Optical Spectroscopy of Xenon-Related Defects in Diamond

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OPTICAL SPECTROSCOPY OF XENON-RELATED DEFECTS IN DIAMOND

by

YURY DZIASHEKO

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for
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Abstract

OPTICAL SPECTROSCOPY OF XENON-RELATED DEFECTS IN DIAMOND

by

Yury Dziashko

Adviser: Professor Anshel Gorokhovsky

The work presents the results of optical studies of Xe-related defect in diamond. This defect is one of a few having narrow zero-phonon line in the near-infrared part of the photoluminescence spectra. It appears in diamond after Xe\(^+\) ion implantation followed by thermal annealing. Given unique physical properties of diamond (hardness, optical transparency in wide spectral range, chemical inertness, high thermal conductivity, low thermal expansion coefficient) and stability of Xe-related center it can be viewed as a potential candidate for the source of single-photons, or as optically manipulated qubit, not unlike nitrogen-vacancy center. However, compared to the latter Xe-related center is not as well understood and it is necessary to gain thorough understanding of its spatial structure, symmetry, electronic states and mechanisms of interaction with the host diamond lattice.

This thesis addresses several questions, in regard to Xe-related center: 1) How efficiently this center is formed in the implantation/annealing process; 2) How does it interact with the host lattice to produce both homogeneous and inhomogeneous shape of the 811.7 nm zero-phonon line; and 3) What is the type and nature of transitions responsible for the 811.7 nm zero-phonon line.

In answering the first question two methods for measuring the conversion efficiency of any kind of optically active defect have been developed and applied to Xe-related center in diamond. The study of line-broadening mechanisms showed how this center interacts with the strain produced by other neighboring Xe-centers, distributed in a plane-like geometry. Also, interaction with vibrational motions of the diamond lattice localized in the vicinity of the Xe-centers is analyzed and the parameters of this pseudo-local mode are found. Finally, using the effects of optical saturation in photoluminescence under excitation with Gaussian laser beams it has been shown that 811.7 nm zero-phonon line is due to absorption and emission by circular magnetic dipole. Also, the site symmetry of Xe-related center has been confirmed as trigonal with the threefold axis oriented along (111) direction in the diamond crystal.
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Finally, I want to express my gratitude to all members of my Final Examination committee for helpful suggestions and support during my work on the thesis.
С глубоким уважением данную работу я посвящаю своему учителю: Зеньковичу Владимиру Ивановичу. Благодаря его труду я смог дойти до этого шага.

This work is dedicated with deepest respect and admiration to my teacher Vladimir Zenkovich. Without his work I would have never dared to venture this far.
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Chapter 1

General Introduction

1.1 Motivation

It is a well-known fact in the field of condensed matter physics that imperfections of crystal lattice can be used advantageously. For example, the results of research and applications of solid-state lasers can be given as sufficient justification for the interest in optical studies of crystal defects. Nowadays the attention to the optically active defects (defined below) in crystals is increasing. The interest is fueled by the advances in both research and technology of diamond and related materials [1, 31].

Diamond possesses unique physical properties, such as: 1) extreme hardness, 2) high thermal conductivity, 3) optical transparency in a wide spectral range, including near-infrared, and 4) chemical inertness which makes it suitable for biological applications. Combined with the progress in fabrication of micro- and nano-sized structures on diamond crystals and availability of large number of optically active defects it is not surprising that a lot of research in solid state optics is devoted to this remarkable material [59, 21, 57, 4].

Optically active defects in diamond are lattice imperfections (e.g. vacancies, carbon interstitials, foreign substitutional atoms, foreign interstitial atoms or combinations of the above given elements) which modify optical properties of diamond and yield new absorption or emission lines. Due to their small dimensions of 1-5 inter-atomic distances, optically active defects in diamond are essentially sub-nanometer sized artificial atoms, not unlike quantum dots. As such they are of great interest in photonics and quantum optics, especially with current intensive work on developing technology for quantum computing [39, 9]. Already a source of single-photons on-demand has been implemented [50].

Among hundreds of known optically active defects in diamond, one currently attracts most of the attention and stands out as the most well-studied: negatively charged nitrogen-vacancy complex (NV-center) [22].
Due to its ease of creation, well-known quantum structure, ability to optically manipulate spin spates, and stable performance in experiments it became a “center of choice” in numerous research projects as well as applications ranging from testing quantum information protocols to creating bio-markers [10, 37, 54].

What makes the Nitrogen-Vacancy center (as well as several others, such as: chromium-, silicon-, and xenon-related optical centers) attractive is the presence of narrow emission lines in the red and near-infrared spectral regions, where diamond itself is transparent. Firstly, the narrowness of observed lines suggests a possibly weak interaction of centers’ electronic (or spin) degrees of freedom with the host lattice, likely allowing one to create long-lived coherent states for these quantum systems. Secondly, these lines are positioned in the part of the spectrum where diamond is transparent, thus making it possible to excite and collect signal from corresponding optical defects. These properties of the lines are essential for successful applications in the field of quantum computing and communication.

Although there are several promising candidates among the optically active defects in diamond, current research is dominated by the studies of nitrogen-vacancy center. This work focuses on another optically active defect in diamond: Xenon-related defect. It appears after Xe$^+$ ion implantation and thermal annealing of diamond. Spectroscopy studies of this center started almost two decades ago [58]. They were motivated by the presence of a narrow zero-phonon line (explained below) at 811.7 nm and a weak phonon side-band, indicative of the weak coupling to the phonons of the diamond lattice. As of today, it is much less studied than the nitrogen-vacancy center, regardless of its comparable (and with respect to the weak phonon side-band even superior) characteristics.

Spectroscopy studies together with numerical modeling, reviewed below, proposed the spatial structure and configuration of Xe-related defect, as well as the tentative energy level structure. However, much still remains unknown. This work aims at expanding our knowledge about this potentially useful optically active defect. It should be noted that methods developed in the studies of Xe-related center and discussed further in the work are of general character and can be applied to any optically active defect, not necessarily diamond-related.

1.2 Literature Review

This section reviews the works done on Xe-related optically active center in diamond. Other works discussing, for example, isotopes of Xe in pre-solar diamonds or defects induced by Xe$^+$ implantation but not related to it are not relevant to the presented work and will not be considered.

