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de Matos Lamelas**

**Aproximação de três frentes a centros coloridos em
diamante: um caso de estudo em cálcio**

**Three-pronged approach to color centers in diamond: a
case study for calcium**





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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Física, realizada sob a orientação científica do Doutor Vitor Brás Sequeira Amaral, Professor catedrático do Departamento de Física da Universidade de Aveiro, e do Doutor Ulrich Wahl, Investigador principal, com agregação, do Departamento de Engenharia e Ciências Nucleares do Instituto Superior Técnico.

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Palavras Chave

Diamante, defeitos de cálcio, defeitos, cálculos *ab initio*, *emission channeling*, absorção, espalhamento de Raman, absorção no infravermelho, fotoluminescência.

Resumo

O diamante é um material com muitos centros coloridos de potencial para aplicação em tecnologias quânticas. Neste trabalho, uma aproximação de três frentes foi desenvolvida para o estudo de defeitos de Ca neste material. Cálculos *ab initio*, medições de *emission channeling* (EC) e óticas foram realizadas de forma a correlacionar resultados, permitindo um melhor conhecimento dos sistemas em questão. Cálculos de teoria do funcional da densidade (DFT) foram utilizados para otimizar a estrutura de 165 defeitos de Ca, incluindo vários pontos de alta simetria da rede do diamante, diferentes números de lacunas e cinco estados de carga. Energias de formação, transição adiabática de carga e de ligação foram calculadas para todas as configurações. Foi possível concluir que a configuração com o Ca no centro da ligação (BC) com duas lacunas apresenta a menor energia de formação, 13.36 eV no seu estado de carga neutro. Foi feita a análise de medições de EC com elétrons precedidas por implantação de baixa fluência de ^{45}Ca (3×10^{12} iões/cm², 30 keV) executadas no ISOLDE. Dos padrões coletados, foi possível concluir uma distribuição aleatória de Ca em torno do BC antes de tratamento térmico, sendo consistente com os resultados de DFT. Depois do tratamento térmico, esta contribuição foi reduzida em favor de outras posições. Amostras de diamante foram também implantadas com Ca estável em KU Leuven e foram caracterizadas opticamente. Depois de tratamento térmico, a partir de medições de fotoluminescência a temperaturas criogénicas foi possível identificar os dois estados de carga típicos do centro azoto-lacuna, em adição a duas linhas para 563 nm e 579 nm. Estas foram atribuídas a auto-interstícios. Da dependência da fotoluminescência com a temperatura foi hipotetizado que a última faz parte da estrutura vibracional associada à primeira. Adicionalmente, apesar de serem detetados sinais da implantação não foi observado nenhum sinal ótico diretamente devido ao Ca.

Keywords

Diamond, calcium defects, defects, *ab initio* calculations, emission channeling, absorption, Raman scattering, infrared absorption, photoluminescence.

Abstract

Diamond is a material with multiple promising color centers for quantum technologies. In this work, a three-approach was employed to study Ca defects in this material. *Ab initio* calculations, emission channeling (EC) and optical measurements were performed such that the correlation of results was possible, to achieve a better understanding of such systems. Density functional theory (DFT) was used to optimize the structure of 165 Ca defects, including multiple high symmetry sites of the diamond lattice, varying number of vacancies and five charge states. Formation, adiabatic charge transition and binding energies were calculated for all configurations. From them, it was possible to conclude that the bond-center (BC) configuration with two vacancies had the smallest formation energy, 13.36 eV for its neutral charge state. Results from β^- EC measurements following low fluence implantation of ^{45}Ca (3×10^{12} ions/cm², 30 keV) performed at ISOLDE were analysed. From the collected patterns, a distribution around the BC site was found in the as implanted state which is consistent with DFT results, and, after annealing, such contribution was reduced in favor of other sites. Diamond samples were also implanted with stable Ca at KU Leuven and were optically characterized. From low-temperature photoluminescence (PL), after heat treatment, it was possible to identify both charge-states of the nitrogen-vacancy defect in diamond, and also two new lines at 563 nm and 579 nm, which were attributed to self-interstitials. From the temperature dependence of the PL signal, the latter is hypothesized to be a vibronic feature of the former. It was concluded that, despite seeing effects of the implantation, no direct optical signal was found from Ca.

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Glossary

AB	anti-bonding	LT	low temperature (14 K)
AIAA	after implantation and annealing	MBPT	many-body perturbation theory
AIBA	after implantation and before annealing	MgV	magnesium-vacancy
BC	bond-center	NEB	nudge elastic band
BIAA	before implantation and after annealing	NR	non-radiative
BIBA	before implantation and annealing	NV⁻	nitrogen-vacancy negatively charged state
C	"C" from its C_{2v} symmetry	NV	nitrogen-vacancy
CBM	conduction band minimum	NV⁰	nitrogen-vacancy neutral charge state
CVD	chemical vapor deposition	ODMR	optically detected magnetic resonance
ΔSCF	Δ self consistent field	PBE	Perdew-Burke-Ernzerhof
DFPT	density functional perturbation theory	PES	potential energy surface
DFT	density functional theory	PL	photoluminescence
DS	$\langle 110 \rangle$ -split	PLE	photoluminescence excitation
DT	a site that is displaced from T as much as DS is displaced from S	PW91	Perdew-Wang 1991
EC	emission channeling	RT	room temperature
FTIR	Fourier transform infrared spectroscopy	S	substitutional
FWHM	full width at half maximum	SiV	silicon-vacancy
GGA	generalized gradient approximation	SnV	tin-vacancy
GR	general radiation	SP	$\langle 100 \rangle$ -split
H3	heat treatment (preceded by irradiation) 3	SSSP	standard solid-state pseudopotentials
H	hexagonal	T	tetrahedral
HPHT	high-pressure high-temperature	TDDFT	time dependent density functional theory
HSE06	Heyd-Scuseria-Ernzerhof 2006	VBM	valence band maximum
LDA	local density approximation	Y	so-called "Yb"
		ZPL	zero phonon line

Chapter One

Introduction

Nowadays, quantum properties are more and more exploited for a multitude of applications, be it in computation, communication or metrology and sensing. Two years ago Google, in collaboration with NASA and Oak Ridge National Laboratory, claimed quantum supremacy and today one can buy an off-the-shelf scanning nitrogen-vacancy (NV) magnetometer that exploits the quantum properties of defects in diamond. This shows the great interest and promise of the field of quantum technology.

Diamond is one of the materials at the center of this quantum technological revolution, since it can host defect energy levels whose properties can be tailored for a wide-range of applications. Semiconductors and insulators with large enough band gaps are ideally transparent, as they do not absorb visible light, however, extrinsic/intrinsic defects can create energy levels within the gap, leading to absorption and emission of light that is not absorbed by the host material. The defects that lead to this kind of energy levels are called color centers [1]. Diamond is a particularly suitable host for such centers due to multiple reasons such as its wide band-gap, (5.470 ± 0.005) eV at 295 K [2], allowing for color centers with visible emission; carbon has a very low mass and stiff bonds leading to a high Debye temperature which minimizes the coupling to lattice vibrations [3] resulting in bright color centers that can be observed at room temperature (RT) [1]; it has naturally low concentration of nuclear spins as ^{12}C has no nuclear spin and ^{13}C , which is naturally 1.1 %, has nuclear spin of 1/2 [3], thus it allows for long spin coherence times, allowing for more operations in quantum computations. Aside from quantum computation, where centers such as the NV center are used as solid-state spin qubits [3, 4], color centers in diamond can also be used in masers for astronomy and deep-space communication [3], nanoscale magnetometry [5], allowing great spatial resolution and sensitivity [3], and single photon sources [1]. For the latter application they offer advantages over trapped ions and atoms, which, in spite of their excellent optical properties, have difficult scalability and integration challenges, and quantum dots which also have excellent optical properties but have low coherence times and it is difficult to produce indistinguishable emission from an ensemble [1].

Color centers in diamond have been extensively studied over the last decades. Optical measurements, such as optical absorption [2, 6–9], luminescence with varying types of excitation, such as light, electric fields and electrons [6, 10–14], and Raman scattering [15, 16] have been performed for many samples of different types, natural and synthetic, bulk and films, and with different treatments, such as irradiation and annealing. A multitude of color centers has been identified and studied such as the NV [11, 12, 17] and the tin-vacancy (SnV) center [18, 19], but many spectral features still have no physical model [20, 21].

Alongside experimental measurements, much theoretical work has also been developed especially in the realm of density functional theory (DFT) calculations. Equilibrium structure, formation and

migration energies, phonon and electronic band structures and other properties have been calculated for pristine diamond and various defects [22, 23]. Initially these calculations were performed at the local density approximation (LDA) and generalized gradient approximation (GGA) level, but with increasing computational power and improvements in computational methods, the use of hybrid functionals and even higher level theories such as many-body perturbation theory (MBPT) have become feasible for defect calculations [24–29] and thus are state of the art. Defect properties can be calculated with various approaches such as the cluster approach (no periodicity but surface influence) [30, 31] and the supercell approach (periodic replicas) [26–29, 32]. More recently methods based on non-equilibrium Green functions have been proposed [33] that eliminate the periodicity of the defect but also consider the crystalline bulk.

The NV center in diamond, more specifically its negative charge state, has been the color center of focus in diamond due to its low spin-orbit coupling, (5.33 ± 0.03) GHz from experiment and 4.8 GHz from theoretical calculations [32], which reduces decoherence with the lattice, and to its spin state that can be polarized and manipulated with a common green laser by RT optically detected magnetic resonance (ODMR) [3]. It has achieved the longest coherent spin lifetime without cryogenics, 75 s in a ten qubit quantum register [4]. However, it also has limitations. Due to its coupling to phonons, at RT, it emits from 637 nm to 800 nm, generating distinguishable photons. Additionally, it is hard to achieve good defect properties on near-surface centers [3]. Negatively charged group-IV-vacancy centers, such as the silicon-vacancy (SiV), have weaker phonon coupling but also have shorter coherence times [34]. SnV centers have become increasingly interesting as it is expected that they have longer coherence times [10]. Contrary to NV centers, in the group-IV-vacancy centers, the impurity is thought to be near a bond-center position [23] and recent β^- emission channeling (EC) measurements have corroborated this expectation [35].

Recently, single-photon emission has been observed for the magnesium-vacancy (MgV) [36] and thus, due to the chemical similarity with Mg, Ca defects might also show similar behavior. Due to its valence and size, intuitively one would expect a similar center structure to MgV, resulting in interesting properties. This element is also a candidate for the so-called ST1 center [10], which show RT ODMR, a property only found on the NV center to date. For these reasons and lack of literature on the subject, it was selected for study. The present work forms part of a more systematic study into the properties of group II elements in diamond, with EC experiments performed for the isotopes ^{27}Mg , ^{45}Ca , and ^{89}Sr . Samples implanted with different fluences of Ca were studied by visible and infrared absorption, photoluminescence (PL) and Raman scattering. EC measurement results with Ca were also analyzed to determine its position in the lattice upon implantation and after annealing. Alongside the experimental work, *ab initio* calculations were performed to predict experimental results and aid in their interpretation.

In the text below, chapter 2 presents the theoretical concepts, followed by how the *ab initio* calculations were performed and their results in chapter 3. In chapter 4, the EC analysis procedure and results are presented and discussed. The same is done for the optical measurements in chapter 5. To finish, conclusions are elaborated in chapter 6, with suggestions for future work.

Chapter Two

Theoretical Background

A wide variety of diamonds can be found in nature and are classified according to their impurity content. The two main types, I and II, are defined based on the N content, as this is the major impurity in diamond. If the N concentration is above 1-2 ppm the diamond is said to be type I, otherwise it is type II [17]. The major categories can be further divided into type Ia, Ib, which contain N aggregates or substitutional single N, called C centers, and IIa, IIb, where N and B impurities are at the detection limit of infrared absorption (IIa) or are detectable (IIb) [17]. Type Ia diamonds are also divided by the majority aggregate form, type IaA if it is A aggregates, a pair of substitutional N, or IaB if it is B aggregates, four N atoms around a vacancy. Type I diamond corresponds to around 98 % of natural diamond [17], however, such is not suitable for quantum applications of color centers due to the very high concentration of impurities, which, for example, lead to more interaction between defects reducing coherence times.

2.1 SYNTHETIC DIAMOND

Synthetic diamonds are more desirable in this regard and can be grown by multiple techniques, such as high-pressure high-temperature (HPHT) and chemical vapor deposition (CVD). In the latter, diamond is grown in non-equilibrium conditions from a gas mixture of a few mole percent of CH_4 diluted in H_2 [17]. This gas mixture is activated by means of, for example, a microwave plasma, an arc jet or a hot metal filament, resulting in free H atoms that drive the growth [17]. It occurs on a substrate that has to be appropriately chosen, with common options being Mo or Si, and pre-treated to encourage diamond nucleation. Tuning the growth parameters such as gas flow, mixture concentration and temperature, the resulting grain size can be adjusted. Single crystals can also be grown with the correct parameters by homoepitaxial growth from a single crystal seed or from very specific substrates such as Ir [17]. The growth is driven by reactions that exchange H from CH_y radicals ($y \in \{1, 2, 3, 4\}$). H also plays an important role in terminating the carbon surface which avoids the formation of graphitic carbon, and removes deposited carbon in non-diamond form [17].

2.2 ION IMPLANTATION

After or during growth, color centers need to be introduced in the diamond for use in quantum applications. This can be achieved with multiple methods, such as delta doping with N during CVD growth [37] or using Fe_3N -C catalyst during HPHT [38]. After growth, color centers can be introduced by ion implantation, electron irradiation or laser processing, for example [37]. Independent of the introduction method usually annealing is required for optical activation of the color centers, be it

to allow diffusion of impurities and vacancies to optically active positions or for the formation of complexes of various point defects.

Ion implantation is the only method that can insert impurities in a reproducible and controlled way into diamond post growth. As such, it is essential for impurities which cannot be feasibly introduced during growth [37]. It is achieved by creating and focusing a beam of ions of the desired species into the material. The energy of the beam, in conjunction with properties of the ion and target, such as the displacement energy, determine the implantation depth, lateral range, called straggle, and the number of intrinsic defects created per implanted ion [37, 39]. Masks can also be used to define planar features [37]. The major difficulty with this technique is the choice of thermal treatment parameters that activate the implanted species.

The implantation process is stochastic and described by Poissonian statistics but deterministic ion implantation can be achieved detecting the ion before or after it enters the material. Post-impact techniques, such as the detection of secondary electrons, require specific material structures and tend to lead to more false positives. Two examples of pre-impact techniques are ion trap detection [40] and mirror charge detection [41]. The former, laser traps and cools each ion, resulting in almost 100 % probability of detection, giving an extremely reliable signal, however, has low implantation rates. The latter use ring detectors that, if triggered above a defined threshold, open a shutter for enough time for only one ion to pass through, thus achieving much higher implantation rates at the cost of high technical demand from the signal processing side [37].

2.3 ANNEALING

After ion implantation, the implanted region contains not only the implanted species but also considerable lattice damage, i.e., broken bonds, vacancies and self-interstitials, that do not correspond to thermal equilibrium. Supplying energy to the system promotes migration of some or all defect types, and repair of the unwanted lattice damage from the implantation process. Such energy is usually of thermal origin [10, 42, 43] but other sources can be used [44]. In diamond, broken bonds can be reformed into sp^1 (polymer), sp^2 (graphite) and sp^3 (diamond), and the competitions between the latter two is of great significant as sp^2 bonds are thermodynamically stable under normal pressure and temperature conditions. As such, diamond requires the annealing to be done under vacuum [45] or stabilizing pressure (HPHT methods) to avoid graphitization, i.e., turning into graphite. This exemplifies a case where the annealing leads to more defects instead of repairing the lattice, as such, annealing parameters much be chosen carefully.

The energy barrier between sp^2 and sp^3 hybridization depends on the density of defects close to the broken bond. Above a critical defect concentration, graphite is predominantly formed and the diamond structure cannot be restored [42]. This establishes a limit for ion implantation, however, for quantum applications the reduced interaction between defects usually places a stricter limit.

The mobility of a defect during annealing can be described by a simple diffusion equation, where a concentration term is considered, but other terms from interactions between defects can also be accounted for, such as electrostatic interaction between charged defects or with dislocations (a type of linear defect) [46]. The diffusion can often be fully characterized by the diffusivity or diffusion coefficient that depends on a attempt frequency, characteristic of the material, and the migration energy barrier between the initial and final position [47]. The migration energy for a given defect can be calculated with DFT using the nudge elastic band (NEB) method [47], as such, the expected diffusion distance for a given annealing temperature and time of a defect can be estimated before any experiment. In combination with the implantation fluence, i.e., the number of ions implanted per

unit area, one can estimate the average distance between implanted ions and if they can be brought together during annealing. Such estimates can also be performed for an impurity and a vacancy which is the structure of the main technological interesting color centers in diamond as mentioned above.

2.4 OPTICAL PROPERTIES

When light shines on samples various phenomena can occur, such as the light beam being reflected, absorbed and scattered. If the medium is excited, be it by light or other method, it may also luminesce, emitting light that can suffer additional processes. In subsection 2.4.1 a brief introduction to the microscopic theory of absorption and emission of light, with focus on defects in semiconductors, is presented, followed by a description of the macroscopic theory of Raman scattering in subsection 2.4.2.

2.4.1 Microscopic theory of light absorption and emission

Optical absorption in materials is caused by transitions between its energy levels. Considering a one dimensional system for simplicity, it can be described by $I(z) = I(0) \exp(-k(\omega)z)$ [48, 49], where $I(z)$ is the radiation intensity as function of position z in the material, $k(\omega)$ is the frequency dependent absorption coefficient. Experimentally, this relation can be expressed by quantities such as the transmittance $T = \frac{I}{I(0)}$ and the absorbance $A = -\log_{10}(T)$, by measuring the light intensity, I , after it has entered, propagated and left the sample. Considering that the absorption happens at particular sites in the material, such as atoms in a solution or color centers in a semiconductor, one can define the absorption cross-section $\sigma(\omega)$ which corresponds to the absorption coefficient per absorption site, i.e., $\sigma(\omega) = k(\omega)/N_{\text{sites}}$, where N_{sites} is the number of such absorption centers [49].

In a solid, the environment is not isotropic nor inert, as such the effects of the material have to be considered. Neglecting external perturbations, the Hamiltonian of the solid system may be written as [50]

$$\mathbf{H}(\mathbf{r}, \mathbf{R}) = \mathbf{T}_N + \mathbf{V}_{NN}(\mathbf{R}) + \mathbf{H}_e(\mathbf{r}, \mathbf{R}), \quad (2.1)$$

where $\mathbf{r}$ and $\mathbf{R}$ are the electrons and nuclear coordinates, respectively, $\mathbf{T}_N$ is the nuclear kinetic energy operator, $\mathbf{V}_{NN}(\mathbf{R})$ describes the nuclear electrostatic interactions which leads to lattice vibrations, and $\mathbf{H}_e(\mathbf{r}, \mathbf{R})$ is the electronic Hamiltonian. The nuclei, due to their much larger mass, respond very slowly to electron's motion, i.e, the nuclei see an average charge distribution of the electrons and the electrons see the nucleus as static. This is the Born-Oppenheimer approximation, and thus the wavefunction of the system can be decoupled in terms of nuclear and electronic motion, $|\psi\rangle = |a\rangle \otimes |\{n\}\rangle \equiv |a, \{n\}\rangle$, where a corresponds to the electron levels, and $\{n\}$ are the occupation number of the lattice vibrational modes. Considering only dipole transitions, the absorption cross-section becomes [49, 51]

$$\sigma(\omega) = \left[\frac{n_r}{\epsilon} \left(\frac{E_{\text{eff}}}{E_0} \right)^2 \right] \frac{8\pi^3\omega}{3c} \cdot \text{Av}_{\{n\}} \left[\sum_{\{n'\}} |\langle b, n' | \boldsymbol{\pi} \cdot \mathbf{r} | a, n \rangle|^2 \delta(\omega - \omega_{ab,nn'}) \right], \quad (2.2)$$

where $\boldsymbol{\pi}$ is the unit polarization vector, with $\hbar\omega_{ab,nn'} = E_{b,n'} - E_{a,n}$ where $E_{a,n}$ and $E_{b,n'}$ are the eigenvalues of the corresponding eigenstates, n_r is the refractive index of the material and ϵ its dielectric constant, E_{eff} is the effective field in the solid, which is different from the field in vacuum E_0 due to the polarization of the material [49]. The average, Av, is over the thermal population of the vibronic (electronic + vibrational) initial state. Eq. (2.2) tells us that there is absorption to the excited state associated with a purely electronic transition, i.e., no change in the phonon occupations, called zero phonon line (ZPL), that is accompanied by transitions involving different number of phonons. In the continuum limit of the phonon modes, the transitions changing the number of phonons lead to a band in the spectrum called vibrational sideband.

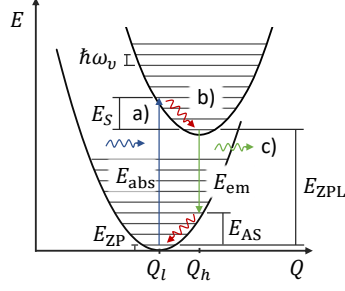


Figure 2.1: Configuration-coordinate diagram of two electronic energy levels (parabolas) with multiple associated vibrational levels (horizontal lines). The abscissa represents the configuration coordinate, in this case, the displacement along a normal mode of the lattice, with two equilibrium positions Q_l and Q_h of the lower and higher energy electronic states, respectively. Three types of processes are present: a) absorption, b) non-radiative relaxation by creation of lattice phonons and c) emission. E_S , E_{AS} , E_{ZP} , E_{ZPL} , E_{abs} and E_{em} are the Stokes, anti-Stokes, zero-point, ZPL, absorption and emission energies.

Representing each component of the wavefunction in the position basis of each subspace, $|\mathbf{r}\rangle$ and $|\mathbf{Q}\rangle$, where $\mathbf{Q}$ represents all normal coordinates of the lattice, $\chi_n(\mathbf{Q}) = \langle \mathbf{Q} | \{n\} \rangle$ and $\phi_i(\mathbf{r}, \mathbf{Q}) = \langle \mathbf{r} | i \rangle$, the matrix elements of the coupling operator from an initial vibronic state i and final state f of the whole system have the form

$$\mathcal{M}_{if} = \int \int \chi_f^*(\mathbf{Q}) \psi_f^*(\mathbf{r}, \mathbf{Q}) \Omega(\mathbf{r}, \mathbf{Q}) \chi_i(\mathbf{Q}) \psi_i(\mathbf{r}, \mathbf{Q}) d^3\mathbf{r} d\mathbf{Q} = \int \chi_f^*(\mathbf{Q}) \Omega_{if}(\mathbf{Q}) \chi_i(\mathbf{Q}) d\mathbf{Q}, \quad (2.3)$$

The matrix elements of the transition operator, $\Omega(\mathbf{r}, \mathbf{Q})$, depend weakly on $\mathbf{Q}$, as such, can be approximated as independent on $\mathbf{Q}$ which is called the Condon approximation and results in

$$\Omega_{if}(\mathbf{Q}) \approx \bar{\Omega}_{if}, \quad \mathcal{M}_{if} = \bar{\Omega}_{if} \int \chi_f^*(\mathbf{Q}) \chi_i(\mathbf{Q}) d\mathbf{Q} = \bar{\Omega}_{if} \cdot M_{if}. \quad (2.4)$$

This greatly simplifies the problem, as only the overlap integrals of different vibrational modes need to be computed, for a given electronic transition. In this approximation M_{if} can be seen as the relative intensity contributed by the vibrational transition of the vibrational modes corresponding to state i and j . Lax [51] has analyzed the effects of the various approximations here presented and found them to be generally good approximations. Additionally, during an electronic transition, the nuclei, due to their mass, in most cases respond very little to the change in the electronic charge density, and will not be in equilibrium, hence the vibrational states with most of the contribution will be such that the classical turning points match the structure of the initial state. This is the Franck-Condon approximation. Mathematically this is equivalent to replacing the sum over n' in (2.2) by a mean value [51]. This is also equivalent to saying that the vertical transition, i.e. without changes in the structure, is the most likely, which leads to a very useful representation of the absorption and emission processes in the so-called configuration-coordinate diagrams (Fig. 2.1). Between absorption and emission, the structure is able to relax non-radiatively by exciting lattice vibrations.

Considering only the Condon approximation and substituting in Eq. (2.2) one gets

$$\sigma(\omega) = \left[\frac{n_r}{\epsilon} \left(\frac{E_{\text{eff}}}{E_0} \right)^2 \right] \frac{8\pi^3 \omega}{3c} \langle \bar{\Omega}_{ab}^2 \rangle_{\text{pol}} \cdot G(\omega), \quad (2.5)$$

$$G(\omega) = \text{Av} \sum_{\{n\}} \sum_{\{n'\}} |M_{nn'}|^2 \delta(\omega - \omega_{ab,nn'}). \quad (2.6)$$

Here $\langle \rangle_{\text{pol}}$ represents the average over the directions of the polarization vector and $G(\omega)$ is called the shape or spectral function and is normalized in respect to ω [49]. For the ZPL it can be shown that the spectral function is Lorentzian [52].

The steps presented above can be performed for emission, dominated by spontaneous emission except in the case of a system similar to a laser, resulting in an emission transition probability W (or equivalently the reciprocal lifetime) given by [49, 51]

$$W(\omega) = \left[\frac{n_r^3}{\epsilon} \left(\frac{E_{\text{eff}}}{E_0} \right)^2 \right] \frac{32\pi^3 \omega^3}{\hbar c} \langle \bar{\Omega}_{ab}^2 \rangle_{\text{pol}} \cdot G(\omega). \quad (2.7)$$

It is worth noting that, despite the same form of $G(\omega)$ for absorption and emission, as the initial and final states are not the same, the spectral function is also different. From these results the absorption and emission spectra can be calculated if $G(\omega)$ is known. For that, let us return to the Hamiltonian of Eq. (2.1). In the Born-Oppenheimer approximation

$$\begin{aligned} \mathbf{H}_e |a\rangle &= E_{e,a}(\mathbf{Q}) |a\rangle, \\ [\mathbf{T}_N + \mathbf{V}_{NN} + E_{e,a}(\mathbf{Q})] |\{n\}\rangle &= [\mathbf{T}_N + \mathbf{V}_N] |\{n\}\rangle = E_{a,n} |\{n\}\rangle, \end{aligned} \quad (2.8)$$

where $E_{e,a}(\mathbf{Q})$ are electronic eigenvalues for eigenstate a as function of $\mathbf{Q}$, and $E_{a,n}$ are vibrational eigenvalues associated with eigenstate a . In the low temperature limit, the mean positions of the nuclei equal their equilibrium position [50], therefore one can expand $\mathbf{V}_N$ in terms of the displacements from the equilibrium position of the lower energy state, up to second order (harmonic approximation) [50]

$$\begin{aligned} & \left[\mathbf{T}_N + \sum_{\nu} \left(\frac{\partial E_{e,a}}{\partial (\sqrt{m_{\nu}} Q_{\nu})} + \frac{\partial \mathbf{V}_{NN}}{\partial (\sqrt{m_{\nu}} Q_{\nu})} \right) \sqrt{m_{\nu}} Q_{\nu} + \right. \\ & \left. + \frac{1}{2} \sum_{\nu, \mu} \left(\frac{\partial^2 E_{e,a}}{\partial (\sqrt{m_{\nu}} Q_{\nu}) \partial (\sqrt{m_{\mu}} Q_{\mu})} + \frac{\partial \mathbf{V}_{NN}}{\partial (\sqrt{m_{\nu}} Q_{\nu}) \partial (\sqrt{m_{\mu}} Q_{\mu})} \right) \sqrt{m_{\nu} m_{\mu}} Q_{\nu} Q_{\mu} \right] |\{n\}\rangle = \epsilon_{a,n} |\{n\}\rangle, \end{aligned} \quad (2.9)$$

where Q_{ν} and m_{ν} are the normal displacement coordinate and the mass, respectively, of vibrational mode ν , and $\epsilon_{a,n} \approx E_{a,n}$ due to the harmonic approximation. The derivatives are evaluated at the equilibrium position and all sums go to the number of normal modes N , but such is not represented for the sake of conciseness. Separating the terms that mix normal modes

$$\left[\mathbf{T}_N + \sum_{\nu} \mathcal{A}_{\nu} \sqrt{m_{\nu}} Q_{\nu} + \frac{1}{2} \sum_{\nu} \omega_{a,\nu}^2 m_{\nu} Q_{\nu}^2 + \sum_{\nu, \mu \neq \nu} \mathcal{B}_{\nu, \mu} Q_{\nu} Q_{\mu} \right] |\{n\}\rangle = \epsilon_{a,n} |\{n\}\rangle, \quad (2.10)$$

where the coefficients $\mathcal{A}_{\nu}$, $\mathcal{B}_{\nu, \mu}$ and the frequency $\omega_{a,\nu}$ are defined by comparison with equation (2.9). For the lower energy state, as the expansion is around its equilibrium, the first order derivatives, the negative of the forces, are null, as such the linear term disappears. Additionally, the energy reference can be defined such that the zeroth order terms are zero for the lowest energy state. Assuming that the $\mathcal{B}_{\nu, \mu}$ are zero as well for this state, the resulting $\mathbf{V}_N$ is given by $\mathbf{V}_l = \frac{1}{2} \sum_{\nu} m_{\nu} \omega_{l,\nu}^2 Q_{\nu}^2$.

Let us consider two cases for the higher energy level, linear coupling and quadratic coupling. For the former, representing $\mathbf{V}_N$ for this state as $\mathbf{V}_h$ one gets [12]

$$\mathbf{V}_h = E + \frac{1}{2} \sum_{\nu} m_{\nu} \omega_{h,\nu}^2 \left(Q_{\nu} + \frac{\mathcal{A}_{\nu}}{m_{\nu} \omega_{h,\nu}^2} \right)^2 - \frac{1}{2} \sum_{\nu} \frac{\mathcal{A}_{\nu}^2}{m_{\nu} \omega_{h,\nu}^2}. \quad (2.11)$$

From this result, one can conclude that linear coupling introduces a shift in equilibrium positions for the higher energy state, compared to the lower energy state, and this shift's magnitude depends on the

coupling strength. The vibronic wavefunction associated with this potential is

$$\psi_h(\mathbf{r}, \mathbf{Q}) = \phi_i(\mathbf{r}, \mathbf{Q}) \prod_{\nu} \chi_{\nu}^{n_{\nu}} \left(Q_{\nu} - \frac{\mathcal{A}_{\nu}}{m_{\nu} \omega_{\nu}^2} \right), \quad (2.12)$$

where n_{ν} is the occupation number of vibrational mode ν [12]. Let us define the Huang-Rhys factor $S_{\nu} = \mathcal{A}_{\nu}^2 / (2\hbar m_{\nu} \omega_{\nu}^3)$ for each mode such that $S_{\nu} \hbar \omega_{\nu}$ is the relaxation energy in mode ν and a total Huang-Rhys factor $S = \sum_{\nu} S_{\nu}$. The former measures how many phonons of mode ν participate on average in the transition and the latter is equivalent but for phonons of any mode. For temperature $T=0$ K, the only initial state that participates is the $n_{\nu} = 0$ state, i.e., with no phonons. With the prior definitions, the amplitude of overlap of the vibrational wavefunctions for $n_{\nu} = 0$ and $n'_{\nu} = 1$ is [12]

$$|M_{01}^{\nu}|^2 = S_{\nu} \exp(-S_{\nu}) \prod_{\mu \neq \nu} \exp(-S_{\mu}) = S_{\nu} e^{-S}, \quad (2.13)$$

therefore, the total relative intensity of the one-phonon sideband is $S e^{-S}$ [12]. For a transition with n phonons involved $|M_{0n}|^2 = S^n e^{-S} / n!$ and $\sum_{n=0}^{\infty} |M_{0n}|^2 = 1$ [12]. The spectral function for the n -phonon sideband, $G_n(\omega)$, can be obtained considering that by absorbing a photon of frequency $\omega = \omega_{\text{ZPL}} + \omega_{\nu}$ on can create $n - 1$ phonons with total energy corresponding to $\omega_{\nu} - \omega'_{\nu}$ and create one phonon with frequency ω'_{ν} , because the modes are independent [12]. Summing over all possible frequency splits

$$G_n(\omega_{\nu}) \propto \int_{\mathcal{L}} G_{n-1}(\omega_{\nu} - \omega'_{\nu}) G_1(\omega'_{\nu}) d\omega'_{\nu}, \text{ with } n > 1, \quad (2.14)$$

where $\mathcal{L}$ are the limits of integration, due to the frequency of the phonons in a material being limited to $[0, \omega_{\text{max}}]$. $\mathcal{L} = [0, \omega_{\text{max}}]$ for absorption and $\mathcal{L} = [-\omega_{\text{max}}, 0]$ for emission.

Due to the phonon coupling, the properties of the ZPL depend on temperature. For linear coupling only the intensity changes with temperature [52, 53]

$$G_0(T) \propto \exp\left(-b \int_{\mathcal{L}} g(\omega_{\nu}) (2\mathcal{P}(\omega_{\nu}, T) + 1) d\omega_{\nu}\right) \propto \exp(-S(T)), \quad (2.15)$$

where $g(\omega_{\nu})$ is phonon density of the states of the center which is related to G_1 by $G_1(\omega_{\nu}) \propto e^{-S} (\mathcal{P}(\omega_{\nu}, T) + 1) g(\omega_{\nu}) / \omega_{\nu}^2$ [53], $\mathcal{P}(\omega_{\nu}, T) = [\exp(\hbar \omega_{\nu} / k_B T) - 1]^{-1}$ is the Bose-Einstein distribution, k_B is the Boltzmann constant and b a numerical factor that depends on the normalization of $g(\omega_{\nu})$ [53]. Note that S can be calculated from $g(\omega_{\nu})$ however such requires that b is also known [53].

Considering now quadratic coupling, $\mathbf{V}_h$ is given by [12]

$$\mathbf{V}_h = E + \sum_{\nu} \mathcal{A}_{\nu} Q_{\nu} + \frac{1}{2} \sum_{\nu} m_{\nu} \omega_{h,\nu}^2 Q_{\nu}^2 + \sum_{\nu, \mu \neq \nu} \mathcal{B}_{\nu, \mu} Q_{\nu} Q_{\mu}. \quad (2.16)$$

The diagonal coupling terms change the frequency of the higher energy state to $\omega_{h,\nu} \neq \omega_{l,\nu}$ and the off-diagonal terms mix the lower energy level vibrational modes. In the limit of long wavelength, the presence of the defect has little influence on the wave propagation and the quadratic coupling can be approximated by the product of independent linear coupling terms, $\mathcal{B}_{\nu, \mu} \propto \mathcal{A}_{\nu} \mathcal{A}_{\mu}$ [12, 52]. In this approximation, the ZPL's intensity $G_0(T)$, full width at half maximum (FWHM) and line shift $\Delta\omega_{\text{ZPL}}(T)$ are [53]

$$\begin{aligned} G_0(T) &\propto \exp\left(-b \int_{\mathcal{L}} g(\omega_{\nu}) (2\mathcal{P}(\omega_{\nu}, T) + 1) d\omega_{\nu}\right) \propto \exp(-S(T)), \\ \text{FWHM}(T) &\propto \int_{\mathcal{L}} g(\omega_{\nu})^2 \mathcal{P}(\omega_{\nu}, T) (\mathcal{P}(\omega_{\nu}, T) + 1) d\omega_{\nu}, \\ \Delta\omega_{\text{ZPL}}(T) &\propto \int_{\mathcal{L}} g(\omega_{\nu}) \mathcal{P}(\omega_{\nu}, T) d\omega_{\nu}. \end{aligned} \quad (2.17)$$

For weak quadratic coupling the relations found for linear coupling hold [53], therefore, from the knowledge of $G_1(\omega_\nu)$ and S (or the previously mentioned proportionality constant) at $T=0$ K, one can reconstruct all the ZPL properties with temperature [12]. Experimentally it is not always feasible to determine $G_1(\omega_\nu)$ however, if it is only non-zero for a sufficiently small range of ω_ν , $\delta\omega$, around ω_0 , such as the case for coupling to a single mode, it can be approximated as a Dirac delta centered at ω_0 , the frequency of the single mode.

2.4.2 Macroscopic theory of Raman scattering

When light passes through a medium it induces a polarization in the medium, i.e., the charge density changes from its equilibrium configuration. This can be seen as a virtual state as it is not an eigenvalue of the Hamiltonian of the system. While in the virtual state the lattice may relax towards the new charge density equilibrium structures, emitting one or more phonons. As the virtual state is not stable it quickly decays to the ground state emitting a photon. It might have the same energy as the original photon if no phonons were created in the virtual state, and this is called Rayleigh scattering, or it might have less energy, having suffered Stokes Raman scattering. Additionally, the system might also have been in a vibrational excited state of the fundamental electronic one and, after the interaction with light, decayed to the vibrational ground state, therefore, phonons were destroyed in the process and the scattered photon has more energy than the incident one, which is called anti-Stokes Raman scattering.

This picture can be made more rigorous considering an elastic susceptibility χ , a rank two tensor which corresponds to the response of the material stress to an applied strain, in this case from the light field $\mathbf{F}$, treated as a plane wave. The elastic susceptibility relates the polarization of the material with the light field, and it is influenced by lattice vibration's atomic displacements, $\mathbf{Q}(\mathbf{r}, t)$. Expanding the susceptibility in powers of the atomic displacements, to first order, the polarization of the material is given by [48]

$$\begin{aligned} \mathbf{P}(\mathbf{r}, t) = \mathbf{P}_0(\mathbf{r}, t) + \frac{1}{2} \frac{\partial \chi}{\partial \mathbf{Q}} \Big|_{\mathbf{Q}=\mathbf{Q}_0} \mathbf{Q}(\mathbf{q}, \omega_0) \mathbf{F}_i(\mathbf{k}_i, \omega_i) \cdot \\ \cdot [\cos((\mathbf{k}_i + \mathbf{q}) \cdot \mathbf{r} - (\omega_i + \omega_0)t) + \cos((\mathbf{k}_i - \mathbf{q}) \cdot \mathbf{r} - (\omega_i - \omega_0)t)], \end{aligned} \quad (2.18)$$

where $\mathbf{F}_i(\mathbf{k}_i, \omega_i)$, $\mathbf{k}_i$ and ω_i are the amplitude, wavevector and frequency of the incident light beam, and $\mathbf{q}$ and ω_0 the wavevector and frequency of the vibrations. The three additive terms correspond to Rayleigh, anti-Stokes Raman and Stokes Raman scattering, respectively. The shift in frequency relative to the incident photon is called the Raman shift or Raman frequency and is the independent variable in a Raman spectrum. The anti-Stokes regime is much weaker in intensity as it requires the thermal population of higher vibrational levels. As such, when Raman scattering is mentioned it is usually meant in the Stokes regime. Higher order terms in the expansion lead to higher Raman scattering involving more than one phonon. From equation (2.18) one can also conclude that a change in elastic susceptibility, and consequently, the polarization due to the vibrations is required for Raman scattering to occur. Although not here detailed, the polarization of the incident and scattered light also plays a role, as the change in polarization might be non-isotropic [48].

In the scattering process, both momentum and energy are conserved, as such, due to the very low momentum of the photon in the visible region, only phonons from the zone center of reciprocal space participate. If higher momentum radiation is involved, such as X-rays, this is no longer the case [48]. For two-phonon scattering, phonons from all the reciprocal zone can participate as long as the sum of their momentum is approximately zero. If the two phonons are identical the resultant spectral feature is called an overtone [48].

2.5 EMISSION CHANNELING

EC is an experimental technique that uses the channeling of nuclear decay products such as α (He nucleus) and β (electrons and positrons) particles of unstable isotopes implanted inside a material to determine their site location [54]. This information can also be collected after different annealing temperatures giving information about the structural changes during heat treatment.

An intuitive idea of the process can be gathered from Fig. 2.2. Consider that an isotope that shows β^- decay is implanted into a crystalline sample. As the radioactive probe decays, electrons are emitted and, due to their negative charge, they are attracted by the positive nuclear charges along the chains of atoms, leading to stable, "oscillatory" trajectories with small angular deflections along the chains, therefore more electrons are collected in these directions, i.e., the electron yield is higher in these directions. If the probe is in a position like in Fig. 2.2b, despite the vertical direction being a channeling direction, due to the vertical chain of atoms, the yield is not increased. This is because, after being emitted in this direction, the electron starts at the top of a "potential valley", which causes larger angular deflections to dominate the movement. This effect is called blocking and more generally it occurs when the charged particle, although in a channeling direction, faces an initial potential that blocks its path. Such channeling and blocking effects depend greatly on the probe position, allowing the determination of its position by measuring the particle yield from a sample [54, 55]. Comparing the probe positions of Fig. 2.2, one can conclude that it is not enough to measure one direction as different probe positions can have the same effect for a particular direction.

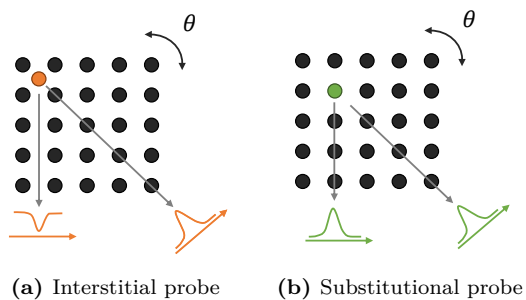


Figure 2.2: 2-dimensional schematic representation of the channeling effects of electrons for a radioactive probe at two different positions in the crystal lattice.

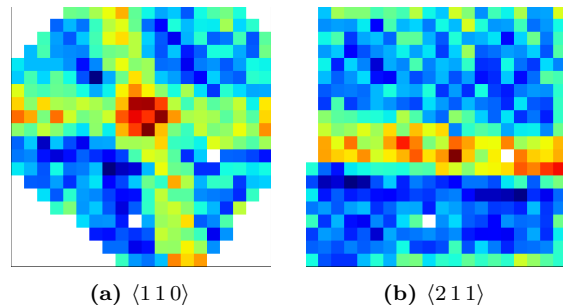


Figure 2.3: Example 2-dimensional pattern resulting from an EC experiment for two crystallographic directions.

Experimentally, a sample is implanted with the appropriate isotope to study a particular chemical species, and then mounted on a goniometer that allows it to be oriented towards a position sensitive detector. Multiple directions, specified by the size of the detector and the geometry of the experimental setup, are measured around major crystallographic directions of the lattice, resulting in 2-dimensional patterns of particle counts around each direction, called channeling patterns (Fig. 2.3). As each pixel of the detector has a slightly different response, before any measurement, they are calibrated against a known source, usually of γ radiation. For short-lived isotopes, with half-life of the order of a few hours or less, the collection of the channeling pattern has to be performed during implantation, in so-called on-line experiments.

The mechanics of the channeling for electrons and positrons are significantly different from those for α particles, as the latter are in good approximation described by classical mechanics, for typical energy ranges. Despite the more complex description, electron channeling is most frequently used in experiments due to the wider availability of appropriate isotopes [55].

To extract atomic sites and respective occupation fractions from a given pattern, a fit to simulated patterns is performed. These simulated patterns are calculated based on the reversibility principle that states that the channeling of a charged particle emitted from within the material is equivalent to the time reversal of the channeling of an identical charged particle entering into the material [54, 55]. For the case of electron channeling, despite the high energies, a quantum mechanical treatment is necessary, as such simulations are performed at the level of many-beam dynamical theory [56, 57]. It is based on the consideration that the electron wavefunction can be split into two components, one relativistic described by a Klein-Gordon equation for the motion parallel to the channeling axis, and another for the perpendicular component, described by Bloch waves resulting from the Schrödinger equation with periodic Doyle-Turner atomic potentials for each atom. The number of so-called beams corresponds to number of Bloch waves considered [55, 57].