To begin, an explanation of how the Xe-related optical center in diamond may be created is needed. One way to introduce an optically active center in diamond is ion implantation, followed by thermal annealing as
1.2. LITERATURE REVIEW

illustrated in Fig. 1.1, A) and B). This is a mature technique that gives control over the spatial placement of impurities and suitable for virtually any ion/crystal combination. However, besides damaging the lattice, ion implantation creates a thin layer of impurities, often close to the surface of the sample. For example, SRIM (www.srim.org) calculations show that for Xe$^+$ ions with energy 180 keV the layer is 16 nm thick and positioned approximately 50 nm below the surface. As a downside, such a thin layer makes absorption measurements challenging.

As the result of ion implantation and subsequent high temperature ($T > 800^\circ$ C, when vacancies become mobile) thermal annealing a new quantum system, consisting of xenon atom and vacancy(ies) is created. The fact that vacancies are involved in this center has been established in [45]. This work studied natural diamonds (type Ia) implanted with 500 keV Xe ions and showed that increasing the implantation dose over $10^{13}$ cm$^{-2}$ leads to the quenching of photoluminescence by irradiation induced defects. Observation of two prominent peaks at 811.6 nm and 794 nm have been reported in [45], together with a weak vibronic sideband (see Figure 1.2). These lines are due to transitions between electronic states of Xe-related defect in diamond. Since this defects is coupled to the diamond lattice, electron-phonon interaction leads to transitions which change not only the electronic state of the defect, but vibrational state of the lattice as well. This is seen as a wide phonon side-band in the photoluminescence spectra. The sharp and narrow part of the spectral line corresponds to the purely electronic transitions, when no phonons are emitted. It is called a zero-phonon line (ZPL) and is seen for example at 811.6 nm in Figure 1.2. According to [45] the intensity of 811.6 nm zero-phonon line increases with the increasing annealing temperature (assuming the annealing time the same and equal to 2 hours) and reaches a plato at about 1400$^\circ$C.

In a later work by Martinovich and Gorokhovsky [44], the results of resonant excitation of Xe-related center in natural diamonds (type Ia) with $\lambda_{exc} = 793.1$ nm and $\lambda_{exc} = 811.7$ nm at $T=8$K were reported. They demonstrated that both 794 nm and 811.6 nm lines in photoluminescence spectra are indeed zero-phonon lines of 0-0 transition. The work also established that the absorption cross-section for 794 nm ZPL is about four times higher than for 811.6 nm zero-phonon line. Based on the results of [44] an energy level scheme, shown in Figure 1.3a, was proposed.

In [6] Bergman, Zaitsev, and Gorokhovsky studied polarized photoluminescence from Xe-related centers in high purity diamond, CVD-grown along (001) crystallographic plane. Room temperature photoluminescence spectra, excited with laser of $\lambda_{exc} = 647$ nm, featured two prominent peaks at 794 nm and 811.7 nm. It was found that these peaks were polarized and the study of their polarization, as the sample was rotated around the axis perpendicular to the (001) plane, allowed to conclude that Xe-related center is of trigonal $C_{3v}$ symmetry, oriented along $\langle 111 \rangle$ direction. Also, within a model of classical dipoles it was possible to assign the following transition types for zero-phonon lines: 811.7 nm is of $\sigma - \pi$, 794 nm is of $\sigma - \sigma$ type.
type transition corresponds the emission due to a linear dipole, while $\sigma$ to a circular one. Figure 1.3b shows the scheme of energy levels involved and the types of the transitions according to [6].

Another work on implantation dose dependence of photoluminescence of Xe-related center in diamond is reported in [7]. It is shown that for implantation doses $10^{10} - 10^{13}$ cm$^{-2}$ the intensity of the 811.7 nm zero-phonon line grows linearly with the implantation dose. This implies that formation of a Xe-related center requires a single Xe atom. Taking into account the results of works [45, 44, 6] a tentative spatial configuration of Xe-related center is proposed: A single Xe atom associated with a vacancy (or vacancies) and forming a structure with trigonal symmetry. The orientation of this defect, according to [6], is along $\langle 111 \rangle$.

Theoretical investigation of Xe-related defects in diamond are presented in [3]. Using numerical calculations with molecular orbital method, electronic structure and stability of a mono-atomic Xe defect was studied. A stable configuration is predicted for a substitutional Xe atom coupled to a vacancy with both Xe and the vacancy lying on the $\langle 111 \rangle$. In the process of relaxation Xe is displaced along $\langle 111 \rangle$ and a Xe-split vacancy (or divacancy) center with trigonal symmetry is formed. According to [3], the stable configuration of Xe-divacancy complex is achieved when Xe is positioned well off-center, being 1.774 Å from the first three neighboring carbon atoms and 2.515 Å from the other three. Thus, the structure of Xe-related center predicted in work [3] lacks inversion symmetry.

Another work which numerically investigates the structure of noble gas impurities in diamond is reported in [30]. Density functional calculations predict that among all considered noble gas atoms (He, Ne, Ar, Kr, and Xe) xenon has the highest formation and migration energies. The latter facts mean high thermal stability and unlikelihood of diffusion of Xe atom at temperatures below 1400°C. Also, a split-vacancy configuration is identified as the most stable, in agreement with the earlier work [3]. In contrast to [3], the orientation of Xe-split-interstitial complex is found to be [001]. Another result of interest is that Xe chemically reacts with diamond lattice (due to its dense packing), releasing energy when it is displaced from high-symmetry tetrahedral interstitial site. In addition, Xe-implantation may change electric properties of diamond introducing donor and acceptor levels within the bandgap of diamond and making it n-type (semi-)conductor.

Thermodynamic stability of Xe-related defect in diamond was also studied in [23]. Substitutional xenon atoms (Xe$_s$), surrounded by either one or three vacancies are considered. In the process of lattice relaxation Xe$_s$-V turns into xenon-split-vacancy complex, with xenon becoming interstitial and the whole structure possesses $C_{3v}$ symmetry. In contrast to previous theoretical works, this split-vacancy configuration has xenon symmetrically placed between two groups of carbon atoms and thus has the center of inversion. “Xe+three vacancies” center is shown to be less stable than Xe-split-vacancy. Another important result of
1.3 Work Overview

In current section a brief overview of this work will be presented. It is to give a reader an overall idea of the research questions that have been addressed and the main results obtained. There are four main topics

the work [23] is the calculated vibrational density of states (vDOS). Xe-split-vacancy defect modifies the vDOS of pure diamond in the spectral region 150-300 cm$^{-1}$, introducing two prominent peaks: at 218 cm$^{-1}$ and 251 cm$^{-1}$. The possibility of their observation in both Raman and infra-red spectra is predicted. The corresponding vibrations are localized near Xe atom, thus the existence of pseudo-localized modes around Xe-related defects are theoretically predicted in [23].
Figure 1.2: a) Zero-phonon line (ZPL) with vibronic side band from Xe-related center in diamond at 8 Kelvin. Implantation dose is $10^3$ cm$^{-2}$. b) Same ZPL at 200 Kelvin together with 794 nm peak. Adopted from [45]
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Figure 1.3: Energy levels scheme and the transition types for Xe-related center in diamond based on the results of work [44] and [6].

discussed in corresponding chapters, supplemented by the appendices in some cases: 1) Conversion Efficiency, 2) Inhomogeneous Broadening of ZPL, 3) Homogeneous Broadening of ZPL, and 4) Optical Saturation in Polarized Photoluminescence.