An important parameter of such simulations is u the root-mean-square displacement of an atom from its equilibrium position. It enters the thermally averaged Doyle-Turner potential used to describe the crystal and thus affects electron energy levels, but also causes dechanneling effects related to the thermal movement of crystal atoms, which represent deviations from ideal periodic conditions [55]. The values for this parameter for the crystal atoms are obtained from literature, the one for the impurity atom is usually estimated, but also larger values can be considered, representing Gaussian distributions of larger width than the thermal one. The simulated pattern gives the normalized yield which is normalized relative to the yield observed if no channeling effects were present, such as the case for an amorphous sample. A direction with unity yield is called a random direction and a uniform pattern is called a random pattern. Experimental patterns contain a fraction corresponding to a random pattern that is always considered during fitting. It acts similarly to a constant in linear regression. Such fraction might be due to radiation background, incoherently scattered electrons, an amorphous region of the sample or a uniform distribution of emitting sites [55].

During the fitting procedure, one also has to account for the instrumental smoothing introduced by the limited resolution of the detector, σ_{detector} , and also the finite size of the implantation beam spot, σ_{spot} . This can be done considering a Gaussian smoothing function with a projected one-dimensional standard deviation of σ , which is calculated from experimental parameters $\sigma = \arctan\left(\sqrt{\sigma_{\text{detector}}^2 + \sigma_{\text{spot}}^2/d}\right)$, where d is the distance to the detector [55]. The resulting fractions, including the random fraction, sum to one, however, the random fraction usually includes a contribution from the background, therefore all fractions have to be corrected. This can be done by estimating the fraction due to γ radiation and the scattering of electrons in the measurement chamber, either by measurement or simulations, however, this procedure also has associated errors resulting in absolute site fractions with errors around 10 % [55]. In this work no such corrections are applied, but instead the relative fractions of just the sites involved in the fit, excluding the random fraction, are considered for comparison between fits.

2.6 DENSITY FUNCTIONAL THEORY

To calculate the properties of solids, in principle and ignoring spin for the moment, one just has to solve the many-body Schrödinger equation, however this is easier said than done. In the Born-Oppenheimer approximation, the dimension of the electronic wavefunction of the system scales as 3^N where N is the number of electrons. For a small molecule such as N_2 , which has fourteen electrons, the wavefunction would have 4782969 dimensions. As such, the wavefunction quickly becomes computationally untreatable. However, all hope is not lost as, thanks to the Hohenberg-Kohn theorem, the ground-state energy of the many-body system can be written as a functional of the ground-state

charge density, a scalar quantity defined over ordinary 3-dimensional space. Associated with this theorem there is also a variational principle that allows one to determine the correct charge density from the minimization of the energy. Such approach is called DFT, and a brief description of it will be given below mainly based on [58] and the lectures from the MaX School on Advanced Materials and Molecular Modelling with Quantum ESPRESSO 2021. For a deeper view of the subject [59] is recommended.

The universal functional of the Hohenberg-Kohn theorem can be decomposed considering an auxiliary system of non-interacting electrons whose charge density is the same as the real system. From this, the energy of the system, E^{DFT} , can be written as

$$E^{DFT}[n] = T_s(\psi_i) + E_{\text{external}}[n] + E_{\text{Hartree}}[n] + E_{\text{xc}}[n] + E_{\text{ions}}, \quad (2.19)$$

where $T_s(\psi_i)$ is the kinetic energy of the non-interacting system with wavefunction ψ_i for the i^{th} electron, E_{external} is the energy due to an external potential to the electrons, i.e., the interaction with the ions, E_{Hartree} is the Hartree energy, i.e., the energy from the electrostatic repulsion of the electrons, E_{xc} is the energy associated with the exchange of electrons and their correlation and finally E_{ions} is the energy of the ions. The charge density, n , is the sum amplitude squared of the non-interacting wavefunctions, which are also referred to as Kohn-Sham orbitals. The analytical form of all terms is known except for the exchange-correlation term. The initial approximation to this term is known as LDA. In this approximation, the exchange-correlation energy depends only on the charge density, and is defined such that its value in a small volume is equal to the value at the same point of the homogeneous electron gas with charge density equal to that point. The approximation can be improved considering also information about the gradient of the charge density in the calculation of the exchange-correlation. Such approach falls under the umbrella of GGA. Contrary to LDA, there are multiple possible approaches to construct a GGA functional such as the Perdew-Wang 1991 (PW91) and the Perdew-Burke-Ernzerhof (PBE) functionals.

From the minimization of equation (2.19) relative to the density and constraining the Kohn-Sham orbitals to be orthonormal one arrives at the Kohn-Sham equations

$$H^{KS}\psi_i(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{external}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.20)$$

where the potential terms V_k are the derivatives of energies E_k of Eq. (2.19), with $k \in \{\text{Hartree, external, xc}\}$. This Schrödinger-like equation can be solved by conventional eigenvalue solvers, however, it is necessary to know the eigenstates to calculate the charge density that defines the Hamiltonian, therefore, it needs to be solved self-consistently, i.e., the charge density is guessed, the eigenvalues and eigenfunctions are determined, then a new charge density is computed, mixed with the old charge density, and used in the next iteration through this process, which stops when a convergence parameter, be it the variation of the charge density, wavefunction or other derived quantities, is below a threshold. Different mixing schemes of the new and old charge density can be considered having different convergence characteristics.

To represent the wavefunction it is necessary to consider a basis. Multiple choices can be made such as Dirichlet wavelets, atomic orbitals and plane waves. A complete basis of the Hilbert space of the problem would be infinite and therefore needs to be truncated since one cannot store nor compute with such a basis in a computer. This leads to errors in the final result, and the size of the basis set has to be adjusted according to the desired accuracy. The smaller the basis set, the smaller is the required memory and also the lower is the computational time as all matrix operations need to be performed for smaller matrices. For the case of plane waves, the truncation can be accomplished by setting a

maximum energy of the plane waves considered in the basis. The higher this cutoff the sharper the variations that can be captured in the wavefunction. This usually leads to a larger basis set when using plane waves than other methods, but they are much simpler to systematically adjust the size of the basis set as only one parameter needs to be tested. Additionally, they do not bias the wavefunction to a particular shape and lend themselves to periodic systems, allowing easy exploitation of reciprocal space to compute certain quantities.

For periodic systems it is not necessary to simulate a large number of atoms, as the unit cell is sufficient along with periodic boundary conditions. A periodic system requires the additional attention of sampling adequately the first Brillouin zone, to be integrated over in the calculation of the total energy. For efficient integration, i.e., using the least amount of reciprocal zone points, so called k-points, for a required accuracy, the Monkhorst-Pack scheme can be used to generate a k-point grid. It takes as input the number of k-points desired for a given direction and returns the k-point coordinates to be used. Note that this set can further be reduced exploiting the symmetry of the system under study. The value of a quantity of interest needs to be tested against increasing number of k-points in each direction to see its variation and determine a satisfactory compromise between accuracy and computational time. This process is called convergence testing and should also be performed for the basis energy cutoff, in the case of plane waves.

When using a plane wave basis, the representation of core electrons is substantially more expensive than that of the valence electrons, as the wavefunctions of the former show much higher frequency variations requiring a much higher cutoff to be represented accurately. However, in terms of chemical bonding, as core electrons are, by definition, much more tightly bound, they feel very little influence of the surrounding environment, and thus can be modeled as screening of the nuclear potential. The resulting combined potential is called a pseudopotential. There exists a wide diversity of pseudopotentials, generated with different assumptions, that require higher or lower energy cutoffs, and that include different correction terms.

The forces on each atom can be calculated from the derivatives of the energy with respect to position. Knowing the forces one can perform structural optimization by moving the atoms to minimize the former. This can be done through multiple optimization algorithms and is sensitive to the initial positions, i.e., they need to be physically reasonable to achieve a physically reasonable result.

2.6.1 Modeling of point defects

Point defects constitute local perturbations to the periodic structure of a crystal, for example vacancies, where an atom is missing from a lattice position, and interstitials, additional atom(s) in a position between the lattice positions. This introduces difficulties into their modeling because, if treated without periodic boundary conditions the properties of the base bulk material might not be correctly captured and surface effects might be present. On the other hand, if treated with periodic boundary conditions, the defect is replicated in each unit cell which is very far from the real situation. In both cases, the problems can be mitigated simulating a larger system, but it leads to much more costly computations when compared to the pristine bulk. One example of the former is the molecular approach where a few layers of bulk material are constructed around the defect and terminated at a surface with its dangling bonds saturated, usually with H [60, 61]. With periodic boundary conditions instead of the unit cell, one simulates a supercell of the bulk material with the defect, the so-called supercell approach [61]. It is not feasible to use supercell sizes that reproduce the physical concentration of defects in a material. Considering typical concentrations of Si doping, $1 \times 10^{13} \text{ cm}^{-3}$ to $1 \times 10^{18} \text{ cm}^{-3}$, even for the upper limit, the supercell would have to be of the order of 100 Å while typical lattice parameters are of the order of a few angstroms. However, it is not necessary to reach

such high separation between defects, as the bulk material screens the defect interaction, as such, smaller supercells can be used. The supercell size is a parameter that needs to be converged, as the distance at which defects feel their periodic replicas depends both on the defect and on the bulk material [61]. The supercell approach is advantageous as it allows the use of optimization related to periodicity, the band structure of the host material is well described with no quantum confinement effects and the results are more straightforward to interpret when compared to other techniques [61]. This is the approach adopted in this work.

When considering a specific point defect, one has to consider multiple charge states as, depending on the Fermi level, the stable charge state can change. To do so, charged supercells need to be considered, but this is problematic because, if nothing is done, the charge of the system would diverge to infinity. To avoid this, charged calculations consider an uniform background of opposite charge, called a jellium background, to make the supercell neutral [61]. This introduces a change in the energy reference level, which has to be corrected so that charged calculations are comparable. Also, spurious electrostatic interaction between defect replicas need also be accounted for. Multiple *a posteriori* correction schemes exist such as the Lany-Zunger [62] and Kumagai-Oba [63]. Recent works also propose changing the self-consistency loop either to do a self-consistent correction [64, 65], or avoid the jellium method all together [66].

One of the key thermodynamical properties of a defect, X , is its formation energy E_f [61, 67]

$$E_f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + q(E_{\text{vbm}} + E_F) + E_{\text{corr}}, \quad (2.21)$$

where $E_{\text{tot}}[X^q]$ is the total energy of the supercell with defect X and charge q , $E_{\text{tot}}[\text{bulk}]$ is the energy of the bulk supercell, n_i is the number of atoms of species i added to form the defect and μ_i is the chemical potential of the same species, which depends on the experimental conditions. The latter are treated as variables in the general formalism and can be varied to represent different experimental situations [61]. They are usually referred to the energy per atom of a reference phase at temperature $T=0$ K. Note that the formation energy is assumed to be independent of the temperature [61]. The remaining term measures the energy required to add or remove electrons to form a given charge state. E_{vbm} is the valence band maximum (VBM) and E_F is the Fermi energy relative to the VBM. Frequently, as the Fermi energy can change a lot depending on other sources of charges (such as defects for a semiconductor), the formation energy is represented as function of E_F . E_{corr} is a *a posteriori* correction term. Besides the electrostatic correction previously discussed, it can also include corrections due to wavefunction overlap, elastic and magnetic interactions, however these are dependent on the specific defect and its properties [61]. An alternative to these corrections is finite-size scaling, where the formation energy is calculated with multiple supercell sizes and extrapolated to the dilute limit [68], however the accuracy of results based just on extrapolation cannot be determined [61], and there is a significant increase in computational cost.

From the formation energy two important quantities can be extracted, the defect concentration in thermal equilibrium, N_X^q , and the adiabatic charge transition level, $E(q|q+1)$ [61, 67]. The former is given by [67]

$$N_X^q = \frac{1}{V} g_X \exp\left(-\frac{E_f[X^q]}{k_B T}\right), \quad (2.22)$$

where V is the volume of the supercell and g_X is the number of equivalent sites in it, and the latter is the energy defined such that $E_f[X^{q+1}]|_{E_F=E(q|q+1)} = E_f[X^q]|_{E_F=E(q|q+1)}$ [67].

Such transition level establishes the threshold values that limit the region of stability of a given charge state. The transition between charge states, if allowed (i.e., the matrix elements of the electric

dipole operator are not zero) can occur via optical excitation, but in this case, as discussed before, the transition is vertical. Therefore, the vertical charge transition levels, differ from the adiabatic ones. The former can be calculated in the same way as the latter but considering the formation energy computed at the structure of the initial state for the two charge states, and thus, have different values depending on the energy ordering of the initial and final states of the transition [61]. Due to the electrostatic interaction in the supercell approach, a correction is also needed for the vertical transitions that is not simply given by correcting each of the formation energies individually [69].

For complex defects, for example a vacancy X and an interstitial Y complex, the binding energy, E_b , can also be calculated from the formation energies, $E_b = E_f[X] + E_f[Y] - E_f[XY]$. If the binding energy is positive, there is an energy gain in forming the complex and thus it is thermodynamically favorable to do so. A positive binding energy does not translate to significant concentration of the complex as the configurational entropy of the pair of isolated defects may be very different from that of the complex [61]. Additionally, in experiment, dynamical energy barriers and competition from other defects might also reduce the concentration of a complex defect.

The optical intra-charge state transitions of the defect can also be calculated including the reconstruction of the phonon sideband. For that, the potential energy surfaces (PESs) of both the ground and excited states need to be computed. The former can be achieved using DFT to calculate the total energy at different structures along a normal mode, i.e., at different amplitudes of such mode. The vibrational modes can also be determined by various techniques such as the force constant method [70] and density functional perturbation theory (DFPT) [71]. Excited state properties can in principle be determined by traditional DFT but the form of the appropriate functionals for that is not known [72]. Higher level theories such as MBPT and time dependent density functional theory (TDDFT) can be used to map the PES, but this comes at great computational cost. An alternative is the Δ self consistent field (Δ SCF) method [67, 73], sometimes also called constrained DFT [29]. It is very similar to DFT however the electron occupations of the system are manually fixed to describe an excited state, at the computational cost of regular DFT. This method was originally only justified for cases where the excited state was the lowest energy state of its symmetry, however, Görling [72] has given it a formal justification in the general case, assuming the use of special unknown orbital-dependent exchange-correlation functional. Recent verification against experiment and TDDFT have shown that for the calculation of optical spectra the use of this method with known functionals provides accurate results [29]. Ignoring the zero-point energy, the ZPL, the energy of maximum absorption and emission intensity, Stokes and anti-Stokes shifts, can be calculated from the two PES, subtracting the appropriate energies as illustrated in the configuration-coordinate diagram (Fig. 2.1).

Jin *et al.* [29] showed that for the structural and vibrational properties, hybrid functionals, more specifically Heyd-Scuseria-Ernzerhof 2006 (HSE06) [74], provided little benefit over standard PBE, however, for energetics and electronic structure, they are essential to get comparable results to experiment. Regular LDA and GGA functionals severely underestimate the band gap of materials, which is usually attributed to self-interaction error and the lack of the expected discontinuity in energy on the addition or removal of an electron [75]. Hybrid functionals are orbital-dependent exchange-correlation functionals that combine specific fractions of traditional LDA and GGA with a fraction of the exact Hartree-Fock exchange [75]. The improved performance of hybrid functionals in the band gap prediction is attributed to a cancellation of errors [75], as such, different hybrids work better for different materials. For the case of diamond, HSE06 has been found to reproduce the band gap very well, to within 0.06 eV of experiment at $T = 0$ K [76], resulting also in experimentally comparable formation energies, optical transitions and other defect properties [26, 29, 67, 76].

Chapter Three

Ab initio Calculations

To study the effect of introducing calcium in the diamond lattice, DFT calculations with various configurations were performed. After experimenting with different software packages, Quantum ESPRESSO [77–79] was selected for the calculations due to its open-source nature, widespread application in literature and ease of use. An additional incentive to its use was the participation in the MaX School on Advanced Materials and Molecular Modelling with Quantum ESPRESSO 2021. Due to the large number of computations required as well as the use of multiple computers for their execution, the need of a central control system became evident. For this, the Aiida Python package was used [80, 81]. The Quantum ESPRESSO [82], Common Workflows [83] and Wannier90 workflows [84] plugins were also used. Small modifications were done to these to better suit this work. A custom plugin was also developed containing workflows to facilitate the convergence tests and defect calculations performed. All calculations for this work were performed between seven 16 thread machines with varying amounts of memory from 16 GB to 64 GB, one 8 thread machine used mostly for the coordination, one 24 thread machine and the ARGUS cluster from University of Aveiro.

PBEsol, a modified version of PBE with better performance for solids, PBE, and HSE06 functionals were used. With the former, the standard solid-state pseudopotentials (SSSP) PBEsol efficiency version 1.1 pseudopotential library [85] was used, and, with the remaining functionals, the SG15 Optimized Norm-Conserving Vanderbilt pseudopotentials [86]. Norm-conserving pseudopotentials were used with PBE instead of either projected augmented wave or ultrasoft potentials from the SSSP library as they include core corrections which are incompatible with hybrid functionals. Thus, for comparable results, both PBE and HSE06 use norm-conserving pseudopotentials.

At the start, convergence tests were performed for the k-point grid and the plane wave energy cutoff, with the primitive unit cells of diamond and metallic face-centered cubic calcium. Monkhorst-Pack grids with the same number of k-points in all direction, due to lattice symmetry, were used. Unless otherwise specified, all calculations used a criteria of 1×10^{-9} Ry/atom for the self-consistent loop, 0.5×10^{-5} Ry/atom and 0.5×10^{-4} Ry/ a_0 /atom for the total energy and total force in relaxation calculations, which correspond to the precise defaults of the Aiida Quantum ESPRESSO plugin.

For diamond, fixed electron occupation was used and, for calcium, cold smearing [77]. With a criterium of a change less than 1 meV/atom, convergence was achieved for 4 and 6 k-points along each direction for diamond and calcium, respectively. For the energy-cutoff a value of 45 Ry and 30 Ry reached convergence for diamond and calcium, with the SSSP library, while for the SG15 pseudopotentials 75 Ry and 60 Ry were required. With the converged parameters and using PBEsol, the lattice constant of both diamond and calcium was calculated by varying the cell volume and fitting a Murnaghan equation of state as implemented in the Pymatgen package [87]. The calculated diamond lattice

constant is $3.5552 \text{ \AA}$, which compares well to experimental measurements, $(3.567095 \pm 0.000017) \text{ \AA}$ [88], achieving a relative error of 0.3 %. In the case of calcium, the calculated and experimental values are $5.4543 \text{ \AA}$ and $(5.5884 \pm 0.0002) \text{ \AA}$ [89], respectively, which, although with a bigger difference, $\sim 2 \%$, still compare reasonably well.

With the converged parameters the electronic band structure of diamond was calculated using the HSE06 functional. To do so a self-consistent calculation was performed, followed by interpolation using maximally localized Wannier functions as implemented in Wannier90 [90], through the Aiiida Wannier90 workflows plugin. The use of Wannier functions for interpolation is required because non-self-consistent calculation are not implemented for hybrid functionals in Quantum ESPRESSO, therefore, direct calculation requires a prohibitively large number of k-points (on the order of 500) for an electronic band structure with reasonable resolution. The results are presented in Fig. 3.1. From them, one can extract a band gap of 5.617 eV , which agrees well with the experimental value of $(5.470 \pm 0.005) \text{ eV}$ [2], resulting in an error of 3 %. Note that the calculated band gap is for 0 K, while the experimental value is for 295 K. As the energy gap increases with decreasing temperature, the error in the calculated value is smaller than the value given.

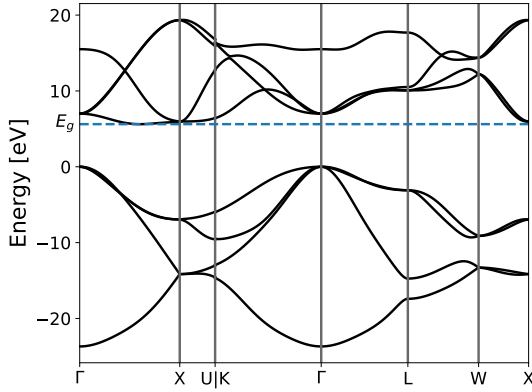


Figure 3.1: Diamond electronic band structure calculated with the HSE06 functional and interpolated using the Wannier functions.

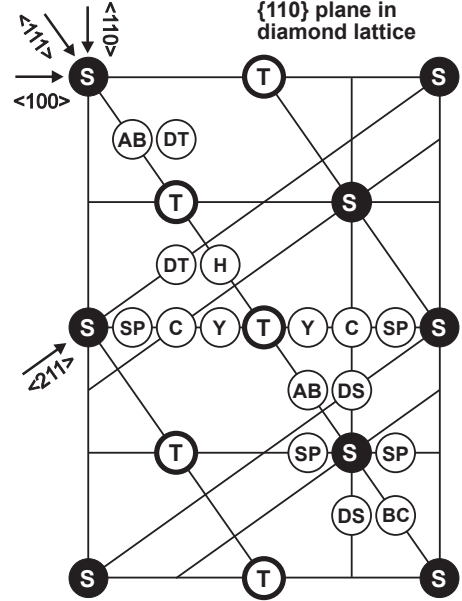


Figure 3.2: Schematic representation of the high symmetry sites of the diamond lattice. Adapted from [35] by Ulrich Wahl.

The vibronic structure of optical centers depends on the coupling to lattice vibration, as such, the phonon density of states of diamond was also calculated with the primitive cell using DFPT as implemented in Quantum ESPRESSO, for comparison with vibronic structures in chapter 5. The calculation was performed using $12 \times 12 \times 12$ grid of q-points (determined to be converged) to calculate the phonon modes and was interpolated to $50 \times 50 \times 50$ for the density of states calculation.