Chapter 2, “Conversion Efficiency”, is devoted to the general question: How efficient is the process of creation of optically active centers? For the ion implantation, followed by high temperature thermal annealing, one may wonder how many implanted ions (say, out of 100) will yield an emitting center? It is a very important characteristic of the process of optical centers’ creation. Generally, one would like to have all ions converted into emitting centers. To this end major factors affecting the efficiency of “ion-to-emitter” conversion must be understood and controlled. But of equal importance is to be able to measure the conversion efficiency – the parameter defined as the fraction $q = \frac{N_{emit}}{N_{impl}}$ of implanted ions that have turned into emitting centers. A method has been developed for this purpose and described in the chapter “Conversion Efficiency”. It is based on exciting an area of the sample with a laser beam and collecting a luminescence signal from ensembles of emitters from within that area. Doing this for various points of the sample is a process called mapping. Statistical processing of such mappings allows one to find the average number of emitters in ensemble. Having determined the total number of the ions implanted into the area being illuminated by the laser beam, one may estimates the conversion efficiency $q = \frac{N_{emit}}{N_{impl}}$. Two variants of such method are discussed in this work, both have been applied to estimate the conversion efficiency.
of Xe-related center in diamond with similar results (q = 30% for a specific ion-implantation+annealing process described in Chapter 2). These results were published in [17, 18, 19].

Next two chapters address the question of interactions between optically active defects and the host crystal lattice. The results of interactions can be seen through the shapes of the spectral lines observed in the photoluminescence spectra collected from ensembles of emitters. At low temperatures the line-shape remains roughly the same and is determined by the inhomogeneity of the host crystal. For example, local variations of the elastic strain may lead to the variations of the transition energies of different emitters in the observed ensemble. The resulting spectral line shape is the statistical effect of “spreading” the ideal single-emitter line-shape in accordance with the inhomogeneity of the crystal. The observed line-shape is called inhomogeneously broadened and it depends on the source of crystal’s inhomogeneity. Chapter “Inhomogeneous Broadening of ZPL” explores a peculiar change of the shape of the 811.7 nm zero-phonon line from Xe-related centers in diamond as one increases the implantation dose of xenon. As shown, it is likely that optically active defects themselves create extra inhomogeneity of the elastic strain. Due to their two-dimensional spatial distribution in the sample (the result of ion implantation with a monoenergetic beam) and their structure involving xenon-ion coupled to vacancy(ies), the inhomogeneously broadened line must have a shape with heavy tails, substantially deviating from Gaussian or Lorentzian line-shapes traditionally considered in literature. The results of these investigations were published in [20].

Chapter 3, “Homogeneous Broadening of ZPL”, deals with the problem of evolution of spectral line-shape with temperature. The increase of the width of the emission line is called homogeneous broadening. It will be present even in the homogeneous crystal and thus it’s temperature-dependent character is the same for all emitters. Various electron-phonon interaction mechanisms have been considered in literature to explain experimentally observed line-shapes. One of them is analyzed in the chapter “Homogeneous Broadening of ZPL” and used to describe the asymmetry of the 811.7 nm zero-phonon line from Xe-related centers in diamond. The model considers emitter as a two-level system coupled to a single vibrational mode of the crystal lattice, localized near the emitter. The reason for the existence of such a mode is given and the parameters of this mode are found. The parameters are based on experimental data as well as numerical calculations of the line-shapes within the mentioned model.

In the final chapter “Optical Saturation in Polarized Photoluminescence” several question are studied: 1) What is the site-symmetry of Xe-related center in diamond? 2) What type of dipole transition are responsible for the 811.7 nm zero-phonon line from that center? 3) What is the nature (electric or magnetic) of the corresponding dipole? Although questions 1) and 2) have been previously addressed in work [6], this work did not consider several important factors, such as optical saturation, possible isotropy of the emitter, and finite aperture of the objective collecting the signal. All these factors have been accounted for to confirm the
results previously obtained: a) Xe-related center has a trigonal symmetry, with the 3-fold axis aligned with the \langle 111 \rangle\ direction of the diamond lattice, b) the light is absorbed by a circular dipole, perpendicular to the orientation of the Xe-related defect, and emitted by a linear dipole, colinear with the defect. The answer to the question 3) is new and establishes a magnetic nature of the absorption and emission. A special emphasis of this chapter is made on effects of optical saturation which become important whenever one is working with intense Gaussian laser beams. Instead of avoiding these effects by working at low power’s of the laser beam, it is shown how optical saturation can be used to gain additional information about emitters.
Chapter 2

Conversion Efficiency

2.1 Introduction

One of the methods to create optically active centers in solids is ion implantation followed by thermal annealing. The process is illustrated in Figure 2.1. This technique allows one to accurately control the spatial distribution of the implanted ions, the dose of implantation, as well as the type of the implanted ion. A variety of combinations of host materials and implanted ions is possible and the search for optical centers with properties suitable for applications is in progress. An important example is the search for a single optical center in diamond which can be used in quantum optics applications [27].

One of the important parameters to characterize the creation of optical centers by ion implantation is conversion efficiency (sometimes the term formation yield is used), understood as the probability to form optical centers in the result of implantation and thermal annealing. It can be defined as the ratio of the density of emitting centers $N_{\text{emit}}$ to the total density of implanted ions $N_{\text{impl}}$:

$$q = \frac{N_{\text{emit}}}{N_{\text{impl}}}.$$  \hspace{1cm} (2.1)

There are two basic ways to measure this parameter:

1. Direct counting of single emitting centers.

2. Collecting signal from an ensemble of emitting centers.

The first approach, while being conceptually easy, is hard to use in most experiments, since it requires a signal-collection system with high spatial resolution, as well as a controlled implantation process allowing implantation of a fixed number of ions [49]. As shown below, to use the second approach one has to establish
Figure 2.1: The process of creating optically active defects in crystal via ion implantation: A) Sample is placed under a monoenergetic beam of ions with a known flux. Exposure time determines the surface density of implanted ions (fluence); B) Numerical (SRIM, www.srim.org) calculation of implantation density profiles for Xe$^+$ ions implanted into diamond. For a monoenergetic beam the resulting distribution of implanted ions is centered around certain depth, determined by the type and energy of the ions, as well as the target material. C) Sample is annealed in vacuum at high temperature ($T > 800^\circ$C for diamond) to remove the damage introduced by ion implantation and to facilitate the creation of optically active defects; D) Some large and heavy ions, such as Xe, are unlikely to diffuse during annealing, therefore the related optically active defects form a thin layer close to the surface of the sample.
the connection between the statistics of the signal (e.g. photoluminescence), collected from an ensemble of emitters, and the statistics of the spatial distribution of those emitters.