The sites from the simulated library of the EC patterns (Fig. 3.2) were considered as possible defect configurations. It contains patterns considering the substitutional (S) site and interstitials at high symmetry points of the lattice. Starting from S and moving along $\langle 111 \rangle$ one finds the bond-center (BC), anti-bonding (AB), tetrahedral (T) and hexagonal (H) interstitials. Again from S but now along $\langle 100 \rangle$ one gets the $\langle 100 \rangle$ -split (SP), so-called "Yb" (Y) and "C" from its C_{2v} symmetry (C) interstitials. Now considering the $\langle 110 \rangle$ direction one arrives at the $\langle 110 \rangle$ -split (DS) interstitial. Also, a site that

is displaced from T as much as DS is displaced from S (DT) was considered. Using the calculated lattice parameter, supercells of the conventional diamond unit cell were constructed for each of the studied defects. Additionally, for each site, configurations with different numbers of vacancies, starting from zero up to the number of nearest neighbor carbon atoms, were analyzed. Due to the large size of the calcium atom compared to the carbon atoms, some atomic positions were adjusted to avoid any overlap between atoms. Such was done considering, as radius, half the interatomic distance from the bulk structure from both materials. Carbon atoms which were closer to the impurity than the sum of radii from both species were displaced along the direction connecting the involved atoms, until this minimum distance was met. Additionally, an isolated vacancy was also considered to serve as a comparison bridge with other *ab initio* and experimental works, in addition to allowing the calculation of binding energies.

As the energy cutoff depends on the species involved, i.e., the pseudopotentials and not the number of atoms of each species, the converged values from the bulk calculations were used for the defect calculations. To converge the number of k-points, a $2 \times 2 \times 2$ supercell, hereafter referred to as a x2 supercell, of the unrelaxed H site was used. The convergence was not tested for all sites as the screening of the interaction with defect replicas should be insensitive to the calcium site, as the amount of pristine lattice between two replicas is the same for different sites. The H was selected as it allows all the numbers of vacancies considered. Also, the k-point grids were shifted half a grid step in every direction to avoid the Γ point. This improves the accuracy of the defect calculations by avoiding the bonding and anti-bonding character at this reciprocal point, originating from the artificial interaction between defect replicas [61].

With the same criterium as above, two k-points along each direction were found to be sufficient. This calculation was repeated up to four vacancies, both in the neutral and the +1 charge states (in units of the absolute value of the electron's charge), as both variables could influence the interaction between replicas, leading to more variation of defect energy levels throughout the reciprocal zone, i.e., changing the required k-point sampling. However, the same result was obtained for all tested configurations, two k-points along each direction are sufficient. Next, the formation energy considering different supercell sizes was calculated for the same site without vacancies and for the two charge states. Note that as the size of the cell increases, the size of the first Brillouin zone decreases, therefore, less k-points are required to achieve the same sampling density. For a given supercell size n , if $4/n$ rounded up k-points are used, a sampling density at least as great as the original x2 supercell is guaranteed. As can be seen from Fig. 3.3, the change in formation energy from a x3 supercell to an x4 supercell is 0.38 eV and 0.42 eV, indicating that larger supercells are required. A calculation with an x5 supercell was attempted however, due to memory limitations it did not succeed. For the x4 supercell, with available computational resources, approximately one day was required for a self-consistent calculation, which need to be performed on the order of twenty times for a single structural optimization. Given the number of configurations considered, such is not acceptable. Therefore, x3 supercells were used for the remainder of the study. The k-point scaling previously mentioned, one would determine that two k-points along each direction are also necessary for at least the same sampling density due to the rounding. As reducing to a single k-point would provide a great computational saving, a k-point convergence test was performed for a x3 supercell of the H site without vacancies, and it was determined that one k-point was sufficient to achieve the criterium above mentioned.

Note that, as x3 supercell does not correspond to convergence, the systematic errors in the computational results, just from this effect, are expected to be of the order of a few tenths of electronvolt, thus the current study should be seen as a screening of possibly interesting configurations,

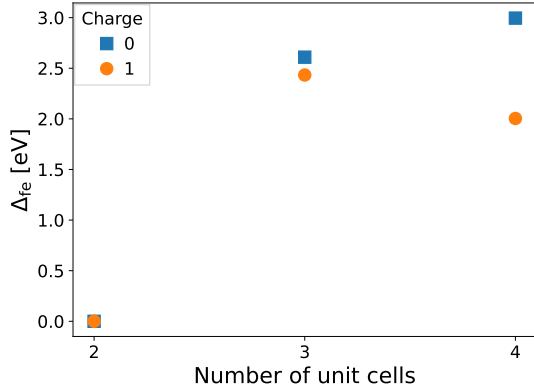


Figure 3.3: Formation energy difference as a function of the supercell size considering the Ca atom at the H site, in the neutral and +1 charge states.

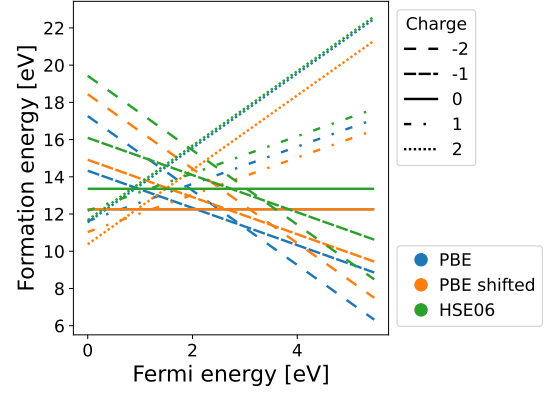


Figure 3.4: Formation energy as function of the Fermi energy for the defect at BC site with two vacancies, for all its charge states. Values presented include charge correction.

and more accurate follow up studies are required for accurate predictions.

For each of the configurations already described, five charge states, from -2 to 2 , were analyzed, resulting in 165 total defects. Structural optimization was performed for every configuration, with 1×10^{-5} Ry/atom and 1×10^{-4} Ry/ a_0 /atom for the total energy and total force stopping criteria, with the PBEsol functional, the converged parameters, x3 supercell, a shifted k-point grid, Gaussian smearing of 0.005 eV and considering collinear spin. A wide variety of structures was obtained covering C_s (26), C_{2v} (56), C_{3v} (23), D_{3d} (24) and T_d (36) point groups. The structures are identified by their initial configuration, i.e., site, number of vacancies and charge, but one should note that the impurity site in the relaxed configurations may not correspond to its initial site. Moreover, some of the relaxed structures of different initial conditions result in similar final structures, as is the case, for example, the S site with one vacancy and BC site with two vacancies, and the S site without vacancies and the BC site with one vacancy. Also, different charge states result in different structures however, for some starting configurations the resulting difference is relatively small, for example for the BC site with two vacancies the calcium stays in the same position while the relaxed carbons atoms show a difference of 0.033 Å for the two extreme charge states. For the H site without vacancies even the calcium shifts by 0.766 38 Å when considering the two extreme charge states.

Using the relaxed structures, the formation energy of all configurations was calculated at the PBE level, and the five charge states of the BC site with two vacancies, the SP and DS sites with one vacancy and the S with 4 vacancies were calculated at the HSE06 level. The latter is still in execution. Due to the computational cost of the hybrid calculations only the Γ point was used for these calculations, as it allows the use of computational tricks to reduce execution time. The PBE computations also use this reciprocal point for comparable results. For charged defects, the correction scheme proposed by Kumagai *et al.* [63] was applied, through the implementation in the Pymatgen package. For this the average site potential was calculated considering half the interatomic distance of the pristine bulks as the radius of each species.

Fig. 3.4 shows the corrected formation energy as a function of the Fermi energy for the BC site with two vacancies, at the PBE and HSE06 level. It also includes the PBE formation energy calculated considering the HSE06 VBM as the reference level for the Fermi energy on top of the charge correction (band edge shifting correction from the Pymatgen library), hereafter referred to as PBE shifted. From

it, one can conclude there is a significant difference between the values obtained at the hybrid level and the remaining calculations. For positive charge states, the shifted VBM leads to closer results to the hybrid functional, but for negative charge states not applying the shift is better. Moreover, depending on the charge state, the difference between the hybrid calculation and the others varies. Therefore, the adiabatic charge states transition energies determined at the PBE level will be different from the hybrid ones. However, in this regard, the shift in the VBM leads to much better results, almost matching the hybrid values (Table 3.1).

Table 3.1: Formation ($E_F = 0$) and adiabatic charge transition energies for the BC defect with two vacancies. Values presented include charge correction.

Charge State	Formation energy [eV]			Transition	Energy [eV]		
	HSE06	PBE shifted	PBE		HSE06	PBE shifted	PBE
-2	19.43	18.44	17.26				
-1	16.09	14.91	14.33	2 1	0.50	0.66	0.07
0	13.36	12.26	12.26	1 0	1.18	1.22	0.64
1	12.18	11.03	11.62	0 -1	2.74	2.66	2.07
2	11.67	10.38	11.55	-1 -2	3.33	3.52	2.94

Looking now just at the stable charge state formation energy of all studied defects (Fig. 3.5), one can see that in general, the higher the number of vacancies the lower the formation energy is. Furthermore, the overlap in energy of many defects is seen. Such is likely due to similar structures

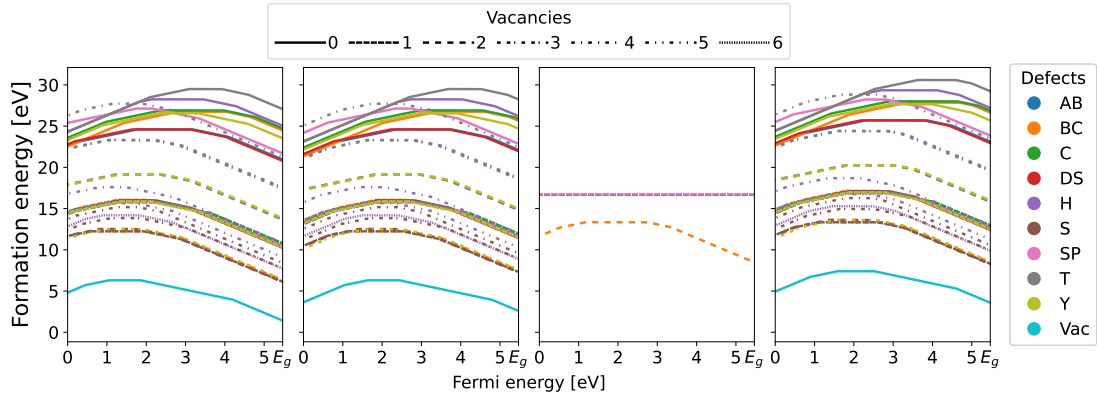


Figure 3.5: Formation energy of the most stable charge state as function of the Fermi energy for all defects. All values are given with charge correction. The plots correspond from left to right to PBE, PBE shifted, HSE06 and PBE with extrapolation from the PBE/HSE06 delta for the BC with two vacancies defect. For the hybrid calculation only the neutral charge state is presented with exception of the BC defect. The single vacancy is referred to as Vac.

after relaxation for different initial configurations. For example, the S site with one vacancy relaxes to the same structure as the BC site with two vacancies, which is similar to the latter. However, this is not always the case, as for example, the AB site with one vacancy has almost the same formation energy as the BC site with one vacancy, but their relaxed structures are different. Note that this overlap is only observed with vacancies which allow more freedom to the Ca atom.

One can also verify that the energy difference, Δ , observed between PBE and HSE06 calculations for the neutral charge states of the BC with two vacancies and the SP and DS with one vacancy defects are similar. Additionally, the relaxed defects do not possess the same symmetry, D_{3d} , C_{2v} and C_s , respectively, as such, one can hypothesize that the correction difference from hybrid calculations, for the remaining defects, should also be similar. Using Δ from the BC defect, the formation energy as function

of the Fermi energy were calculated (right most plot in Fig. 3.5). Comparing the vacancy results with literature, one finds that the obtained formation energies, considering the hybrid extrapolation, are closer to the results in [26] than the original PBE results, but a difference of $\sim \pm 0.5$ eV is observed for all charge states. Such might be due to the use of x3 supercell, while a x4 supercell was used in [26]. In terms of adiabatic charge transition energies, when comparing to results from [26], the hybrid extrapolation leads to an overestimation of the quantities of the same order of magnitude. For this case, PBE results are in better agreement for all transition except from -1 to -2 , nonetheless, it still gives better results on average when compared to hybrid extrapolation.

Table 3.2: Formation ($E_F = 0$) and adiabatic charge transition energies for a single vacancy. Values presented include charge correction. Δ is the energy difference between the HSE06 and PBE calculations for the BC defect with two vacancies.

Charge State	Formation energy [eV]			Transition	Energy [eV]		
	PBE + Δ	PBE shifted	PBE		PBE + Δ	PBE shifted	PBE
-2	14.52	13.53	12.36				
-1	9.93	8.75	8.16	2 1	0.88	1.03	0.44
0	7.40	6.30	6.30	1 0	1.58	1.62	1.04
1	5.82	4.68	5.27	0 -1	2.52	2.44	1.86
2	4.95	3.65	4.82	-1 -2	4.60	4.78	4.20

The binding energies were calculated for all defect complexes considering three scenarios for charged defects: 1) the charge was considered to be already on the Ca defect before the addition of any vacancy; 2) the charge was considered to be captured during the addition of the vacancies; 3) the charge was considered to be supplied by unit charged vacancies, either positive or negative depending on the final charge. Note that these scenarios are not exhaustive as, for example, part of the charge could come from the Ca and the remaining from charged vacancies, or the vacancies could have greater than unit charge. For the scenarios considered, all complexes were found to have positive binding energies, ranging from 10.23 eV to 61.73 eV (S site with 1 vacancy and +2 charge; H site with 6 vacancies and -2 charge), 5.26 eV to 60.78 eV (S site with 1 vacancy and -2 charge; H site with 6 vacancies and +2 charge) and 0.21 eV to 58.47 eV (S site with 1 vacancy and -2 charge; H site with 6 vacancies and neutral charge) for scenarios 1,2 and 3, respectively. For all cases, it was found that having all the charge already on the Ca atom can be energetically more favorable, and is at least equally favorable, than the vacancies bringing all the charge. Note that the values given were calculated with hybrid extrapolation, as such approach provides more accurate formation energies, as discussed before.

Let us now focus on a single defect configuration, the BC site with two vacancies, as it was found to be a major contribution in the EC measurements to be discussed in chapter 4. For this configuration the vertical charge transition energies were calculated and are presented in Table 3.3. The charge corrected formation energies were used in this computation, which although not a rigorous correction [69], provides an estimate with error smaller than the sources already discussed. The resulting values show small differences between absorption (increase in the number of electrons in the system) and emission. This can be attributed to small change in equilibrium structures between charge states, as already mentioned.

For the configuration in question, despite the similar structure for all charge states, significant variation is seen in the Kohn-Sham energy levels (Fig. 3.6). For all charge states, several energy levels are observed near the conduction band. These are likely a result from the over estimation of the band gap from the HSE06 with the used parameters (5.617 eV). They show a majority of the charge density distributed over the carbon atoms, having band-like character. For the -2, -1 and 2 charge states, a

Table 3.3: Vertical charge transition energies for the BC site with two vacancies neutral defect. The values were obtained from the difference of charge corrected formation energy.

Transition	Energy [eV]		
	PBE + Δ	PBE shifted	PBE
2 1	0.60	0.75	0.16
1 2	0.51	0.66	0.08
1 0	1.24	1.29	0.70
0 1	1.20	1.24	0.66
0 -1	2.76	2.68	2.09
-1 0	2.75	2.67	2.08
-1 -2	3.35	3.54	2.95
-2 -1	3.29	3.48	2.89

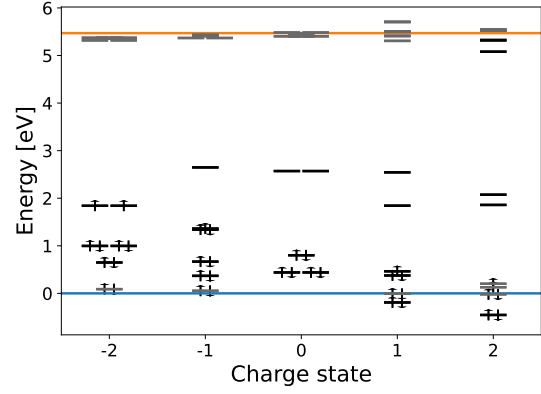


Figure 3.6: Kohn-Sham energy levels inside the diamond's gap for all charge states of the BC site with two vacancies defect, calculated with HSE06. The arrows represent the occupation of each level according to each electron spin. The blue line corresponds to the VBM and the orange one to the experimental conduction band minimum (CBM). The energy levels localized in the defect are represented as black and the remaining as grey.

similar situation occurs near the valance band. The remaining levels show a localized character on the defect (Fig. 3.7). For the neutral configuration, in order of increasing energy, a doubly degenerate

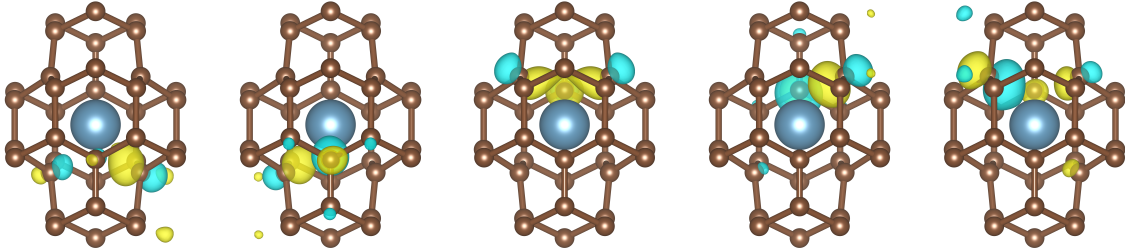


Figure 3.7: Isosurfaces of the charge density contribution of the wavefunctions corresponding to localized states on the BC site with two vacancies neutral defect. The isosurfaces were traced for 0.02 electrons/ $\text{\AA}^3$ and are ordered from left to right in increasing energy. The color represents the sign of the wavefunction, yellow is positive and blue is negative. The isosurfaces are obtained from calculations with the HSE06 functional. The structure is oriented such that the horizontal in-plane axis corresponds to the $\langle 110 \rangle$ direction and the vertical in-plane axis the $\langle \bar{1}11 \rangle$.

filled level is verified followed by a non-degenerate level also filled. A higher lying empty doubly degenerate level is also present. Although not shown, at the PBE level, the energetic ordering of the filled localized states is swapped. Comparing with the remaining charge states one can see that the -2 state is similar to the neutral one, with the order of the lowest lying levels swapped, and a reduced energy separation with the higher energy degenerate level. The remaining charge states show a different behavior. All defect localized levels are non-degenerate and organized into two pairs with closer energy and a fifth level with a bigger energy difference. Note that one of the five localized levels seen in the energy gap for non-positive charge states becomes part of the valence band for the positive charge states. The irreducible representation of the wavefunctions was not determined. However, given

the D_{3d} point group of the defect, the doubly degenerate levels correspond to either the E_g or the E_u irreducible representations, the non-degenerate levels are associated with the A_{1g} , A_{2g} , A_{1u} and A_{2u} , with the pair intuitively being of the same inversion symmetry.

Depending on the charge state, the number of unpaired electrons changes. For odd defect charge one unpaired electron is observed as expected and for even defect charge paired spins are verified with the exceptions of the +2 charge state. For the latter, two non-localized states have an unpaired spin. Such can be intuitively considered reasonable due to the very small energy difference between the two levels, indicating that the cost of pairing the spins is greater than the energy separation of the two levels, however, further calculations are required to confirm such hypothesis. This could be done, fixing the occupation of degenerate levels to the paired and unpaired case to determine the cost of pairing two spins, which could then be compared with the energy delta between the two observed levels.

To better understand the effect of the charge state on the spin polarization of the system, the spin polarization of the charge density was determined for each charge state (Fig. 3.8). Starting from the

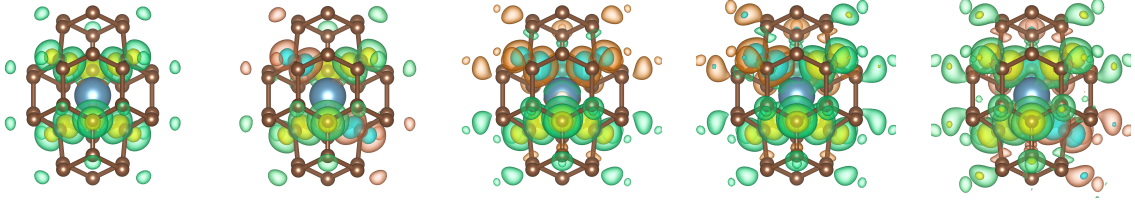


Figure 3.8: Isosurfaces of the spin polarization of the charge density for the BC site with two vacancies defect from -2 to 2 charge. The isosurfaces were traced for $+(-)$ 0.1 electrons/ $\text{\AA}^3$ in yellow (blue) and for $+(-)$ 0.02 electrons/ $\text{\AA}^3$ in green (orange). They are ordered from left to right in order of increasing charge. The isosurfaces are obtained from calculations with the HSE06 functional. The structure is oriented such that the horizontal in-plane axis corresponds to the $\langle 110 \rangle$ direction and the vertical in-plane axis the $\langle \bar{1}11 \rangle$.

neutral state, one can see that increasing the charge results in higher spin density and greater bonding between the calcium and the diamond matrix. This is consistent with the chemical picture since, as electrons are removed, due to the electron affinities of C and Ca, they are removed from the Ca, which then attracts electrons from the neighboring C atoms, i.e., ionic bonding. Additionally, part of the calcium electrons, meaning the charge density closer to the calcium, show spin up polarization while other show spin down polarization, leading to both signs in the spin polarization of the C matrix. For negative charges states, the spin polarization is reduced. Moreover, the spin polarization of the Ca electrons is now all the same, leading to polarization to a single spin outside Ca. For the -1 charge state, no spin polarization was observed, however this is not expected as the -2 charge state still shows it. Such result is to be analyzed.

One of the goals of this work was to calculate the emission spectra of intradefect transitions for the most likely defect configuration. For this the equilibrium structure of both the ground and excited states are required. The former was already calculated for all configurations but the latter still needs to be computed. Additionally, the vibrational modes and their dispersion are also required for such reconstruction, which is computationally very expensive. This is work in progress. The phonon bandstructure of the BC site two vacancies neutral defect was calculated through DFPT as implemented in Quantum ESPRESSO, for an x2 supercell and a single q-point. These parameters, comparing with the work from Jin *et al.* [29] are far from converged, however, this calculation already required 10 full days with available computational resources. The same calculation with an x3 supercell would required on the order of 10 months to complete with the same computational resources.

Chapter Four

Emission Channeling

A natural type IIa diamond sample was implanted at RT with ^{45}Ca (half life 163 days) at 30 keV with a fluence of 3.5×10^{12} ions/cm² for electron EC measurements. The implantation and measurements were performed at CERN's Isotope mass Separator On-Line facility, ISOLDE [91], by Ulrich Wahl, João Guilherme Correia and Ângelo Costa. The experiments were performed as implanted and after annealing at 600 °C and 900 °C. A position-sensitive pad Si detector with 22×22 pixels of 1.3×1.3 mm² each [92] was used, placed 286.8 mm away from the sample. The spot size was approximately 1 mm in diameter resulting in a experimental smoothing described by $\sigma = (0.090 \pm 0.006)^\circ$.

Due to unknown alignment of the surface normal to any crystallographic direction, alignment was difficult, reducing the amount of useful data collected. As such, only the $\langle 110 \rangle$ and $\langle 211 \rangle$ directions as implanted and after 900 °C annealing have sufficient counts for proper statistics. Moreover, from the occupation of lattice sites found for this experiment and discussed below, the $\langle 111 \rangle$ and $\langle 100 \rangle$ patterns are expected to show such weak effects that they are almost impossible to find.

To extract possible lattice sites and their respective occupation fractions that led to a pattern, the experimental result has to be fitted against a library of simulated patterns. The library used in this work was precomputed containing patterns from $\pm 3^\circ$ with steps of 0.05° for both angular axis and for $\langle 110 \rangle$ and $\langle 211 \rangle$ directions. Besides the sites discussed in chapter 3, the simulated library also contains patterns considering displacements, D , from one interstitial site towards another in steps of 0.05 or 0.1 of the total displacement, depending on the case. At 293 K diamond has a one-dimensionally projected root mean square displacement $u_1(C) = 0.0435 \text{ \AA}$, giving a Debye temperature of $T_D = 1860 \text{ K}$ [93]. For calcium $0.03491 \text{ \AA}$ was used. This value corresponds to $u_1(^{67}\text{Cu})$ for which the many-beam simulations had already been computed. It is not feasible to repeat the calculation for every impurity as it requires several months. Additionally, for Ca, assuming $T_D(^{45}\text{Ca}) \sim T_D(^{12}\text{C})\sqrt{12/45}$ [35], and considering an harmonic oscillator model of frequency $\omega \sim k_B T_D / \hbar$, one gets an estimate of $u_1(^{45}\text{Ca}) = 0.03613 \text{ \AA}$ which is only marginally different. For the S and BC sites, patterns varying $u_1(^{45}\text{Ca})$ from $0.01 \text{ \AA}$ to $0.95 \text{ \AA}$ were also considered. They model a Gaussian distribution around such sites over the thermal distribution. In total, 245 simulated patterns were considered for each crystallographic direction.

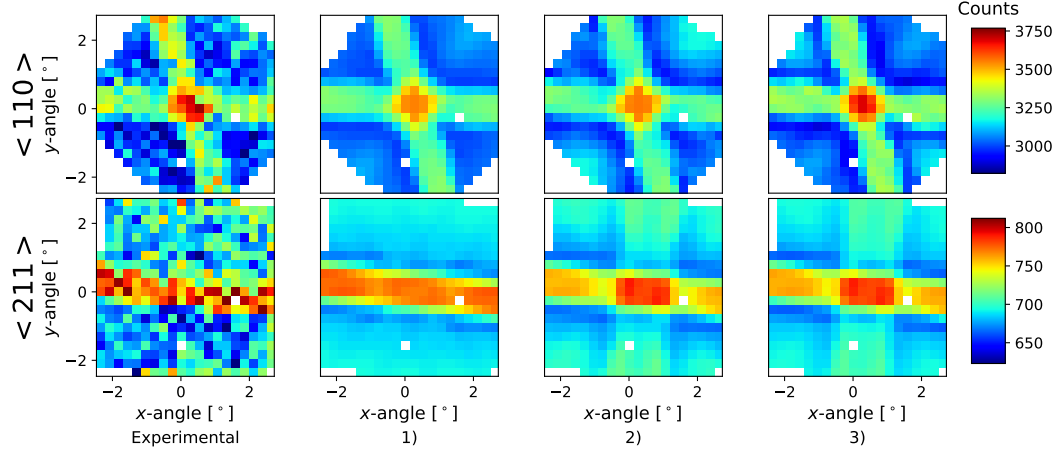
To fit the experimental patterns the PyFDD software [94] was used. To execute a fit, bad pixels from the detector are ignored and an initial guess for the pattern orientation is given. The angular range was limited to $\pm 2.7^\circ$ due to this orientation.

The experimental pattern might be due to a single site or a combination of sites, thus creating a sizable search space, 14 766 395 possible combinations for the library used and considering up to three-site fits. To narrow down the search to plausible physical models a systematic procedure was employed. First a single-site fit was performed for all patterns in the library. The results were filtered

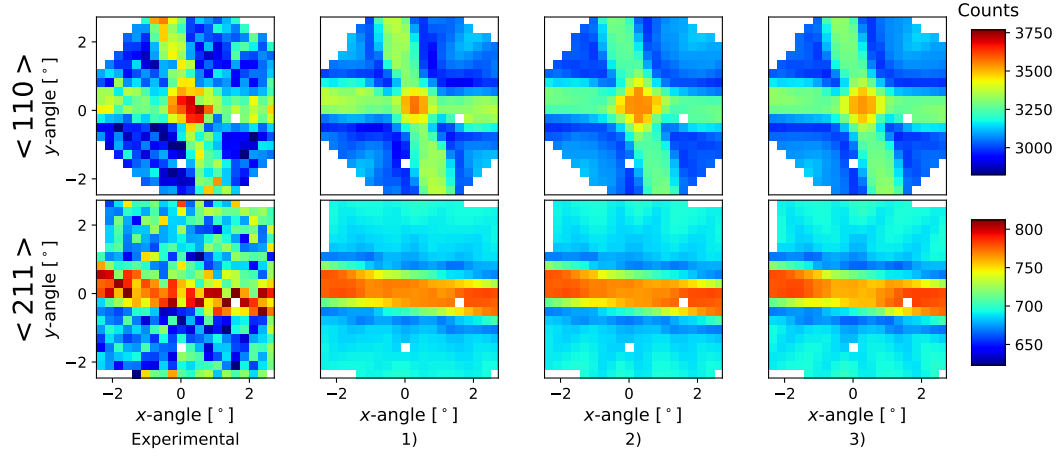
by physical considerations. First, the fractions resulting from the fit had to be consistent for both directions, which was translated to the absolute value of the difference between the relative fraction of each site in each direction being less than 10 %. Note that in a single-site fit, as the relative fractions are always unity, no pattern is excluded. Second, fits resulting in exactly 0 and 1 for the corresponding fraction were discarded, as the former represents no contribution from the pattern and the latter represents no random fraction which is not physical, as background sources, described before, are certainly present in experimental conditions. Values outside $[0, 1]$ are not allowed by PyFDD during the fitting process. Also, fits for which the fitting algorithm failed were discarded.

The filtered patterns were then grouped. Here a group contains the simulated patterns of two interstitial sites and the displacements between the two. For the BC and S sites, the various values of $u_1(Ca)$ also constituted a group each. The groups were scored using a scoring function applied to the average reduced chi square χ_{red}^2 over the crystallographic directions of all group elements. A wide variety of scoring functions can be used such as the median or the mean of the scores of the group elements. In this work the mean after the removal of statistical outliers was used. From the limited experience gained by fitting the current data it was found that the results were similar compared to the mean and the median, giving the same top groups but with the ordering slightly changed. Thorough testing of the effects of this choice ought to be done but this is out of the scope of this work. With the group scores, new fits with two sites were performed. The elements of the three highest scoring groups were considered for one site, and the entire library except the aforementioned for the other. The three best groups were used instead of just the first to minimize the influence of the scoring function and because the ordering might change considering an additional site. The filtering and scoring procedures were repeated to select the patterns for a three-site fit. In this case only the elements of the best group were considered due to computational time limitations. The results were once more filtered and scored. No more than three-site fits were considered due to little improvement in the group metric on three-site over two-site fits.

Fig. 4.1 shows the as implanted experimental patterns obtained as well as the fits of the best element of the three highest scoring groups. For the single-site fits, looking at the $\langle 110 \rangle$ direction one would conclude that despite the ordering, the third ranked group led to a better result as it shows contrast similar to the experimental pattern, both in the central region as well as in the low count borders. However, in the top-left and bottom-right corners, corresponding to the (110) planes, it shows an increase in counts relative to the other corners which is not seen in the experimental pattern. Additionally, in the $\langle 211 \rangle$ direction it results in a central region with higher counts compared to the high-count band observed, which corresponds to the (111) planar effects. Such is not the case in the experimental pattern. The best group does not show any such problems, however it has much lower contrast. Also, it can explain a larger fraction of the observed pattern (Table 4.1). Note that the specific pattern presented corresponds to an uncorrected fraction of 94 % which is too high, resulting in corrected fraction over 100 % with typical correction factors, as such, another element of this group has to be considered. Looking now at the two-site fits in the as implanted state, one can see the addition of another site worsened the fit for the high-count central region of both directions. Its size is reduced for $\langle 110 \rangle$ and a low spot is now observed for $\langle 211 \rangle$. Such is not the case for the fit from second ranked group, which is very similar to the best single-site fit, but with marginally better contrast in the low count region. Additionally, from Table 4.1, the relative fractions of the two-site fits are close to one for one of the sites and zero for the other. Therefore, the inclusion of another site provides little increase in explanation power of the model and thus, the single-site fit is preferred, indicating that in the as implanted state Ca shows a distribution around the BC site. The u_1 of the distribution can



(a) Single-site fits: 1) BC; 2) SP $\rightarrow$ C; 3) S $\rightarrow$ BC.



(b) Two-site fits: 1) (S $\rightarrow$ BC) + BC; 2) C + BC; 3) (DT $\rightarrow$ C) + BC.

Figure 4.1: Best fitting pattern of each each of the three highest ranking groups, as implanted. The corresponding parameters are presented in Table 4.1.

be estimated considering the variation of the metric with this parameter (Fig. 4.2). For the $\langle 211 \rangle$ direction, smooth behavior is observed as a function of u_1 and a broad minimum is observed. For the $\langle 110 \rangle$ direction, jumps are observed near the minimum indicating difficulties in the automated fitting procedure of PyFDD. Also, a significant fraction of the results was excluded by the filtering process (crosses in Fig. 4.2), indicating that the criteria used might be too strict. A likely culprit is the consistent occupation fraction criterion because, if n sites are occupied, the occupation fraction in a fit with less than n sites can change significantly from one direction to another, as the relative importance to the pattern of each site in each direction can be different. Further investigation into this effect is required. Considering the 90th percentile of the metric of the filtered fits one gets $u = (0.39 \pm 0.01) \text{ \AA}$, where the uncertainty is given as the standard error. Note, that such estimate is affected by the problems already discussed for $\langle 110 \rangle$, thus the given standard error is likely an underestimation of the real value, because the minimum verified for the $\langle 211 \rangle$, which has smooth behavior, is broader.

Following annealing the behavior does not change significantly as similar angular anisotropy is observed for both directions (Fig. 4.3). The total number of counts per pixel changes but such is a consequence of different measuring times for both situations. Comparing the fitted patterns, a similar situation to the as implanted state is observed for the single-site fits, where the third-ranked shows

Table 4.1: Parameters of the best fitting pattern of each of the three highest ranking groups, for the as implanted state. The total fraction corresponds to the sum of non-random fractions and is not corrected for any background contribution. The relative fractions correspond to the fractions from the fit relative to the total fraction.

Number of sites	Rank	Description	D	u_1 [Å]	Relative fractions	Total fraction	χ_{red}^2 $\langle 110 \rangle$	$\langle 211 \rangle$
1	1	BC	0.0	0.44	1.00	0.94	2.61	1.17
	2	SP $\rightarrow$ C	0.1	0.03491	1.00	0.39	3.70	1.34
	3	S $\rightarrow$ BC	0.6	0.03491	1.00	0.25	3.31	1.34
2	1	S $\rightarrow$ BC	0.75	0.03491	0.02	0.67	2.53	1.16
		BC	0.0	0.36	0.98			
	2	C	0.0	0.03491	0.05	0.72	2.55	1.16
		BC	0.0	0.36	0.95			
	3	DT $\rightarrow$ C	0.8	0.03491	0.13	0.60	2.57	1.16
		BC	0.0	0.28	0.87			

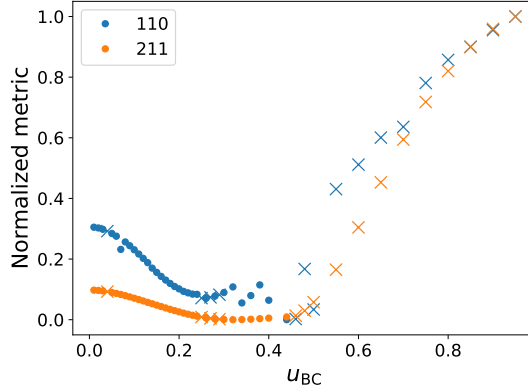


Figure 4.2: Metric (average χ_{red}^2 over directions) normalized (to the $[0, 1]$ interval) over all group elements as function of u_1 of the BC site used in a single-site fit to the as implanted patterns. The crosses correspond to patterns excluded by the filtering process.

the best contrast but suffers in anisotropy along the (111) plane. The best-ranked fit shows lower contrast and more uniform (111) planar effects but with too little counts. Considering two-site fits significantly improves the situation for $\langle 211 \rangle$ and also has contrast closer to the experimental data for $\langle 110 \rangle$. Comparing with the three-site fits, one sees visually worse results with the exception of the fit from the third-rated group which is very similar two the two-site patterns. Such shows that several site combinations provide fits of similarly good quality, so it is not possible to favor one particular case, however, they point towards a larger contribution from an intermediary displacement from S to BC and a contribution from in between DS and C. There is also a possible contribution from a distribution around BC (third-ranked three-site fit), but with u_1 smaller than the as implanted state. As can be seen from Table 4.2, the relative fractions either the two- or the three-site fit have a large contribution close the BC site, consistent with a small change local environment of the Ca during the annealing.

Considering the three-site fit, one can hypothesize that the Ca further away from the BC moves first and towards the DS or S site. Looking at the formation energies obtained in chapter 3, this is not expected as the BC and S achieve lower energies. However, such is only the case if complexes can be formed. If such is not the case, looking at the case without vacancies, the DS site provides an energetic advantage over the BC site, which is even greater for the S site. As such, one can hypothesize movement

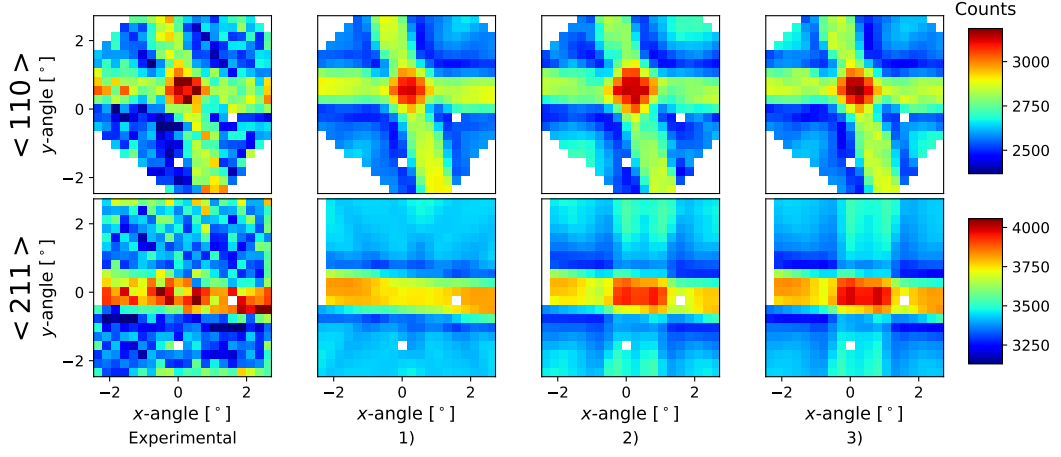
Table 4.2: Parameters of the best fitting pattern of each of the three highest ranking groups, after annealing at 900 °C. The total fraction corresponds to the sum of non-random fractions and is not corrected for any background contribution. The relative fractions correspond to the fractions from the fit relative to the total fraction.

Number of sites	Rank	Description	D	u_1 [Å]	Relative fractions	Total fraction	χ^2_{red} $\langle 110 \rangle$	$\langle 211 \rangle$
1	1	BC	0.0	0.28	1.00	0.57	2.51	4.46
	2	SP $\rightarrow$ C	0.1	0.03491	1.00	0.46	3.17	4.79
	3	S $\rightarrow$ BC	0.6	0.03491	1.00	0.29	2.59	4.81
2	1	S $\rightarrow$ BC	0.65	0.03491	0.66	0.43	2.55	4.31
		DS $\rightarrow$ C	0.5	0.03491	0.34			
	2	S $\rightarrow$ BC	0.65	0.03491	0.56	0.39	2.52	4.37
		DS	0.0	0.03491	0.44			
	3	SP	0.0	0.03491	0.50	0.41	2.43	4.43
		BC	0.0	0.14	0.50			
3	1	T $\rightarrow$ H	0.1	0.03491	0.01	0.40	2.42	4.07
		S $\rightarrow$ SP	0.9	0.03491	0.49			
		BC	0.0	0.12	0.50			
	2	S $\rightarrow$ SP	0.9	0.03491	0.55	0.37	2.43	4.14
		S	0.0	0.27	0.02			
		BC	0.0	0.03	0.43			
	3	S $\rightarrow$ BC	0.6	0.03491	0.41	0.42	2.51	4.36
		DS $\rightarrow$ C	0.3	0.03491	0.26			
		BC	0.0	0.18	0.33			

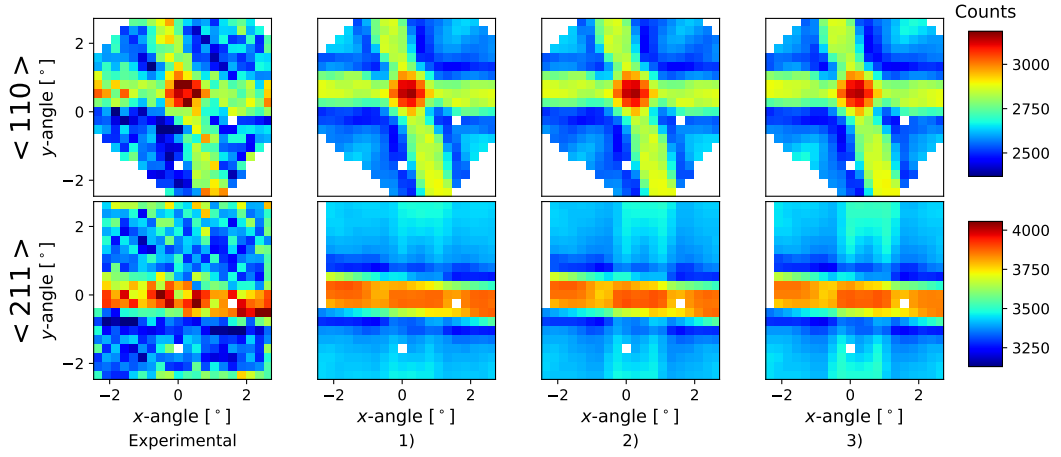
from the BC to the S that passes close to DS, likely due to a higher energy barrier in between BC and S, than in between BC and DS and DS and S. Such implies that a migration of the vacancies from the Ca sites during annealing is consistent with DFT and EC results. Due to the positive binding energy of Ca defects, such would only happen if there was competing defect. The most likely candidate are C interstitials. N is also possible as it preferentially captures vacancies during annealing [9], however, from simulation of ion implantation, shown in chapter 5, the number of vacancies created is far too great for N to be a major culprit in this type IIa diamond sample. Such hypothesis can be verified or negated by performing EC experiments with high purity diamond, and NEB calculations could be used to check the described path. Note that the DS site without any vacancies is not thermodynamically stable, as during structural relaxation it converged into the AB site. Such, might be the cause of the relatively low fraction of this site in the three-site fit, as well as its displacement from the ideal DS site.

An alternative hypothesis is that the lowest energy configuration was not included in the DFT calculations. Due to the large number of vacancies after implantation and the positive binding energies obtained, one could consider complexes with even more vacancies. Starting from BC with two vacancies, for the addition of the next closest vacancy, in the orientation of Fig. 3.2, one would tentatively expect that the calcium would be displaced towards SP. Such would be consistent with the third-ranked two-site fit and the first- and second-ranked three-site fits.

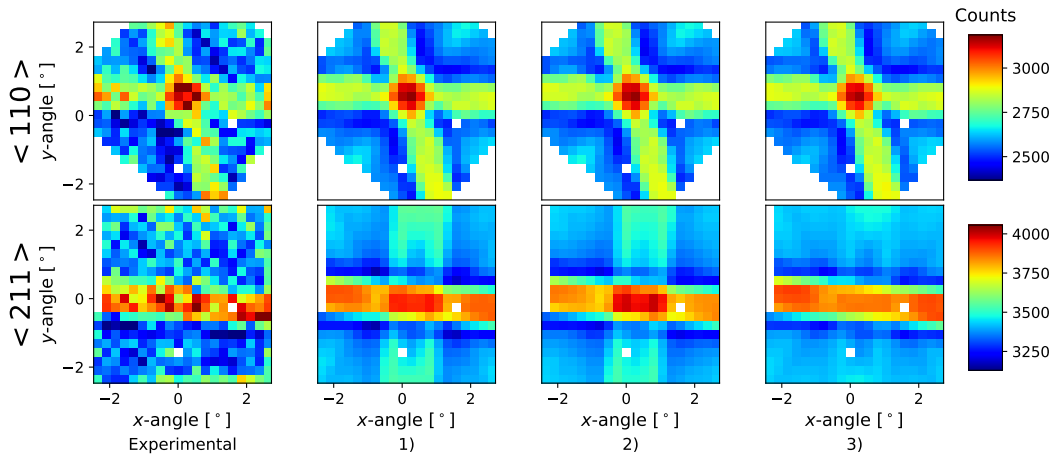
Note that, although the uncorrected total fractions from non-random fractions are generally less than 50 % for the after annealing patterns, they can be close to 100 % after correction. Due to the loss of counts orienting the sample, the count rate at the end of the measurement was very low, therefore, the background may account for a large percentage of the collected pattern, which could result in correction factors greater than 2. New measurements are currently in progress to improve this.