In this chapter an approach to relate the statistics of the signal and the number of emitting centers is discussed. The relationship found is non-trivial and, as is shown further in the work, is determined by the experimental conditions. This statistical method is applied to estimate the conversion efficiency of the model center: Xe-related optical center in diamond.

2.2 Theoretical Background

Experimental conditions, described in section 2.3, allow us to use the following model assumptions:

1. All optical centers are positioned in a plane close to the sample’s surface.
2. Spatial distribution of emitters is uniform, with the surface density $\rho_0$.
3. Spatial distribution of emitters is random and follows Poisson distribution.

Two types of laser excitation, illustrated in the Figure 2.2, will be discussed: a) an easy to understand case of “flat-top” excitation with a uniform beam and b) more realistic Gaussian beam with the intensity distribution $I = I_0 \cdot e^{-r^2/w^2}$ ($w$ defines an effective laser beam size) and total power $P = I_0 \pi w^2$. The photoluminescence signal is collected from a circular-shaped “useful” area with the radius $R$. The radius of the useful area $R$ can be written in terms of the effective size of the laser beam $w$ as $R = kw$, where $k$ is the dimensionless size of the useful area.

When optical saturation needs to be taken into account, it will be done so by means of the intensity dependent absorption coefficient:

$$\alpha(P) = \frac{\alpha_0}{1 + P/P_S},$$

(2.2)

were $P_S$ is the saturation power and $\alpha_0$ is the unsaturated absorption coefficient. The expression (2.2) describes saturation for a resonant excitation in multi-level system [13]. In our model it will be used for an arbitrary excitation as long as it gives a reasonable approximation of the experimental results.

The signal from the useful area around a given point on the sample is given by the sum of contributions from each emitter inside that area: $S = \sum_{i=1}^{N} X_i$, where $X_i$ is the signal from an individual center and $N$ is the number (random!) of optical centers inside the useful area. The total signal $S$ is also a random quantity, described by the Compound Poisson distribution with the following properties [42]:

$$\bar{S} = \bar{N} \cdot \bar{X}, \quad \sigma_S^2 = \bar{N} \cdot \bar{X}^2.$$

(2.3)
The difference between regular and compound Poisson is in the expression for the variance $\sigma^2_S$. For the former, the variance is proportional to the square of the average signal $\bar{X}^2$ from a single emitter, while for the compound Poisson it is proportional to the average of the squared signal $\bar{X}^2$. The average number of optical centers is therefore

$$\bar{N} = \beta \cdot \frac{\bar{S}^2}{\sigma^2_S}, \quad \beta = \frac{\bar{X}^2}{\bar{X}^2}. \hspace{1cm} (2.4)$$

Here we introduce a dimensionless factor $\beta$, which obviously depends on the excitation beam profile $I(r)$. The evaluation of this factor for two aforementioned cases is presented below.

### 2.2.1 Flat-Top Excitation

Flat-top excitation is the only case when the average of the squared signal $\bar{X}^2$ equals to the square of the average signal $\bar{X}^2$, and therefore $\beta = 1$. In this case the total signal is simply the product of the number of emitters inside the useful/working laser spot and the signal from one emitter: $S = N \Delta X_1$. The connection between the statistics of spatial distribution of the emitters and the statistics of signal is trivial. Since the former is assumed to be Poissonian ($\sigma^2_S = N \cdot X_1^2$) one can find the average number of emitters inside the useful area and the signal from a single emitter:

$$\bar{N} = \frac{\bar{S}^2}{\sigma^2_S}, \quad X_1 = \frac{\sigma^2_S}{\bar{S}}. \hspace{1cm} (2.5)$$

This is similar to the determination of the electron charge using the shot-noise analysis.

Comparing (2.4) and (2.5), one can see that $\beta$ has the meaning of the correction factor which “upgrades” the Poisson distribution of the total signal from regular to compound.

The signal from a single emitter $X_1$ depends on the excitation power $P$, the sensitivity of detection $\sigma$, as well as on the quantum yield of luminescence $Q$:

$$X_1 \propto P \cdot Q \cdot \sigma. \hspace{1cm} (2.6)$$

In contrast, in (2.4) the estimated average number of optical centers does not depend on the quantum yield $Q$ (this can seen from the fact that both $\beta$ and the ratio $\bar{S}^2 / \sigma^2_S$ have the constant factor $Q^2$ canceled). What really matters is whether the optical center emits with detectable intensity (i.e. contributes into the total signal $S$), regardless of its quantum yield.
Figure 2.2: a) Flat-Top excitation with uniform distribution of power inside the laser spot. The total collected signal $S$ is directly proportional to the number of emitters inside the working area. b) Gaussian Beam has non-uniform power distribution and therefore the relation between the statistics of the total signal $S$ and the number of emitters inside the working area is not linear anymore. For Poissonian distribution of emitters on the surface of the sample it may still resemble the Flat-Top case when one introduces correction coefficient $\beta$, dependent on the experimental conditions as explained in this chapter. c) Value of the correction coefficient $\beta$ as the function of the dimensionless working area size $k \equiv R/w$. Three levels of optical saturation $\gamma$, proportional to the power of the laser beam, are considered: low, moderate and high.
2.2.2 Gaussian Beam Excitation

In the case of the excitation with a Gaussian beam \( I(r) = I_0 \cdot e^{-r^2/w^2} \) the total signal from an ensemble of emitters is given by the following sum of signals from single emitters (see Figure 2.2):

\[
S = \sum_{i=1}^{N} X_1 e^{-r_i^2/w^2}.
\]

(2.7)

Here \( X_1 \) is the signal from a single emitter, when it is positioned in the center of the laser spot. The absorption coefficient \( \alpha(I(r)) \) now becomes dependent on the position within the laser spot and can be written as

\[
\alpha = \frac{\alpha_0}{1 + \gamma e^{-r^2/w^2}}.
\]

(2.8)

The dimensionless ratio \( \gamma \equiv I_0/I_S \) is the saturation parameter. It is proportional to the total power of the laser beam \( P = I_0 \pi w^2 \) and inversely proportional to the laser spot area: \( \gamma = P/(\pi w^2 I_S) \).