(a) Single-site fits: 1) BC; 2) $SP \rightarrow C$; 3) $S \rightarrow BC$.



(b) Two-site fits: 1) $(S \rightarrow BC) + (DS \rightarrow C)$; 2) $(S \rightarrow BC) + DS$; 3) $SP + BC$.



(c) Three-site fits: 1) $(T \rightarrow H) + (S \rightarrow SP) + BC$; 2) $(S \rightarrow SP) + S + BC$; 3) $(S \rightarrow BC) + (DS \rightarrow C) + BC$.

Figure 4.3: Best fitting pattern of each each of the three highest ranking groups, after 900 °C annealing. The corresponding parameters are presented in Table 4.2.

Chapter Five

Optical Measurements

For the optical measurements four free-standing single-crystal type IIa diamond samples grown by CVD were used. The samples were acquired from Element Six (marketed as single-crystal plate) and are $3\text{ mm} \times 3\text{ mm} \times 0.25\text{ mm}$. They are rated at less than 1 ppm and 0.05 ppm of N and B, respectively, and with $\{100\}$ top faces [95]. Unless otherwise stated, the heat treatments and measurements described in this chapter were performed at University of Aveiro.

Three of the samples were uniformly implanted at KU Leuven by Malven Tunhuma and Lino Pereira, with stable Ca at 50 keV and different fluences: $4 \times 10^{12}\text{ ions/cm}^2$ (diamond A), $2 \times 10^{13}\text{ ions/cm}^2$ (diamond B), $1 \times 10^{14}\text{ ions/cm}^2$ (diamond C). The remaining sample, diamond D, was used as control during annealing and thus left without implantation.

The SRIM software [39] was used to determine the expected implantation profile. The default parameters for C and Ca were used considering a density of 3.51524 g/cm^3 for diamond [96]. For the implantation conditions described, an average penetration depth of $283\text{ \AA}$ with a straggle of $80.7\text{ \AA}$ was obtained. The maximum concentration of Ca corresponds to $4.79 \times 10^5\text{ (atoms/cm}^3\text{)}/(\text{ions/cm}^2)$ and the creation of ~ 430 vacancies is expected for each implanted ion.

As mentioned in chapter 2, thermal annealing is required after ion implantation and it was done as follows: the sample was sealed in a quartz tube with five Ar purges and a pressure less than $1.33 \times 10^{-5}\text{ mbar}$ (lower limit of the sensor used). With the tube sealed at one end and connected to the vacuum system at the other, the vacuum was pulled. The sample was then isolated from the rest of the vacuum system by a valve. No further pressure measurements were performed after this stage. The tube was then sealed at the valve end with an oxy-acetylene torch. After sealing, the sample was heated in a tubular oven to 900°C during 30 min, starting with the oven hot. After which it was left to cool at RT for about 30 min. These parameters were selected to be comparable to what is experimentally viable in the EC setup, as to preferentially induce the same Ca positions for both sets of measurements. Diamond A was also annealed as described before implantation to verify if it led to any change in the set of optical measurements performed.

In the following sections measurements will be grouped according to the treatment the corresponding samples had received. In chronological order: before implantation and annealing (BIBA); before implantation and after annealing (BIAA); after implantation and before annealing (AIBA); after implantation and annealing (AIAA).

PL measurements were performed both at RT and at low temperature (14 K) (LT) using as excitation the laser lines at 325 nm (power density $I_0 < 0.6\text{ W/cm}^2$) from a Kimmon IK Series He-Cd laser, 405 nm and 532 nm from solid-state lasers. The latter two have controllable power output, which was measured with a Ophir StarLite laser power meter. After excitation, the light emitted from the

diamonds was dispersed by a Spex 1704 monochromator (1 m, 1200 gr/mm) and detected by a cooled Hamamatsu R928 photomultiplier. RT PL and photoluminescence excitation (PLE) spectra were also recorded for all samples using an Fluorolog-3 Horiba Scientific setup with a 450 W Xe lamp followed by a double additive grating Gemini 180 monochromator (1200 gr/mm and 2 x 180 mm) in the excitation and a triple grating iHR550 spectrometer in the emission (1200 gr/mm and 550 nm). Appropriate high-pass filters were also used, however no signal was observed above system artifacts due to the low sample luminescence combined with the low excitation density. RT micro-Raman and micro-PL measurements were also performed using a Horiba Jobin Yvon HR800 spectrometer equipped with a 600 gr/mm grating, with the 442 nm laser line, using a 50x objective in multiple positions for each sample. These measurements are equivalent to their macroscopic counterparts but only collect light from a spatial volume of a few micro-meters cubed. Transmittance measurements were performed with a Shimadzu UV-2100 spectrometer from 190 nm to 850 nm. The infrared absorption was also measured using a Bruker Vertex 80v FTIR spectrometer at a magnification of 10x. For diamond B, PL measurements with excitation power and temperature were also performed.

For the laser-excited PL measurements optical filters were used depending on the excitation wavelength. Unless otherwise state, all spectra with 325 nm were collected using an appropriate notch filter after the laser and a high-pass filter at the slit of the monochromator. For the 405 nm and 532 nm excitation only an appropriate high-pass filter was used. Moreover, all laser-excited PL spectra were corrected for the optics and spectral response of the system.

5.1 STRUCTURAL CHARACTERIZATION

Fig. 5.1 shows photographs of the samples AIBA and AIAA (BIBA and BIAA for diamond D) taken with an optical microscope at 50x magnification. As can be seen, the samples were initially

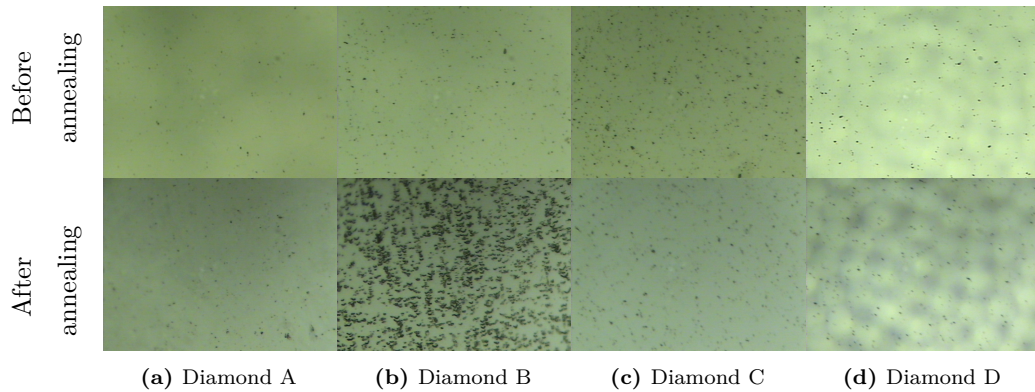


Figure 5.1: Optical microscope photos of all diamond samples AIBA and AIAA (BIBA and BIAA for diamond D) at 50x magnification.

visibly similar, being mostly clear with a distribution of black spots. After the annealing, all samples remained similar with exception of diamond B, for which an increase in size and density of the spots was observed. Due to this increase, the possibility that such spots were surface graphitization due to oxygen [45] was initially entertained, however, from interference effects present in the Fourier transform infrared spectroscopy (FTIR) spectra discussed below, the thickness of such spots is expected to be in the micro meter range. If it was graphite, it should be detectable in the Raman measurements performed, however no vibrational modes of graphite were detected. As these spots were also observed in the virgin state of diamond D it is possible that they are carbon compounds adsorbed during the

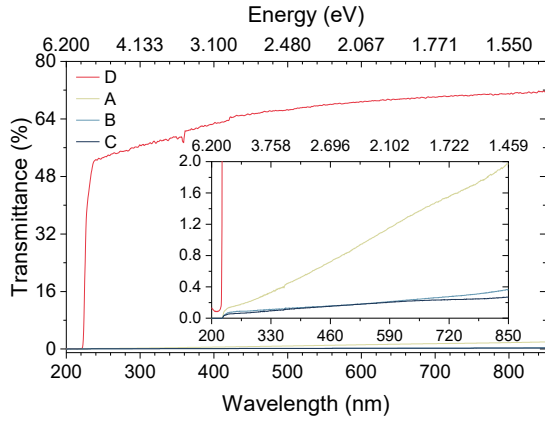


Figure 5.2: RT transmittance for all samples AIAA. An artifact of the lamp change of the particular spectrometer is also present at 360 nm, caused by the different intensities of the two lamps used to cover the spectral range.

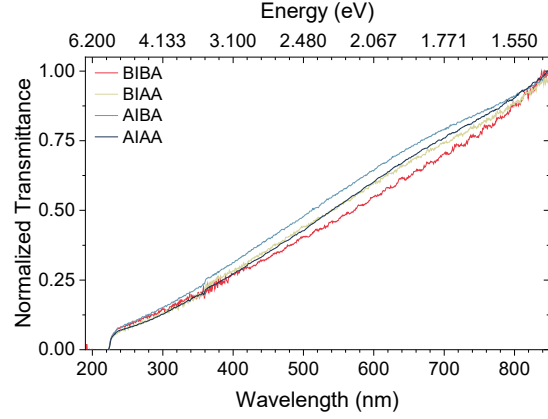


Figure 5.3: RT normalized transmittance for diamond A at the different processing stages. An artifact of the lamp change of the particular spectrometer is also present at 360 nm, caused by the different intensities of the two lamps used to cover the spectral range.

growth process. The increase of such contamination, during the annealing performed, is plausible, as the samples were cleaned using ethanol, allowing for residual ethanol to be present during annealing.

In visible absorption (Fig. 5.2) the characteristic diamond band edge can be seen at ≈ 223 nm (≈ 5.56 eV). No other absorption features are present in the spectra, which confirm the classification of the samples as type IIa diamond [97]. The transmittance of the implanted diamonds is much lower than that of the virgin sample, and it seems to decrease with increasing implantation fluence, however, samples B and C, despite a difference of half an order of magnitude in fluence, show similar transmittance. A possible explanation is the transformation observed for sample B. The behavior at the different processing stages is similar for diamond A (Fig. 5.3), meaning that the used annealing and implantation parameters do not result in novel active centers in the studied spectral region. The annealing before implantation led to a broad increase in relative transmittance. Another broad increase was seen after implantation, and it was reversed after subsequent annealing, i.e., within detectability by this technique, the annealing was effective at restoring the lattice. For the remaining samples no information is available before implantation, as they were received already implanted. Comparing the before and after annealing visible absorption (Fig. 5.4), small differences, as the ones described before, are observed for diamonds C and D (not implanted), but not for diamond B, for which, the absorption slope changes considerably after and before annealing, possibly due to the modifications this sample suffered.

In the Raman spectra of all samples AIAA (BIAA for diamond D) (Fig. 5.5), three sharp vibrational maxima were identified at $(1330.9 \pm 0.5) \text{ cm}^{-1}$, $(2463 \pm 5) \text{ cm}^{-1}$ and $(2666 \pm 2) \text{ cm}^{-1}$, and three broad contributions at $(1670 \pm 40) \text{ cm}^{-1}$, $(1910 \pm 20) \text{ cm}^{-1}$, $(2299 \pm 10) \text{ cm}^{-1}$. The uncertainties given are the sample standard deviation from the variation of the respective spectral features for the different samples and measurement locations. The $(1330.9 \pm 0.5) \text{ cm}^{-1}$ line has a calculated FWHM of $(8.5 \pm 0.2) \text{ cm}^{-1}$, $(8.4 \pm 0.8) \text{ cm}^{-1}$, $(7.94 \pm 0.02) \text{ cm}^{-1}$ and $(8.3 \pm 0.4) \text{ cm}^{-1}$ for diamonds A, B, C and D, respectively. These values were extracted from Voigt least squares fits with linear baseline. Such feature corresponds to the first order Raman scattering resulting from triply degenerate $\text{TO}(X)$ phonons [15, 20], and, as can be seen, its width is very similar in all samples. The remaining lines correspond to second order Raman scattering, overtones and two-phonon processes (Table 5.1).

Table 5.1: Experimentally observed Raman lines and the corresponding theoretical phonon frequency values, as well as experimental values obtained by Solin *et al.* [15]. The phonon modes are labeled by the corresponding high symmetry point(s) in the first Brillouin Zone.

Process	Theory (cm^{-1})	This work (cm^{-1})	Solin <i>et al.</i> [15] (cm^{-1})
TO(X)	1324 ^a	1330.9 ± 0.4	1332.5 ± 0.5
LA(L) + TA(L)	1632 ^b	1670 ± 40	
A2(W) + A1(W)	1949 ^b	1910 ± 20	1907 ^d
L(X) + TO(X)	2319 ^b	2299 ± 10	2254
2 $\Sigma(0)$	2460 ^c	2463 ± 5	2461
2O(Γ)	2646 ^b	2666 ± 2	2667

^a [98] ^b [22] ^c [15] ^d Calculated by Windl *et al.* from Solin *et al.* data

In terms of the second order spectral region, the samples show variation amongst them, especially diamonds B and D. Results for diamonds A and C are very close and substantially lower than diamond D, almost 5 times less normalized intensity in terms of average. Sample B shows, in some spots, intensity within the variation of sample D, indicating that they have closer structures, i.e., the experimental discrepancy observed for this sample might also have allowed for more structural repair. Diamonds B (only AIAA) and D also show another sharp feature slightly below the first order Raman line, only present for some measured spots, at $(1293 \pm 2) \text{cm}^{-1}$. This position is compatible with the first order Raman scattering considering ^{13}C [16, 99, 100]. Additionally, the shift observed for first order Raman is slightly larger than the one expected for a concentration of ^{13}C in the natural isotopic ratio, 1.1 % [16, 99, 100]. From Chrenko's [16] results, assuming that it is the only contribution, a concentration of $(9 \pm 2) \%$ ^{13}C would explain the observed deviation, which is much larger than expected. Such might be caused by systematic errors in the measured values, however, they should be small, as the apparatus was calibrated against the same reference sample before each measurement session. If these features are indeed from ^{13}C , the concentration of this isotope in the samples is not uniform as the intensity of the $(1293 \pm 2) \text{cm}^{-1}$ line changes with the location within the sample. Also, the Raman

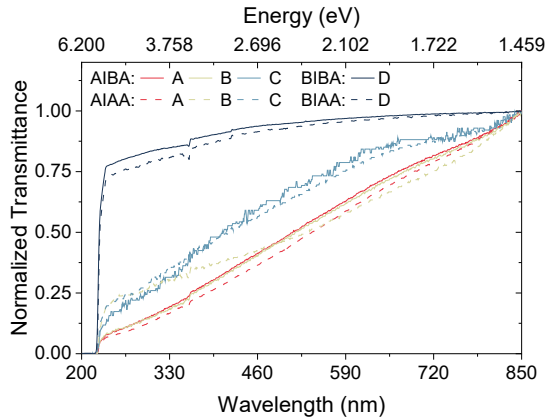


Figure 5.4: RT normalized transmittance for all samples at the different processing stages. An artifact of the lamp change of the particular spectrometer is also present at 360 nm, caused by the different intensities of the two lamps used to cover the spectral range. Normalization is relative to the intensity at 850 nm.

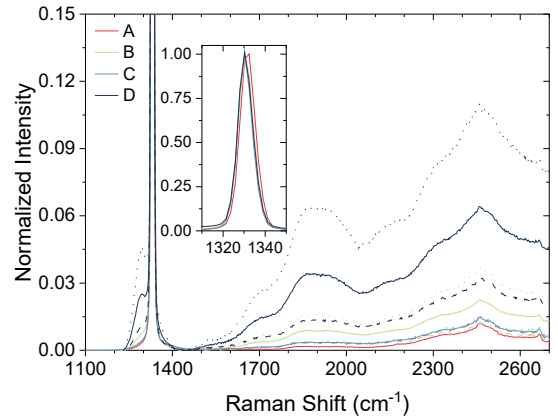


Figure 5.5: RT Raman spectra of all samples AIAA (BIAA for diamond D) averaged over different measurement locations. The dashed lines correspond to the maximum and minimum values, over locations, observed for each sample. A linear baseline was fitted near the first observed line and subtracted. A zoom of this line is also shown in the inset.

spectra of diamond A show no significant difference over the processing stages (Fig. 5.6). The relative intensity of the second order signal varies but less than variability of different measurement spots.

From FTIR spectra of all samples one can see that the characteristic type IIa diamond infrared absorption is observed [101] with additional contributions superimposed (Fig. 5.7). For all samples,

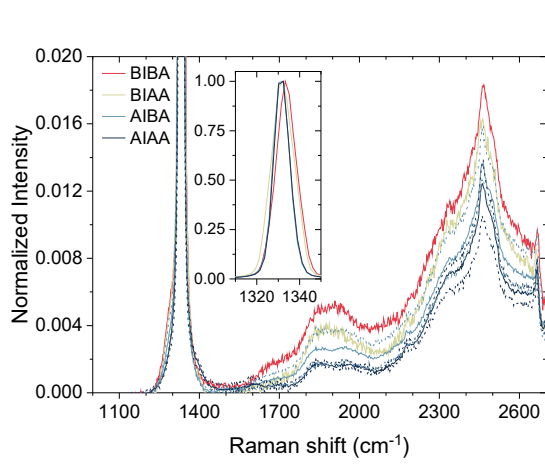


Figure 5.6: RT Raman spectra of diamond A for the different processing stages. Intensity normalized to the first order diamond Raman line, better shown in the inset. A linear baseline was fitted near this line and subtracted. The dashed lines correspond to the maximum and minimum values, over locations, for the corresponding treatment stages.

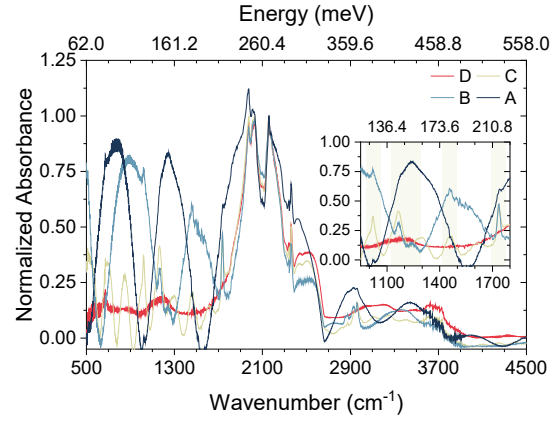


Figure 5.7: RT FTIR normalized infrared absorbance spectra of all samples AIAA (BIAA for diamond D) for the different processing stages. Air water vapor contributions were removed as implemented by the collection software OPUS from Bruker. An exponential baseline was adjusted and subtracted. The inset shows a zoom in one-phonon region of diamond, with shaded areas highlighting matching maxima for the three implanted samples.

oscillations, of differing amplitudes and frequencies, are observed. The lower frequency oscillations, considering normal incidence, are consistent with interference from a material with thickness of around $5\text{ }\mu\text{m}$ for samples A and B, and $15\text{ }\mu\text{m}$ for samples C and D, calculated with the refractive index of diamond. It could be caused by the surface contamination previously described. Note that the refractive index of the associated compound(s) might be different from diamond, however, considering a range of refractive index 1 to 5, one still gets thickness of the order of a few micrometers. Additionally, oscillations of periodicity $\sim 8\text{ cm}^{-1}$ are seen and correspond to a diamond thickness close to 0.25 mm which is the sample thickness. Especially distinct for diamond D, the oscillations are less clear for diamonds A, B and C indicating higher surface roughness. Three lines from 2340 cm^{-1} to 2360 cm^{-1} are observed for all samples and are likely an artifact resulting from CO_2 [102].

For sample D, a small band is observed at approximately 1170 cm^{-1} with some structure. This spectral region is associated with A, B and C centers [103]. Due to the high frequency oscillations in the FTIR signal, spectral decomposition into each center's component, as described in [103] was not possible, however, this indicates the presence of such defects in the sample, even before any modification done during this work, which implies a higher concentration of N than expected for type IIa diamond. It is worth noting that no abrupt cutoff was seen in FTIR measurements at the one-phonon maximum energy of diamond, $\sim 165\text{ meV}$, as was the case in [103]. Such cutoff was observed for two-phonon phenomena in the Raman measurements ($(2666 \pm 2)\text{ cm}^{-1}$ line).

For the implanted diamonds, the N center structure is not visible, but it could be underneath the previously mentioned oscillations. Instead, five lines were observed at $(1019 \pm 2)\text{ cm}^{-1}$, $(1170 \pm 8)\text{ cm}^{-1}$,

$(1250 \pm 20) \text{ cm}^{-1}$, $(1450 \pm 3) \text{ cm}^{-1}$ and $(1740 \pm 3) \text{ cm}^{-1}$. The first two have been assigned to intrinsic point defects (vacancies and interstitials) [103]. The $(1250 \pm 20) \text{ cm}^{-1}$ line is assigned to C–N vibration with a nitrogen-vacancy pair [101]. The $(1450 \pm 3) \text{ cm}^{-1}$ has been reported in literature in irradiated and annealed diamonds, however, not for type IIa diamond [104]. It has been hypothesized that it is due to a substitutional N that exchanges its position with an interstitial C during the annealing [104]. McNamara *et al.* [101] also observed a line at 1450 cm^{-1} and attributed it to O–CH₃, N–CH₃ deformations and sp^3 CH₂ scissor. N was already expected as discussed before. O is also plausible due to the precursors used in CVD growth of diamond, and it is also reinforced by the presence of the line at $(1740 \pm 3) \text{ cm}^{-1}$ assigned to the C=O stretch [101]. The presence of H in the samples is possible. The structure observed near 2960 cm^{-1} has been linked to vibrational modes of H containing defects [6, 101, 105]. Considering the line positions listed by McNamara *et al.* [101], associated with different orbital hybridization, carbon-hydrogen groups and symmetry of the C–H vibrations, a least squares fit was performed to a combination of Voigt profiles with a linear baseline in this spectral region. It was found that the model explains very well the observed signal and the fitted line centers match very closely the expected values [101], supporting this assignment.