A special feature of the Gaussian excitation is the absence of complete saturation of the total signal \( S \) [13]. The signal grows as \( \ln(1 + \gamma) \) due to the increase of the size of the useful/working area under the laser beam. This is different from flat-top excitation, when the signal saturates as \( \gamma/(1 + \gamma) \).

Calculating the average of the signal \( \bar{X} \) and the average of the squared signal \( \bar{X}^2 \), the expression for the correction factor \( \beta = \bar{X}^2/\bar{X}^2 \) can be presented in the following form (see Appendix A for the details of derivation):

\[
\beta = k^2 \ln\left( \frac{1 + \gamma}{1 + \gamma e^{-k^2}} \right) - \frac{\gamma(1 - e^{-k^2})}{(1 + \gamma)(1 + \gamma e^{-k^2})} \ln^2\left( \frac{1 + \gamma}{1 + \gamma e^{-k^2}} \right)
\]

(2.9)

Thus, the correction factor \( \beta \) depends on the size of the useful area given by dimensionless radius \( k = R/w \), as well as on the level of optical saturation \( \gamma \). The behavior of the correction factor as a function of the dimensionless radius of the useful area \( k \) is shown in the Figure 2.2c for three levels of saturation: low \( \gamma = 0.01 \); medium \( \gamma = 1.0 \); high \( \gamma = 100 \). As can be seen, the larger the saturation parameter, the closer one gets to the flat-top case.

Two saturation limits can be recovered from the expression 2.9:

1. \( \gamma \to \infty \), flat-top case with \( \beta = 1 \).
2. \( \gamma \to 0 \), non-saturated case with \( \beta = k^2 \coth\left( \frac{k^2}{2} \right) \).

For medium and low saturation levels the correction factor \( \beta \) depends on the size of the useful area \( k \), therefore a criterion for its determination is needed.
2.2. THEORETICAL BACKGROUND

Figure 2.3: Effective/useful size of the sample that contributes into the total collected signal $S$ increases both with the level of optical saturation $\gamma$ as well as with signal-to-noise ratio.

2.2.3 Useful Area Size

One possible way to choose the effective size $k = R/w$ of the area under the laser beam which contributes to the total signal most is to use the ratio of the signal from the optical centers to the noise, which is always present in the measurements. Figure 2.4 illustrates this idea.

The sample’s surface around the laser spot can be divided into the inside of the circle of the radius $R = kw$ (“useful area”), and the outside. Since the intensity in the Gaussian beam quickly decreases with the distance $r$ from the center of the laser spot, the signal from the outside of the circle is small compared to the total signal: $S_{out} = S_0 \ln(1 + \gamma e^{-k^2})$ and $S_{total} = S_0 \ln(1 + \gamma)$. The contribution $S_{out}$ can be neglected when it is equal of less than background noise which is always present in the measurements. The signal $S_{out}$ may even be totally lost if, for example, spectra are smoothed to remove the noise. If one denotes the signal to noise ratio as $SNR$ then, equating $S_{out} = SNR$ and solving this equation for $k$, one obtains the expression for the dimensionless radius of the useful area $k$:

$$k^2 = \ln \left[ \frac{\gamma}{(1 + \gamma)^{1/\text{SNR}} - 1} \right]. \quad (2.10)$$

Figure 2.3 demonstrates how the effective size $k$ of the useful area grows with the saturation level $\gamma$ for three levels of signal-to-noise ratios: blue curve $SNR = 5$; green curve $SNR = 20$; red curve $SNR = 100$.

To estimate the conversion efficiency, one has to calculate the average number $N_{emit}$ of emitting centers inside the useful area, and the average number $N_{impl}$ of ions implanted into the same area. The latter is determined by the implantation dose $\rho_0$ and the size of the useful area $R = kw$: $N_{impl} = \rho_0 \pi R^2 = \rho_0 \pi k^2 w^2$. 
The expression for the quantum efficiency is then given by

\[ q = \frac{N_{\text{emit}}}{N_{\text{impt}}} = \frac{\beta S^2}{\pi w^2 k^2 \rho_0}. \]  

(2.11)

In an experiment one has to establish the effective size of the laser spot \( w \), the saturation parameter \( \gamma \) and collect the signal at different points on the sample to determine the statistics of the total signal, summarized by \( S^2 \) and \( \sigma_S^2 \). The next section elaborates on the experimental procedure.
2.3 EXPERIMENT

The model presented above has been applied to Xe\(^+\) ion implanted diamond. As has been mentioned earlier, the interest in the Xe center originates from the fact that this center is one of a few (Ni, Si, Cr, Xe) centers in diamond having sharp emission lines in the infrared spectral region. At low temperatures, the photoluminescence spectra features a single zero phonon line at 811.7 nm and a weak phonon sideband. The room temperature luminescence consists of a zero phonon line at 811.7 nm and a weaker line at 794 nm (see Figure 2.7). Previous studies showed that vacancies are involved in the formation of this defect [45], it contains a single Xe ion [7], and is a \langle 111 \rangle oriented defect [6]. These results are in agreement with the previous calculations [3], which concluded that due to its large size, the Xe ion generates stresses and yields a stable configuration in the semi-divacancy site V-Xe-V.
2.3.1 Sample and Setup

The sample studied was a single crystal CVD film grown along the (001) crystallographic plane and implanted with Xe\(^+\) ions having energies 180keV at doses of \(1.0 \times 10^{10}\) and \(1.1 \times 10^{11}\) ion/cm\(^2\). Following the Xe\(^+\) implantation, the annealing at 1400° C was applied for 1 hour. SRIM simulation (see www.srim.org) shows that the Xe centers form a thin (9.6 nm) layer close to the surface of the sample. Spectra were collected in a backscattering geometry (Figure 2.5) using Horiba-JY T64000 spectrometer equipped with a confocal microscope and the cover glass corrected objective x60, N.A. = 0.7, a XYZ scanning stage, a half-wave plate to control polarization of the incident laser light with \(\lambda = 514.5\) nm, and a LiN2 cooled CCD detector. In the cubic diamond lattice there are four equivalent \langle111\rangle directions, therefore the crystal and the polarization of the laser light were oriented in a way that insured equal excitation of Xe centers in all orientations. To increase the signal/noise ratio, the sample was placed in the optical cryostat and cooled to \(T = 80\) K.

2.3.2 Laser Spot Size and Saturation Level

To measure the size of the laser spot \(w\), the knife-edge method has been used [29]. It is based on the variation of Raman signal intensity as one scans across the border between graphitic and diamond phases of the sample. These two phases have different Raman spectra (see Figure 2.6): a graphite-like phase shows broad band centered at 1380 and 1600 cm\(^{-1}\), while diamond exhibits a sharp line at 1331 cm\(^{-1}\). A thin layer of graphite-like phase was introduced in the diamond sample by irradiation with a high dose of implantation. For a Gaussian beam, the intensity of the 1600 cm\(^{-1}\) band during linear scan in the direction perpendicular to the phase border changes with the position \(\xi\) according to the expression:

\[
I_{1600}(\xi) = \frac{I_{\text{max}}}{2} \left(1 - E_{\text{rf}} \left(\frac{\xi - \xi_0}{w}\right)^2\right),
\]

where \(\xi\) is the coordinate of the center of the laser beam, and \(\xi_0\) is the position of the border. One can find \(w\) by fitting formula (2.12) to the experimental data (see Figure 2.6). The measurements revealed a slight ellipticity of the laser spot, with the approximate values of \(w_x = 0.47 \pm 0.04\mu m\) and \(w_y = 0.33 \pm 0.04\mu m\). The 20% error in the determination of the product \(w_x \cdot w_y\) turned out to be one of the major sources of uncertainty in the conversion efficiency.

Representative luminescence spectra collected from the sample at room and LiN2 temperatures are shown in Figure 2.7a. Measuring intensity of the 811 nm zero-phonon line at various excitation powers one obtains “saturation curve” (shown in Figure 2.7b). The saturation parameter \(\gamma\) can determined from such curve by fitting formula (2.12). The saturation parameter in discussed mapping experiments was equal \(\gamma = 0.6P\) and
2.3. EXPERIMENT

Figure 2.6: Determining the laser spot dimensions by scanning a sharp border between two carbon phases: diamond and graphite. a) Raman signal collected from pure diamond (blue, light) and from graphite phase (black, dark) at room temperature. Note the absence of the wide peak at 1600 cm\(^{-1}\) for pure diamond, this peak is characteristic to graphitic phase. b) The intensity of the 1600 cm\(^{-1}\) peak as the function of the laser spot position as it crosses the phase border. The solid line shows the fit of the formula (2.12) to determine the size of the laser beam.
Aperture-free measurements

<table>
<thead>
<tr>
<th>$\rho_0$, cm$^{-2}$</th>
<th>$\gamma$</th>
<th>$k$</th>
<th>$\beta$</th>
<th>$S$, c/s</th>
<th>$\sigma_S$, c/s</th>
<th>$N_{\text{emit}}$</th>
<th>$N_{\text{impl}}$</th>
<th>$q$</th>
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<tr>
<td>$10^{10}$</td>
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<tr>
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<td>2.49</td>
<td>1.73</td>
<td>92.5</td>
<td>12</td>
<td>102</td>
<td>302</td>
<td>0.34</td>
</tr>
<tr>
<td>$10^{12}$</td>
<td>0.96</td>
<td>2.21</td>
<td>1.97</td>
<td>43.8</td>
<td>2.52</td>
<td>607</td>
<td>2380</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 2.1: Conversion efficiency estimated from several confocal micro-luminescence mappings using aperture-free approach.

varied from 0.47 up to 60 depending on the excitation power $P$.

2.4 Results and Discussion

Having determined the effective laser spot size $w$ and saturation level $\gamma$ as the function of the excitation power $P$, a series of mappings have been performed. A single mapping implies the measurements of photoluminescence spectra from Xe-related centers at different points on the sample’s surface. These points were arranged in a square 2D array. A regular map consists of 20x20 points, separated by 2–4 $\mu$m from each other. In Figure 2.8a a representative map is shown. Each pixel is visualized with pseudo-color, corresponding to the intensity of the 811.7 nm peak.

After the accumulation of the map, the statistics of the peak intensity was extracted and analyzed (see Figure 2.8b for the histogram of the signal): the average of the signal, it’s variance, and the signal to noise ratio were determined. The correction factor $\beta$ was calculated using the expression 2.9 and the average number of emitting centers was estimated as $N_{\text{emit}} = \beta \frac{S}{\sigma_S^2}$. The number of implanted ions is given by $N_{\text{impl}} = \pi k^2 w_x w_y \rho_0$, therefore one can estimate the conversion efficiency $q = \frac{N_{\text{emit}}}{N_{\text{impl}}}$. Results are shown in the Table 2.1 for accumulated maps measured under different conditions. The signal to noise ratio was of the order $10^2$. Based on the data gathered from these and other mappings, one concludes that the conversion efficiency is close to 0.30 with 20% relative error.

The main reason for the absence of total conversion ($q = 100\%$) is most likely the lack of sufficient vacancy-ion interaction during thermal annealing. For example, in [52], similar question is discussed for NV$^-$ center. Also, analysis of the role of the vacancies is performed in the Appendix A.0.3. The main conclusion is that the number of vacancies available for “capture” is the critical parameter in the formation of optically active defects. To increase the conversion efficiency one needs to perform additional post-implantation treatment of the sample: bombardment with high energy electrons or protons, for example, to create more vacancies. This may require several cycles of implantation and annealing, since too high concentration of vacancies may irreversibly damage the diamond lattice.
2.4. RESULTS AND DISCUSSION

Figure 2.7: a) Photoluminescence (PL) spectra of Xe-related centers in CVD diamond at LiN2 and room temperatures. PL was excited with 514.5 nm line of Ar/Kr gas laser. b) PL signal intensity (both peak and integral) grows with the increased incident laser power, never reaching the saturation regime due to the Gaussian beam profile of the excitation. Power of 100 a.u. corresponds to approximately 5 mW focused on a micron-sized spot. The logarithmic law for the collected signal is an important feature of the Gaussian beams which must be properly accounted for to correctly determine the level of optical saturation.

\[ S = 115 \cdot \ln(1 + 0.6 \cdot I_l) \]
Figure 2.8: A result of a typical micro-luminescence mapping: a) spatial distribution of a photoluminescence signal from Xe-related optical centers in diamond. Signal has been collected at $T = 80$ K from 400 points arranged in a 20x20 matrix. b) Histogram of the measured signal (peak intensity). Main parameters to extract from it are the average and the standard deviation of the signal. These are used to find the average number of the emitting centers inside the working area of the laser beam $\bar{N} = \beta S^2/\sigma_S^2$. 
2.4. RESULTS AND DISCUSSION

2.4.1 Confocal Aperture Method

Analysis in A.0.2 indicates that the errors in determination of the effective size of the laser spot \( w \) and the size of the useful area \( k \) are the main sources of uncertainty in the conversion efficiency \( q \). To increase the accuracy, one has to use a method which is less sensitive to these parameters. As described below, one possible way to accomplish this is to “force” the size of the useful area. In a set up with confocal microscope this can be done by changing the size of the confocal aperture. If \( M \) is the magnification of the system from the sample to the plane of confocal aperture, then one can make the aperture’s size comparable to the size \( M \cdot w \) of the image of the laser spot. Working at high saturation levels will create an almost uniform excitation profile within the area defined by the aperture. Since the accurate measurements of the laser spot size \( w \) are not required this can be a more accurate way to measure the conversion efficiency. However, this approach required taking into account diffraction effects.