Other authors [38, 106] have assigned the C–H vibrations to 1405 cm^{-1} and 3107 cm^{-1} lines, however these are not observed in this work, which is expected since they are not observed in CVD diamond [105]. The spectral features just described are not seen in diamond D, i.e., they were originated during the processing, either by contamination or by optical activation, as hydrogen can easily be incorporated during growth from the CVD precursors. Hydrogen-nitrogen complex defects give rise to lines also in this spectral region [6], but are not seen despite the presence of both elements in the samples.

5.2 PHOTOLUMINESCENCE

The RT PL spectra of diamond A shows a broad luminescence band and one well-defined line is distinguishable at $(575.5 \pm 0.1) \text{ nm}$ (Fig. 5.8). Through the well-established literature of optical defects in diamond, this line can be assigned to the ZPL of the NV center in its neutral charge state [11, 12, 20, 21, 107, 108]. The associated vibronic band is also visible, especially the interaction with a phonon mode of approximately 44 meV. In BIBA conditions this mode is not distinguishable and the band is less intense relative to the ZPL, which means that structural changes occurred during this annealing as previously discussed. After the implantation, no PL signal was observed for diamonds A and C at RT. Diamond B showed no measurable luminescence after implantation but, after subsequent annealing, the nitrogen-vacancy neutral charge state (NV⁰) optical center was observed similar to the luminescence of diamond A before implantation (Fig. 5.8).

Using the same experimental set-up as in the Raman measurements it was also possible to observe the samples' RT micro-PL (Fig. 5.9). The spectral features are much clearer than in the macro PL measurements due to the better collection efficiency of the Raman experimental setup. Two ZPL were identified, the already discussed NV⁰ line and another at 504.6 nm (Fig. 5.9). The latter is assigned to the heat treatment (preceded by irradiation) 3 (H3) center, formed by a vacancy trapped in an A aggregate [11, 20]. Indication of the presence of this type of aggregates was already seen and discussed in the FTIR measurements. As was the case in the macro-PL, almost no influence from the heat treatment was observed. The main difference is the increase in relative intensity of the H3 center ZPL. This could be caused by the annealing process, as, due to the relative migration energies of a vacancy and a substitutional nitrogen, $(2.3 \pm 0.3) \text{ eV}$ and $(5.0 \pm 0.3) \text{ eV}$, respectively [109], and at relatively low annealing temperature, the majority of the diffusion is from the vacancies, which preferentially

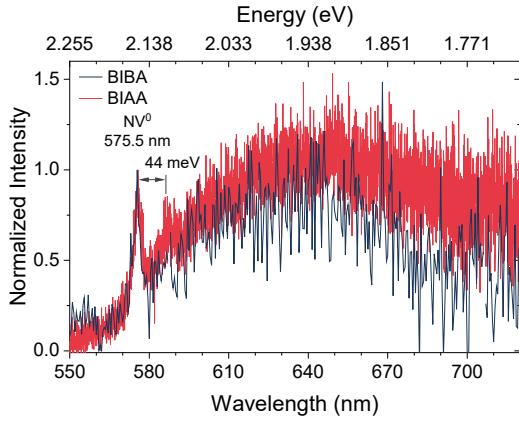


Figure 5.8: RT PL spectra of diamond A for the different processing stages in the spectral region associated with the NV center. Excitation with the 325 nm laser line.

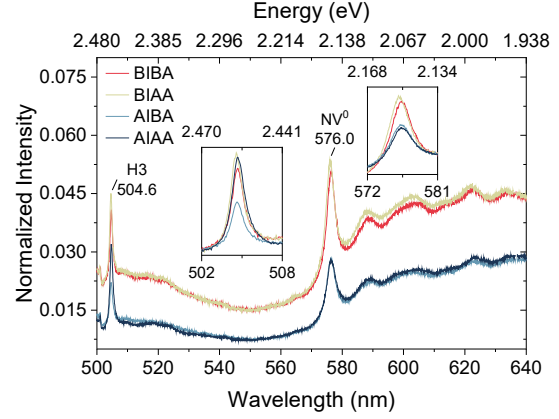


Figure 5.9: RT micro-PL spectra of diamond A for the different processing stages. Intensity normalized to the first order diamond Raman line. Excitation with the 442 nm laser line.

get trapped at nitrogen sites [9]. In this work, only an increase of H3 luminescence was observed, i.e., the vacancies were only trapped at A aggregates, at least at a detectable level. Davies *et al.* [9] also found that A and B aggregates were the only trapping points for type I diamond, which is consistent with no increase in NV intensity. Although a higher concentration of N was found by FTIR, the visible absorption of the samples is consistent with the type IIa classification from the supplier [97]. In type IIa diamond, Clark *et al.* [8] and Davies *et al.* [9] suggest that the main process should be the formation of vacancy pairs. This process can usually be evaluated by the decrease in the intensity of the lines of the general radiation (GR) center placed at 1.665 eV and 1.673 eV [7–9, 11], but, with the used excitation conditions, these lines were not visible in the PL as will be discussed below.

In PL at cryogenic temperatures, the ZPL becomes clearer and the intensity of the vibronic band is strongly reduced, which reinforces the classification as a phonon sideband (Fig. 5.10a). Only a phonon mode with approximately 46 meV is still distinguishable from the background. This corresponds to the same mode observed at RT. The slight difference can be explained by the different wavelength step used in both measurements, which leads to slightly different line positions. Comparing the different processing stages, a small reduction in the relative intensity of this phonon-assisted process is observed. A possible explanation is the variation of the measurement spot, as it was not recorded, meaning that different samplings of defect centers are analyzed, which could have slightly different local environments, leading to slightly different coupling to lattice vibrations. Additionally, the optical path alignment at different treatment stages, and between different samples, is not the same leading to small variation in the results. One could also think that this difference results from damage done to the lattice during the processing. Ideally, the phonon intensity BIAA should be greater than at BIBA however, the annealing parameters used might have not been sufficient to remove most of the lattice damage and even create some defects. In AIAA a partial recovery of the phonon-assisted process is observed.

The spectrum AIBA was measured using a 532 nm laser because the He-Cd laser had to be repaired at the time. The former was not available at the time of BIAA and BIBA which difficults the comparison of the different processing stages. The NV⁰ center is more efficiently excited with this wavelength [110], in addition, no filter was used in this measurement, as such, narrower slits were used to avoid photomultiplier saturation. With the reduction of the slit width, a narrower line is observed for the NV⁰ center implying that the width observed in the remaining measurements is limited by the

experimental setup and not the real width of the ZPL of the center. As no filter was used in the AIBA measurement, a spectrum without any sample was collected to isolate the contributions from the laser. As indicated in Fig. 5.10a, the main Raman line of diamond is observed with this excitation as well as a line at (636.84 ± 0.01) nm, which can be assigned to the nitrogen-vacancy negatively charged state (NV^-) center [11, 12, 20, 21, 107, 108]. This charge state is only excited above approximately 450 nm [110, 111] and thus not visible with the other excitation lines used.

Fig. 5.10b shows a line at 736 nm for BIBA, which is not visible for the remaining stages. This line

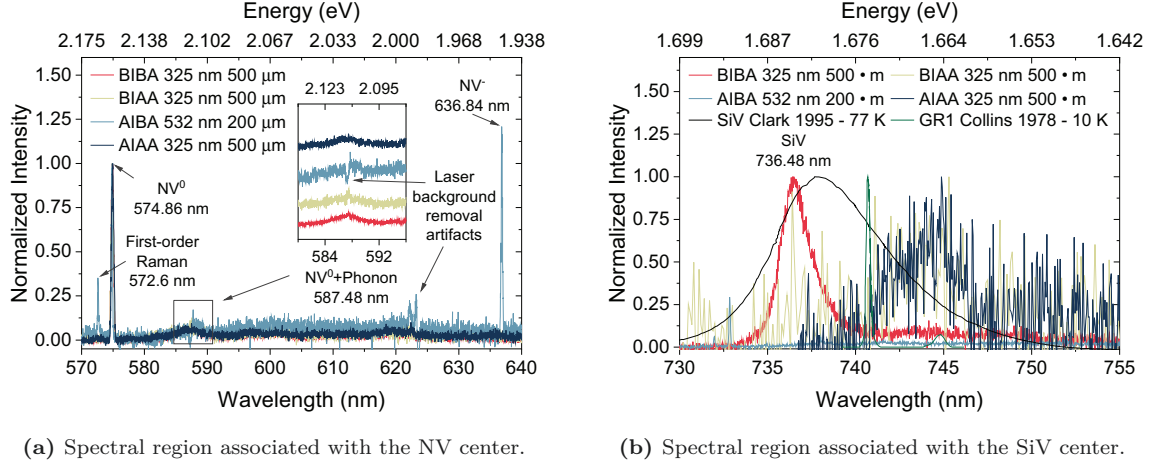


Figure 5.10: LT PL spectra of diamond A for the different processing stages. The spectra for AIBA was measured without any filter, and the signal from just the laser excitation was removed. Polynomial, up to second degree, baselines were subtracted. The inset shows a zoom in the NV^0 center one-phonon region. In the SiV spectral region, spectra from Clark *et al.* [112] and Collins [7] are superimposed to facilitate comparisons. The legend for each experimental line shows the treatment stage, the excitation laser line and the slit width used.

can be associated with the SiV center [20, 112]. The match with the results from Clark *et al.* [112] is not exact but is very close in position and also in asymmetry. The difference in width might be at least partially explained by the different temperature of each measurement. It is worth noting that the fine structure observed by Clark *et al.* is not visible, but this is due to the combination of grating and slits used in this particular measurement, which do not allow the separate lines to be resolved. In literature, the intensity of the center reaches a minimum with annealing near 900 °C [112], which is consistent with its disappearance in this work.

In AIBA the observation of the GR center was expected, more specifically the GR1 as this center, which corresponds to a neutral paramagnetic vacancy [9], is created by irradiation. This absence might be due the excitation energy, as for 532 nm (~ 2.33 eV) the excitation efficiency is roughly 25 % of that closer to the line (~ 650 nm) [113]. In AIAA and AIBA, there seems to be some signal that does not match the SiV center. Its position matches the second line of the GR1 center, however, at the measurement temperature (14 K), the other line, at 741 nm, should be much more intense (Fig. 5.10b), therefore, it cannot originate from the GR center. As the signal is similar in magnitude to the noise, it is plausible that it is a measurement artifact.

In LT PL of all samples the ZPL and vibronic structure of the NV^0 and NV^- centers are visible (Fig. 5.11a). Their intensity correlates with the implantation fluence (Fig. 5.11b) which is expected, as higher fluence leads to more lattice damage, i.e., more vacancies are generated, which can then be captured to form more NV centers. Note that the relative intensity of the two ZPLs is not constant with fluence, the NV^- center is relatively much more intense in diamond B. This might be due to the

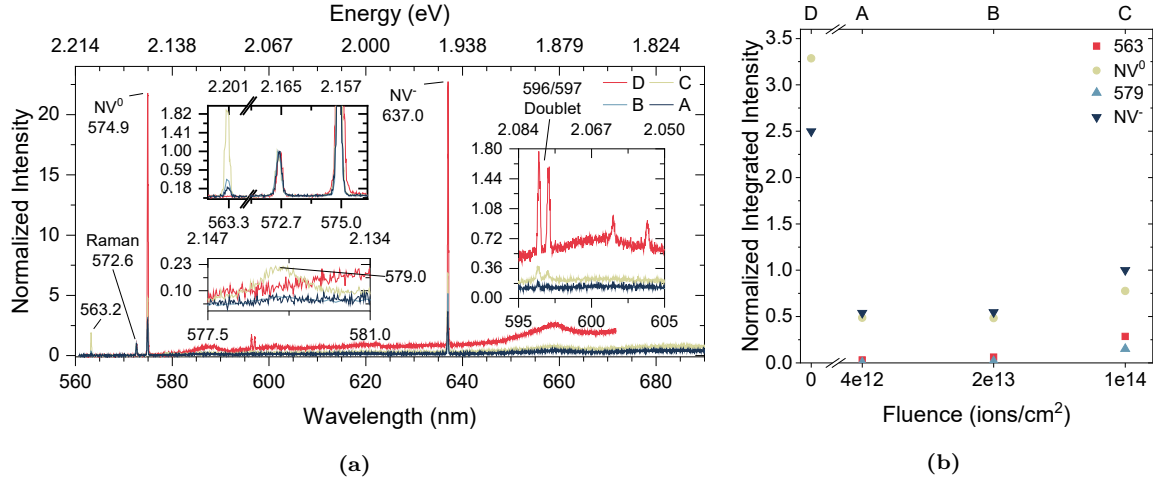


Figure 5.11: LT PL spectra (a) of all samples AIAA (BIAA for diamond D). Excitation with the 532 nm laser line at ~ 35 mW and 200 μm slits. A constant baseline was subtracted and the spectra were normalized to the first order Raman scattering line. The insets show zooms around different lines of interest. The normalized integrated intensity (b) is also shown and was extracted by individual least squares fits to Voigt profiles with a linear background near each line.

modifications of this sample during annealing, as annealing in the presence of O has been shown to convert NV^0 to NV^- [114].

By the logic outlined above, one would expect that the intensities of the NV center should be higher in the implanted samples and not in the reference. This is not necessarily the case, as the implanted calcium also knocks some nitrogen from its substitutional position, which is mostly not restored, due to the low annealing temperature combined with the high migration energy [109]. Additionally, most of the vacancies created during the implantation were captured at C interstitials and A aggregates during annealing, not forming new NV centers. Such leads to a reduction of NV centers for the studied samples. Due to the fluence used, this effect should be a small contribution. One could consider the creation of new recombination pathways due to the implantation and annealing, reducing the fraction through the NV center. Such pathways are usually non-radiative (NR), and therefore, the PL intensity is reduced, however, from the temperature dependence study presented in section 5.2.2, little to no contribution from NR was found for the NV^0 center.

For sample D, five additional lines are observed. A line at (588.68 ± 0.02) nm (uncertainty from the experimental spectral resolution), observed in CVD diamond containing nitrogen after irradiation, has been assigned to an interstitial-type nitrogen-related defect [20, 43]. A doublet at (596.38 ± 0.02) nm and (597.10 ± 0.02) nm which is a common marker of CVD diamond observed in samples containing N [115–117]. This doublet is barely visible for diamonds A and B, and shows higher intensity in diamond C. This behavior is similar to the one described for the NV center. The two remaining lines, at (601.46 ± 0.02) nm and (603.82 ± 0.02) nm have been previously reported in literature [20, 21, 118] for CVD diamond, however, no physical model was associated. These were not observed in the remaining samples.

For the implanted diamonds two additional features are observed, a line at (563.28 ± 0.02) nm (FWHM $(7.3 \pm 0.2) \times 10^{-4}$ meV), hereafter called the 563 line, and another at (579.04 ± 0.02) nm (FWHM (0.0050 ± 0.0003) meV), referred to as the 579 line. The former has been reported in literature after high-energy irradiation with light atoms, in cathodoluminescence after irradiation with 82 MeV C ions [20], in PL after irradiation with 300 keV electrons [43] and 1.8 MeV He^+ [119] and in electroluminescence after irradiation with 6 MeV C^{3+} [14, 120]. Note that in [120] the line is reported as 565 nm. Such

difference is not significant as the measurements were performed at different temperatures, which, from the results of section 5.2.2, can explain ~ 1 nm of the difference, additionally, from the position of the NV center lines one can estimate a systematic shift in the current work of ~ 0.5 nm, bringing the results within ~ 0.5 nm of each other. No definite physical model has been ascribed to the center, but it is thought to be caused by self-interstitials. Forneris *et al.* [14] has put forth a more concrete model of pairs of nearby interstitial atoms along the $\langle 100 \rangle$ axis. The 579 line has also been reported in [14, 43, 120] and a strong correlation with the 563 line was found by Forneris *et al.* [14] who proposed that they are part of the same defect family or different charge states of the same complex. From the FWHM difference observed in the current work (one order of magnitude), by comparison with the NV center in which both charge states show very similar FWHM, the latter hypothesis is considered unlikely. An additional hypothesis is that it is part of the vibronic structure of the 563 line. It would imply a phonon mode with ~ 59.9 meV which is plausible considering the one-phonon cutoff of diamond, ~ 165 meV. A phonon with higher energy than this value would not be expected as the proposed defect for this center is not lighter than C because it is formed by one or multiple C atoms, therefore, there should not lead to localized vibrational modes [121]. If such hypothesis is correct, the correlation with fluence of both lines should be very close. From Fig. 5.11b one can see that the difference in integrated intensity of both lines is not constant, however, this could be due to the 579 line for samples A and B being barely detectable. Closer steps in fluence or higher fluences would be required to see if the correlation with fluence is the same for both lines. Although not shown, the 563 line was also seen with the 325 nm and 405 nm laser excitation lines, when good optical alignment was achieved, meaning that, although less efficiently, the optical center is also excited with higher energies.

Assuming that this assignment is correct, one has to conclude that no direct optical signal from a calcium defect was observed. This might be due to a combination of factors such as measurement system sensitivity and implantation and annealing parameters. Lühmann *et al.* [10] assigned a ZPL at 557.2 nm and an associated vibronic band, measured at RT, to calcium, neither of which were observed. Such a difference might be due the annealing temperature as Lühmann *et al.*'s samples were annealed up to 1600 °C, much higher than this work, 900 °C, therefore, the calcium related defects might be present but not be optically active.

Using the theoretical model presented in section 2.4.1, the ZPL and the vibronic structure of the NV^0 and NV^- centers were individually fitted, with a constrained trust region method as implemented in the Scipy library [122]. Before any fit, the experimental data was divided by the cube of the energy (Eq. (2.7)). Ideally one would normalize the integrated spectral function of the luminescence, eliminating a fitting parameter, however, in this work, the entire luminescence band of the center could not be isolated from other luminescent sources, therefore, only part on the luminescence of each center was used in fitting, as such the integrated spectral function of the center $M = \int_{-\infty}^{\infty} G(\omega) d\omega$ was used as a fitting parameter. For each center and sample combination, the ZPL was first individually fitted to a pseudo-Voigt profile. This profile was selected as the ZPL is a Lorentzian from the theoretical model but the experimental measurement process introduces some Gaussian broadening. The pseudo-Voigt profile also allows to determine the fraction of each contribution. The resulting amplitude G_0 , in combination with an initial guess for M from the integral of the fitted data, was used to estimate an initial $S = -\ln(G_0/M)$.

The one-phonon band shape was initialized from the experimental spectrum using a window with smoothed edges from K-nearest neighbor smoothing. Before smoothing, the window was zero outside the range from the ZPL to 70 % the one-phonon energy cutoff, and a line with slope such that it was unity at ZPL and zero the other bound, inside the range. The full energy cutoff was not used to

minimize the influence from higher phonon process through the smoothing process. Initially, a unity square function was considered in the same range but it led to overestimation of the contribution from high energy modes, resulting in a blow up of the calculated spectrum to lower energy, greatly difficulting the convergence of the fit.

The one-phonon band shape was represented by n Gaussian functions, used as basis functions and not imposed by any model. In principle, other basis could be selected, but it might need more or less fitting parameters. Discrete Fourier series and Chebyshev polynomials were tested but required many more parameters and still achieved inferior results. Also, G_1 should be zero outside the range from the ZPL to the one-phonon cutoff energy, which was enforced constraining G_1 to be less than 1×10^{-8} at the bounds of the physical interval. Theoretically, G corresponds to G_∞ , however, due to the normalization from Eq. (2.4.1), above a certain $n_{\max}$, the contribution is negligible. $n_{\max}$ was selected such that the relative contribution of $G_{n_{\max}+1}$ to the band intensity is 0.1 %, considering an $S=10$, which is sufficiently large compared to the initial guess and values verified during fitting.

All fitting parameters were bounded to physically reasonable values. The amplitude of the Gaussian functions was limited to be positive, however, the physical constraint would be that G_1 is non-negative. The former bounds guarantee such constraint while being much easier to implement. For the experimental data used, the reduction in the completeness of the basis due to such bounds has little effect. Note that, in the fits performed, S was used as a parameter instead of the constant of Eq. (2.15) to avoid numerical problems derived from insufficiently sampling of the Bose-Einstein distribution close to zero energy separation, and is much easier to bound to reasonable values. As the area normalization of G_n is derived from S (Eq. (2.4.1)) the parameters were constrained so that G_1 has unit area. It is multiplied by the correct factor and the remaining G_n are normalized during the band calculation.

In addition to the model of the vibronic band, a background was also fitted. Such is necessary due to the presence of other emission sources beside the center being fitted. Ideally, one would simultaneously fit the other emission sources, but it requires their identification. In this work, such complex approach was not implemented, but constant or linear backgrounds were considered. The former allows for situations in which there is little visible influence from other emissions, and the latter can account for a background from a broad band, as in the center emission region, it can be approximated by a line.

The number of Gaussian functions used to represent G_1 was also varied, from two to eight, for all samples, and up to 20 for diamond B, to determine the minimum number of parameters that lead to a satisfactory result. For the NV^0 center, the 579 line and the 596 nm doublet were masked off, and 3 Gaussian functions with a constant background were found to be sufficient. For the NV^- , center 8 Gaussian functions were required in addition to a linear background. Note that the influence of the NV^0 center on the NV^- fit was analyzed however, negligible influence was found, as the NV^0 shows almost no intensity in the NV^- region for the resulting fit. Additionally, the slope obtained from the NV^- fit is negative (considering energies), i.e., the source of the background luminescence of the NV^- center emits mainly at a lower energy than the center emission, and thus, cannot be the NV^0 center.

The resulting fits capture the general structure of the centers (Fig. 5.12a), however, some of the features are not well modeled, as is the case for the second distinct phonon line observed for the NV^0 defect and the slope near the ZPL. The latter is likely a consequence of the Gaussian basis in conjunction with the bounding of G_1 , because, as the Gaussian functions cannot decay fast enough, they cannot be closer than a certain distance to the ZPL, and thus, the low energy phonons are badly captured with this representation. Also, the sharp feature associated with the one-phonon energy cutoff is not well captured with such a smooth basis. This could be improved by adding sharp functions to the Gaussian basis, or switching completely to another basis. For the NV^- center of diamond A,

an additional line is observed to longer wavelengths from the first phonon interaction, which is not observed in the experimental data but its magnitude is covered by the measurement noise, justifying its presence. Also, one can see the spectrum for diamond B was not as well fitted near the phonon line, showing lower intensity.