As follows from (2.4), the general expression for the correction factor is \( \beta = \frac{X^2}{\bar{X}^2} \). The signal \( X \) from an individual optical center, positioned at a point \( r \) of the sample, is given by \( X = c \cdot I(r) \cdot \alpha(I) \cdot A(r) \). Here \( c \) is a constant that depends on the sensitivity of detection and on the quantum yield of the luminescence of the optical centers (assuming that all optical centers have equal yields of luminescence, the measured conversion efficiency \( q \) does not depend on the yield value); \( I(r) \) is the illumination profile, given by the power density distribution within the laser beam; \( \alpha(I) \) is the absorption coefficient; the factor \( A(r) \) accounts for the effects of a confocal aperture. Because of the aperture and the effects of diffraction only part of the signal from a single emitter reaches the detector, which implies that \( A(r) \leq 1 \).

The confocal arrangement used is shown in Figure 2.9. The aperture size should be smaller than the image of the focal spot: \( d < M \cdot w \), where \( d \) is the aperture size, \( w \) is the focal spot size, and \( M \) is the magnification of the optical system. Together with high level of optical saturation, this will make the excitation of optical centers almost uniform everywhere in the useful area determined by the aperture. This regime of measurements does not require the exact knowledge of the focal spot size \( w \) and is, therefore, unaffected by the errors in \( w \).

An optical center, being a point-like emitter, has an image of a finite size \( r \) at the aperture (see Figure 2.9b). This image, determined by the objective of the microscope, defines a point spread function of the optical system with the characteristic size \( \delta = \frac{0.6098 M \lambda}{NA} \), here \( \lambda \) is the emission wavelength, and \( NA \) is the numerical aperture of the objective [43]. As indicated in the Figure 2.9, this increases the effective size of the useful area because some emitters projected outside of the aperture may still contribute part \( A(r) \) of their signal \( X \) to the total detected signal.

In contrast to the aperture-free method, uniform flat-top excitation (i.e. \( I(r) = \text{const} \)), does not lead to
CHAPTER 2. CONVERSION EFFICIENCY

Figure 2.9: Using a confocal aperture to impose the shape and the size of the working/effective laser beam spot. a) The image of the sample’s surface is magnified $M$ times at the confocal aperture. If the the size of the confocal hole $2d$ is smaller than the magnified laser spot size $Mw$ it essentially defines what part of the image goes to the detector. b) With a small confocal aperture one needs to take into account the effects of diffraction. The latter allows the emitters slightly outside of the borders of the aperture to still contribute into the total collected signal $S$ due to finite size of image of the point-like emitter (point-spread function of the optical system).
the Poisson statistics of the total signal. It means that the correction factor $\beta$ does not equal unity and is determined by the effects of the aperture and the diffraction: $\beta = \frac{A^2}{\bar{A}^2}$. Fortunately, for the given shape and size of the aperture and a particular form of the point spread function, the factor $\beta$ can be calculated numerically with an arbitrary precision. To this end one needs, for example, to simulate the experiment with a known number of emitters $N$ ($N = 1000$ was used in our simulations). In each trial $N$ points are randomly positioned inside a useful area of a certain size $R$. Summation of all signals from the individual emitters, with the effects of non-uniform excitation and the presence of aperture accounted for, yields the set of signals $S_1, S_2, \ldots, S_n$ for a number of trials. Their values vary due to the random distribution of the emitters inside the useful area. The factor $\beta$ is then given by $\beta = N\sigma^2_S/S^2$ and can be calculated with an arbitrary precision. See B for an example of a computer program that can be used to evaluate $\beta$.

Table 2.2 summarizes the results of the measurements using this approach. The mapping procedure is the same as for the aperture-free method, the only difference is in the calculations of the correction factor $\beta$ and the area of the working/effective laser spot as defined by the confocal aperture.

<table>
<thead>
<tr>
<th>Confocal aperture measurements</th>
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<td>$\rho_0$, cm$^{-2}$</td>
</tr>
<tr>
<td>10$^{10}$</td>
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<tr>
<td>10$^{10}$</td>
</tr>
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</table>

Table 2.2: Conversion efficiency estimated from micro-luminescence mappings using confocal aperture method.

2.5 Conclusion

A method for the determination of the probability of implanted ions to form optical centers has been proposed. The method is based on the statistical analysis of the measured signal from many ensembles of emitters. The method is applicable to any type of optical center and is independent of their quantum yield. The analysis revealed that the method is sensitive to the errors in the size of the focal spot of the laser used to excite the centers, and requires an unambiguous criterion for choosing the useful (working) area. The approach was applied to Xe optical centers in a high purity CVD diamond crystal, and the conversion efficiency was estimated as 0.30 with 20% relative error. The alternative and more accurate approach, based on the ability of a confocal aperture to change the useful area of the sample, has been also studied. Both methods produced agreeing results. At high saturation the confocal mapping using an aperture is preferable in situations when accurate measurements of the focal spot $w$ are not possible. This method is nearly insensitive to experimental errors in $w$. However, the necessity of numerical calculations of the factor $\beta$
makes the confocal aperture method more laborious.
Chapter 3

Inhomogeneous Broadening of ZPL

3.1 Introduction

Narrow zero phonon lines (ZPL) in photoluminescence spectra of optical centers in solids are best observed at low temperatures when phonon-induced broadening is negligible and the peak intensity is high. But even then the observed line width in most cases is much larger than the natural line width. This additional broadening is the result of static interaction between the optical center and host environment. The spatial variations of the environmental parameters (e.g. strain or electric field) result in the spread of the transition energies of emitting centers. Collecting a signal from an ensemble of such emitters one can determine the envelope of this spreading. The latter represents the inhomogeneously broadened line, as illustrated in Figure 3.1 Random strain fields can be produced by various types of defects present in a given sample such as: point defects, dislocations, point-defect aggregates, etc. It is hard to attribute a given line shape to a specific defect type unless its effects are dominant. In this chapter we study the features of inhomogeneously broadened lines due to various “point-like” (as defined below) defects and investigate how the change in the distribution geometry of defects changes the shape of the inhomogeneously broadened line. The results obtained are then used to explain the observed peculiar behavior of the 811.7 nm zero-phonon line from Xe-related centers in diamond.