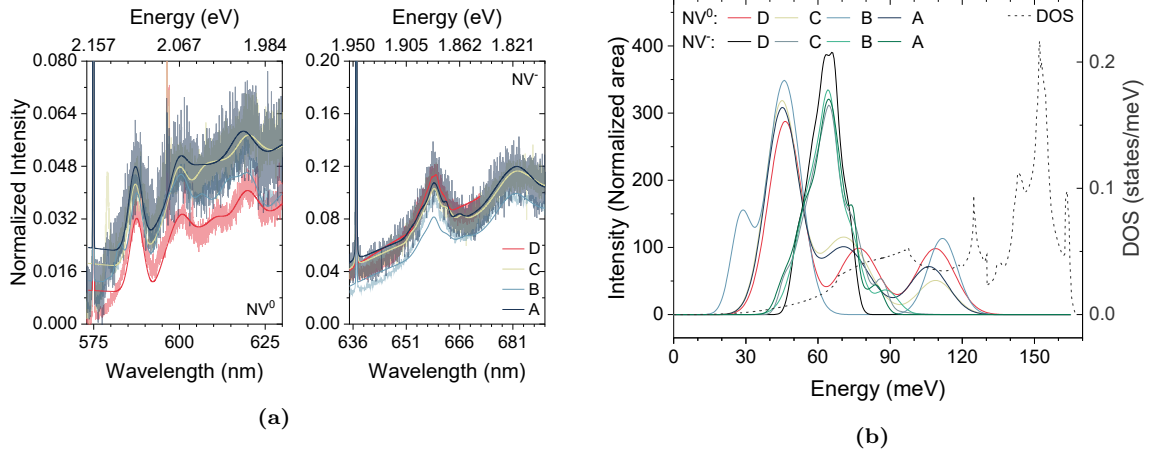


Figure 5.12: Vibronic structure reconstruction (a) and one-phonon spectral function (b) from the least squares fit of the vibrational structure observed in LT PL of Fig. 5.11a. The phonon density of states (DOS) of diamond is also shown.

The inter sample variation is also observed in the G_1 but main features are present for all samples (Fig. 5.12b). In the NV⁰ defect three main lines are observed, (45.6 ± 0.6) meV, (73 ± 3) meV and (109 ± 2) meV. Comparing with the phonon density of states of diamond (Fig. 5.12b), one concludes that the first line corresponds to coupling to a defect-derived phonon mode, a quasi-localized vibrational mode [123], while the remaining can be attributed to lattice modes. Comparing with the results from [123], the obtained G_1 is significantly different, not showing the increase towards the one-phonon energy cutoff nor the abrupt decline for such energy. For the NV⁻ center a single main line, with non-Gaussian shape is observed at (64 ± 7) meV which is consistent with literature [123, 124]. This line corresponds to the characteristic quasi-localized vibrational mode of the NV⁻ center [123].

The average Huang-Rhys factor, over all samples, was determined to be 2.7 ± 0.1 and 1.6 ± 0.1 for the NV⁰ and NV⁻ centers, respectively. For the NV⁰ center, the obtained value is in good agreement with literature [125], however, for the NV⁻ center it is severely underestimated [12, 32, 125]. A factor might be the different temperature, however, the major contribution is likely from the linear background used, which reduces significantly the required band intensity. For a constant background, one gets a factor of 3.7 ± 0.4 which overestimates the expected value. Such is an indication that there is in fact superimposed background from another source.

5.2.1 Dependence on excitation power

The behavior with excitation power of the lines observed with the 532 nm excitation line (Fig. 5.11a) was studied for diamond B. From 5.13a an approximately linear behavior was verified for all lines. The intercepts for all lines were not found to be statistically different from 0 as expected. Relative to the Raman line, the 563 showed a very small increase in intensity with power of $(3.3 \pm 0.5) \times 10^{-5} \text{ mW}^{-1}$. On the other hand the NV⁰ and NV⁻ showed an increase of $(2.4 \pm 0.4) \text{ mW}^{-1}$ and $(3.7 \pm 0.5) \text{ mW}^{-1}$. As no saturation was observed, this implies that excitation efficiency of the 532 nm light is highest for the NV⁻ center, lower for the NV⁰ center and much lower for the 563 line. No trend was found in the line widths and shifts with power.

Analyzing now the integrated intensity ratio between the ZPLs of two charge states of the NV center (Fig. 5.13b) one can conclude that it changes with excitation power. This effect is known

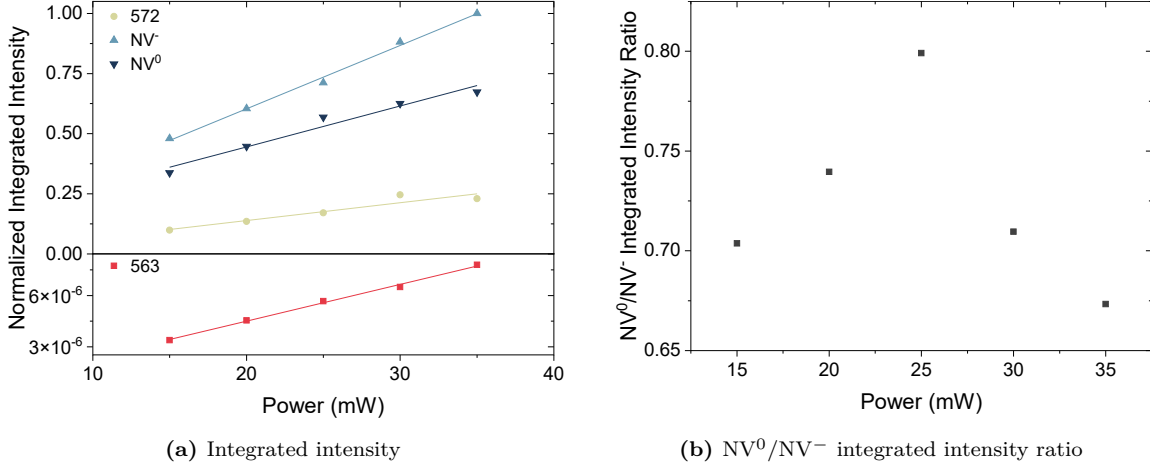


Figure 5.13: Diamond B AIAA ZPLs as function of excitation power. Obtained from a Voigt profile least squares fit to LT PL experimental data from excitation with the 532 nm laser line.

[107, 108, 126] and has been attributed to the presence of nearby electron traps, usually considered a single substitutional N with which an electron is exchanged by tunneling during optical excitation [107]. In literature however different behaviors have been reported. In this work, the NV⁰/NV⁻ ratio is non-monotonic with power, increasing initially, reaching a maximum for 25 mW (estimated 350 mW/cm²) and then decreasing. In [107] is showed a monotonic increase of this ratio in type Ib HPHT diamond with a 532 nm laser line excitation, reaching saturation close to 5 W (estimated 3×10^5 W/cm²). Ref. [126] showed, in natural type IIa diamond implanted with N, that under excitation with 514 nm NV⁰ centers convert to NV⁻, therefore, one would expect the decrease of the NV⁰/NV⁻ ratio with laser power. Additionally, it was concluded that the large variation in conversion rates was consistent with the electron donor hypothesis. In [108] was found that for both a CVD bulk diamond and a type Ib HPHT bulk diamond the NV⁰/NV⁻ ratio decreased with increasing excitation power from a 532 nm excitation line, also the opposite trend was observed addressing single NV centers in type Ib nanodiamonds. As such, one can conclude that there is high variability between samples in the relative concentration of the two charge states with excitation power. One could consider different electron traps in different samples or even in the same sample, that could accept an electron from a NV⁻ center or donate an electron to a NV⁰ center, thus controlling the majority charge state.

5.2.2 Dependence on temperature

Lines' behavior observed with the 532 nm excitation line (Fig. 5.11a) with temperature was studied for diamond B. Fig. 5.14 shows the temperature dependence of the maximum intensity, peak position and FWHM of the observed lines. Fig. 5.14 also shows the least square fit to the quadratic coupling model of the same quantities using the single mode approximation of Eq. (2.17) which results in

$$\begin{aligned}
 \text{FWHM}(T) &= \text{FWHM}(0) + M_{\text{FWHM}} \exp\left(\frac{\omega_0}{k_B T}\right) \left[\left(\exp\left(\frac{\omega_0}{k_B T}\right) - 1 \right)^2 \right]^{-1}, \\
 \Delta\omega_{\text{zpl}}(T) &= \Delta\omega_{\text{zpl}}(0) + M_{\Delta} \left[\exp\left(\frac{\omega_0}{k_B T}\right) - 1 \right]^{-1}, \\
 G_0(T) &= G_0(0) \exp\left(-2M_G \left[\exp\left(\frac{\omega_0}{k_B T}\right) - 1 \right]^{-1} \right),
 \end{aligned} \tag{5.1}$$

where $\text{FWHM}(0)$, $\Delta\omega_{\text{zpl}}(0)$ and $G_0(0)$ are the respective quantities at $T=0\text{ K}$, ω_0 is the mode frequency, and M_{FWHM} , M_Δ and M_G are numerical factors. The terms $\text{FWHM}(0)$ and $\Delta\omega_{\text{zpl}}(0)$ are not derived from the quadratic coupling model. The former is experimentally observed and caused by various kinds of broadening such as lifetime broadening, broadening due to variations of the local structure of the center and experimental broadening. The latter is a consequence of the reference line position

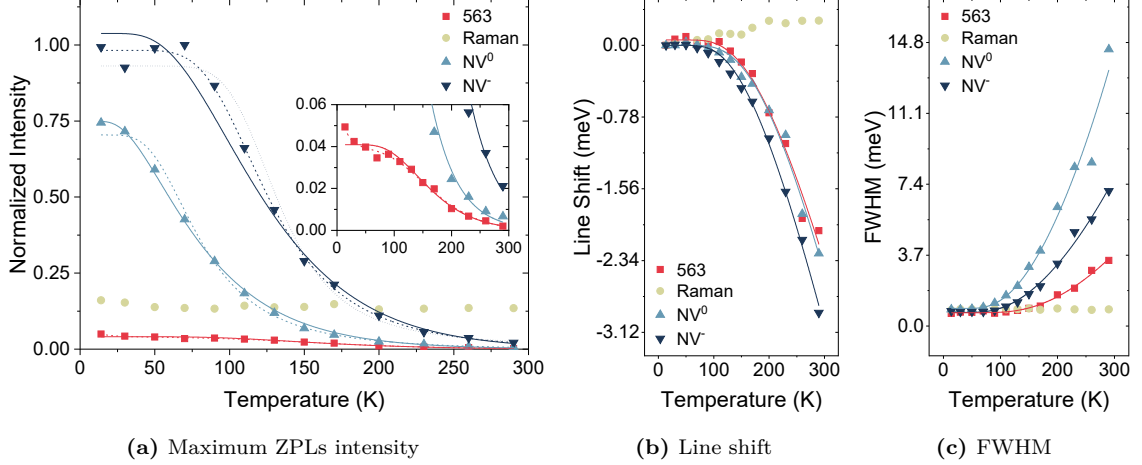


Figure 5.14: Maximum ZPLs intensity, line shift and FWHM of the NV center and the 563 line as function of temperature. Excitation with the 532 nm laser line. The values were extracted from the spectra by a least squares fit to a Voigt profile with a linear background. A least squares fit to the quadratic coupling model within the single mode approximation is also shown as a solid line. For the maximum ZPLs intensity, the dashed line is equivalent but also considering NR process and the dotted line only considers such processes.

used in the calculation of the shift, in this case for the position at 15 K. The resulting parameters are summarized in table 5.2. Note that for the intensity, to improve numerical accuracy in the error estimates, the natural logarithm of the ZPL intensity was fitted.

Table 5.2: Fitting parameters of the least squares fit for the 563, NV^0 and NV^- lines to the quadratic coupling model assuming coupling to a single mode. The parameters for a fit considering NR processes.

Source	Parameters	NV^-	NV^0	563	Units
FWHM	M_{FWHM}	19 ± 6	40 ± 20	26 ± 7	meV
	ω_0	0.039 ± 0.005	0.04 ± 0.01	0.060 ± 0.006	eV
	$\text{FWHM}(0)$	0.72 ± 0.09	0.9 ± 0.3	0.70 ± 0.04	meV
	Adjusted R^2	0.991	0.97	0.991	
$\Delta\omega_{\text{zpl}}$	M_Δ	-17 ± 2	-22 ± 5	-17 ± 5	meV
	ω_0	0.049 ± 0.002	0.059 ± 0.005	0.054 ± 0.007	eV
	$\Delta\omega_{\text{zpl}}(0)$	0.0 ± 0.3	0.0 ± 0.9	0.06 ± 0.04	meV
	Adjusted R^2	0.996	0.986	0.98	
G_0	$\ln(G_0(0))$	0.04 ± 0.06	-0.29 ± 0.01	-3.20 ± 0.05	
	ω_0	0.024 ± 0.002	0.0106 ± 0.0007	0.039 ± 0.004	eV
	M_G	3.2 ± 0.5	1.4 ± 0.1	6 ± 1	meV
	Adjusted R^2	1	0.995	0.989	
$G_{0,\text{NR}}$	$\ln(G_0(0))$	-0.02 ± 0.02	-0.35 ± 0.05	-2.3 ± 0.6	
	M_G	3.2 ± 0.5 (Fixed)	0.7 ± 0.3 (Fixed)	6 ± 1 (Fixed)	
	ω_0	0.042 ± 0.004	0.010 ± 0.009	0.037 ± 0.002	eV
	M_{NR}	70 ± 30	13 ± 5	2 ± 2	
	ΔE	0.049 ± 0.005	0.021 ± 0.003	0.0007 ± 0.0005	eV
	Adjusted R^2	0.999	0.998	0.993	

The line shift and FWHM model describe very well the experimental data (Figs. 5.14b and 5.14c), which can also be seen from the obtained coefficient of determination, R^2 (Table 5.2). For the NV^0 and 563 lines, the intensity of the ZPL is also well described, however such is not the case for the NV^- , for which the observed decay is steeper than expected from quadratic coupling. Such might be attributed to the participation of NR decay processes which compete with the luminescent transition. NR processes can be modeled as thermally activated processes [127], therefore

$$G_{0,\text{NR}}(T) = G_0(0) \cdot \frac{G_0(T)}{G_0(T) + M_{\text{NR}} \exp(-\Delta E/k_B T)}, \quad (5.2)$$

where M_{NR} is a numerical factor that determines the relative efficiency of the NR process, also accounting for the multiplicity of the energy levels, and ΔE is the activation energy of such processes. Fits considering this model are also shown in Fig. 5.14a as dashed lines. To achieve such fits the parameter M_G was fixed to the value obtained in the fit considering only the quadratic coupling. Such was necessary due to M_G and M_p having similar effects on the final curve, leading to uncertainty in their combined determination as the effect of increasing one might be from the other. The inclusion of NR processes provides a much better description of the observed behavior for the NV^- , serving as strong evidence for the participation of NR processes. Such result is consistent with the electronic structure of the NV^- center, which leads to a NR transition between the triplet excited state and a singlet excited state. This transition is at the heart of ODMR verified for the center [50, 67]. It is also possible to see that the dependence on temperature of the ZPL is not simply given by the thermal activation of the NR processes (dotted line in Fig. 5.14a). For the NV^0 center the consideration of NR processes worsens the fit, providing evidence against them in this case. The 563 line temperature dependence is also better described including NR processes, but they are considerable different from those in the NV^- center as can be seen from the two orders of magnitude difference in ΔE and M_{NR} .

Comparing the resulting values of the single mode energy, one can conclude that they are not statistically different (at 95 % confidence) when comparing results from lineshift and FWHM, however this is not the case when comparing with results from the intensity models. This difference is most likely an indication that the physical system does not couple only to one mode, therefore, for each of the properties one gets the majority of the contribution from different modes, given that the weight function, related to the thermal population, is different for each property. The effective mode obtained from the line shift and FWHM fits is consistent with the first distinct mode observed in Fig. 5.11a for the NV^0 and NV^- centers and matches the 579 for the 563 line, giving further evidence to support that the former is a part of the vibronic structure of the latter.

For a more rigorous treatment one ought to consider the one-phonon spectral functions from Fig. 5.12b. In conjunction with Eq. (2.17) one can calculate the behavior of the ZPL intensity, lineshift and FWHM with temperature. Such calculations were performed, however, due to the zero slope near the ZPL, already mentioned, one arrives at almost no thermal variation from LT to RT, as the states with energies that could be populated do not exist in the model G_1 . As such, the correction of the representation capability of the selected basis has to be tackled first before sensible predictions can be made for the temperature dependence of the various ZPL characteristics. The aforementioned improvements are work in progress.

Chapter Six

Conclusion and future steps

In this work a three-pronged approach to the study of color centers was employed. *Ab initio* calculations, EC and optical measurements were performed giving complementary information about the system in study, Ca defects in diamond.

DFT calculations were performed at the PBE level for 165 possible defect configurations and a select few, based on EC input, were studied at the HSE06 level. It was verified that different initial configurations relaxed into similar structures and the most energetically favorable defect with calcium corresponds to the BC site with two neighboring C vacancies. Shifting the formation energies by the difference between HSE06 and PBE calculation for BC configuration, allowed vacancy formation energies within 0.5 eV from hybrid calculations in literature. A similar deviation is expected for the remaining results using this approach. The BC defect was studied for several charge states (-2 to 2). It shows D_{3d} symmetry and introduces five defect-localized levels in diamond's energy gap, with two exceptions. For the positive charge states, 1 and 2, the lowest lying localized level is below the VBM. No defect levels were found sufficiently close to the band edges for thermal ionization at RT. To predict the charge state of the Ca defect experimentally observed, one could follow the procedure outlined by [26], considering also N defects which are present experimentally as observed in the optical measurements. Additionally, due to the charge state behavior observed with optical excitation power for the NV center, which depends on nearby impurities, the simulation of a Ca defect accompanied by a substitutional N might provide useful insights into its charge state.

The experimental results from EC using ^{45}Ca before annealing are consistent with the formation energies obtained from DFT. In the as implanted state, a Gaussian distribution around the BC site was found, which could be caused by nearby implantation defects that cause static displacement of the Ca atom. After annealing, small changes were observed, consistent with the visible absorption measurements, and no concrete assignment was possible as multiple configurations lead to similar quality fits. The collected patterns required additional sites to be explained, which have to have formed during annealing. However, the BC is the minimum energy configuration from DFT, which is inconsistent with the creation of a significant fraction of other sites. Two hypothesis were presented to explain such inconsistency. One could consider the migration of vacancies away from Ca and towards other defects, mainly C interstitials. This would in turn make the DS and S sites more energetically favorable, which would be consistent with some of the models from the EC fits. Another option is that the lowest energy calcium defect was not found in the simulations performed. Due to the large number of vacancies after implantation, determined from the SRIM calculations, and the positive binding energies obtained, one could consider complexes with more vacancies. Starting from the BC site, from symmetry considerations, one would expect that Ca would be close to the SP site, which is

also observed in some of the best EC fits for the after annealing patterns. DFT calculations with more vacancies are thus a logical next step for correlation with EC measurements.

The filtering process used in the EC analysis provided good results, guiding the analysis for the current work, however, a significant fraction of patterns was discarded. As such, the criteria used might be too strict. Careful tuning of the criteria parameters as well as the scoring function used is of vital importance for wider application of the method described. One might also ponder another criterium, limiting the total fraction to be within a range, considering a predetermined correction factor, such that the corrected total fraction is close to 100 %.

Diamond samples were implanted with stable Ca, annealed and studied optically. In the Raman measurements no vibrational modes were observed besides the ones characteristic of diamond. From the FTIR results, the concentration of N in non-implanted diamond was found to be greater than expected for type IIa diamond, as signal characteristic of N aggregates was observed. Such observation could not be done for the implanted samples due to large oscillation in their FTIR signal, which are likely due to surface contamination. Additionally, the fingerprint of C-H vibrational modes was observed in the implanted samples.

In the PL measurements, luminescence from the NV^0 and NV^- was observed in all samples. In the implanted samples, lines at (563.28 ± 0.02) nm (FWHM $(7.3 \pm 0.2) \times 10^{-4}$ meV) and (579.04 ± 0.02) nm (FWHM (0.0050 ± 0.0003) meV) were observed. These were not present before implantation nor in the control sample. Through comparison with literature the former has been linked with intrinsic defects, and is observed for different implantation and irradiation conditions. The latter, seen often in the presence of the former, has been hypothesized to be part of its vibronic structure by comparison with the NV centers, and later supported by its behavior with temperature. From the theoretical analysis of temperature dependence of the intensity of the NV^- center ZPL, it was possible to demonstrate the presence of NR processes which is consistent with energy levels dynamics of the center.

For both charge states of the NV center, the vibronic structure was fitted considering the theoretical model of vibronic coupling, capturing well the main features. However, the one-phonon energy cutoff was not captured and significant deviations close to the ZPL were obtained, which were caused by the combination of the constraints placed during fitting and the basis functions used to represent the phonon coupling. Such limitation of the representation precludes the reconstruction of temperature behavior of the ZPL's parameters. Additionally, the fitting method could also be extended to treat both charge states simultaneously, and considering the experimental data at different temperatures to achieve a self-consistent result. The 563 and 579 lines could also be incorporated, which could provide further evidence in the assignment of the 579 line as part of the vibronic structure of the 563 line. Testing different fitting algorithms might also provide improvements as, depending on the initial parameters, nonsensical fits were often obtained, implying a high sensitivity to initial conditions, therefore, algorithms which value more the exploration of the parameter space, although more time consuming, could prove to yield better results.

In conclusion, considering the assignment of the 563 and 579 lines, no direct optical signal was observed from the Ca. To aid in the verification of this assignment and also on the experimental pursuit of calcium defects, *ab initio* calculation of the optical transitions for Ca BC defect is considered to be an important next step. These should also include the consideration of the Jahn-Teller and dynamic Jahn-Teller effects, which result in structural deformation, affecting also EC results.

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