Xe$^+$ ions implanted into a diamond crystal form optically active centers after the high temperature annealing [45]. The spectroscopy studies of this center have been reported in [45, 6, 7]; they suggest a V-Xe-V or Xe-V$_3$ configuration with a trigonal symmetry [6, 7]. The latter configuration has been confirmed by the density functional theory calculations [3, 23]. Implanted at a fixed energy and annealed, Xe$^+$ ions form a thin planar layer of optical centers below the crystal surface. According to SRIM calculations (www.srim.org), for
Figure 3.1: The origin of inhomogeneous broadening: Collecting signal from ensemble of identical emitters (black dots) coupled to the environment (star-shaped figures represent defects). Inhomogeneity of environment leads to the spread of the transition frequency $\omega_0 + \Delta$. The observed envelope defines inhomogeneously broadened line.

Figure 3.2: Depth profiles, according SRIM(www.srim.org) simulations, of the Xe atoms (right peak) and the vacancies (left peak) for the Xe$^+$ implantation at 180 keV in diamond. Number of ions $N = 40 000$. 

$Xe^+$ into diamond at 180 keV
Longitudinal Range=46.1 nm
Longitudinal Straggle=8.1 nm
3.1. INTRODUCTION

Figure 3.3: Full width at half maximum (FWHM) of the 811.7 nm zero-phonon line in photoluminescence spectra from Xe-related centers in diamond at various temperatures. The implantation dose is $1.1 \cdot 10^{11}$ cm$^{-2}$. Excitation wavelength is 514.4 nm.

used energy of 180 keV, the thickness of this layer is about 16 nm while the depth is 46 nm (see Figure 3.2). During thermal annealing irradiation induced point defects (vacancies and self-interstitials) diffuse in depth and significantly anneal out [2]. Diffusion of large atoms like Xe is much less studied, but it is generally accepted that the migration range is no more than a few C-C distances [26]. We assume an almost planar geometry of the Xe optical centers distribution even after the thermal annealing. These centers may also act as defects and lead to the inhomogeneous broadening additional to the broadening due to the residual irradiation induced and inherent lattice defects. Low temperature ($T < 20$ K) photoluminescence spectra from Xe-related center indicate that the ZPL at 811.7 nm is inhomogeneously broadened (see Figure 3.3); for implantation doses $\geq 10^{13}$ ion cm$^{-2}$ it was shown in [45]. Our measurements at lower implantation doses (see section 3.3) confirmed its inhomogeneous shape and found unexpected changes from Lorentzian to another symmetric but non-Lorentzian line shape with substantially more pronounced tails when one increases the implantation dose. Figure 3.10 demonstrates the effect. This type of behavior is absent in the standard version of the statistical theory of inhomogeneous broadening reviewed in [56].

In this chapter, we consider the following possible causes of the non-standard behavior of the ZPL:

1. The planar geometry of the distribution of defect(s).
2. Complex structure of the defects.

Monte-Carlo simulations have been used to study the problem of inhomogeneous broadening for the planar geometry and various complex structures of the defects.

### 3.2 Theoretical Background

The strain field of a point defect in an elastic isotropic medium is given by the following expression [56]:

\[ \epsilon_{ij} = \frac{S}{r^3} (\delta_{ij} - 3x_i x_j / r^2), \]  

(3.1)

where \( S \) denotes the strength of the defect (\( S < 0 \) for a vacancy and \( S > 0 \) for a large substitutional atom). A pair “vacancy-large substitutional atom” separated by a displacement vector \( \mathbf{d} \) constitutes what can be called a point dipole if \( \mathbf{d} \) is small. The orientation of such structure is specified by \( \mathbf{d} \). Assuming that strains add linearly, the total strain tensor for such configuration equals to

\[ \epsilon_{ij} = S_1 \epsilon_{ij}(r) + S_2 \epsilon_{ij}(r + \mathbf{d}). \]  

(3.2)

For the low concentration of defects the condition \( \mathbf{d}/r \ll 1 \) is satisfied and the strain tensor can be approximated by the first terms in the Taylor series:

\[ \epsilon_{ij} = (S_1 + S_2) \epsilon_{ij}(r) + S_2 \mathbf{d} \nabla \epsilon_{ij}(r). \]  

(3.3)

When the strengths of the substitutional atom and the vacancy are \( S_1 = S \) and \( S_2 = -S \), respectively, the first term in (3.3) vanishes and the components of the strain tensor can be written as

\[ \epsilon_{ij} = \frac{S}{r^3} \Phi_{ij}(\mathbf{d}, \theta, \phi), \]  

(3.4)

\( \Phi_{ij}(\mathbf{d}, \theta, \phi) \) being the angular part. (See C.0.6 for the details of derivation). If the “net strength” is not zero then such a configuration possesses a monopole moment \( \epsilon_{ij} \propto 1/r^3 \) and behaves like a regular point defect. In a similar way, one can show that at the low concentration of point-like bi-dipole defects (two vacancies on both sides of a large substitutional atom) strain field has the form \( \epsilon_{ij} = \frac{S}{r^3} \Theta_{ij}(\mathbf{d}, \theta, \phi) \) if the net strength \( S_1 + 2S_2 \) of this defect is zero. Otherwise \( (S_1 + 2S_2 \neq 0) \), the monopole term \( \epsilon_{ij} \propto 1/r^3 \) dominates and the whole structure behaves like a regular point defect.
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Figure 3.4: The element of a Monte-Carlo ensemble modeling the inhomogeneous broadening: an emitter in a spherically-shaped crystal of the radius \( R_1 \) surrounded by point-like defects. The latter cannot approach the emitter closer than \( R_0 \). Defects create elastic strain field which couples to the emitter to produce a shift of the transition energy \( \omega_0 + \Delta \), where \( \Delta \) fluctuates when the defects are randomly distributed around the emitter.

### 3.2.1 Numerical Model

Monte-Carlo type simulations have been used to study the problem of inhomogeneous broadening numerically. In these simulations an ensemble of \( 10^6 \) independent emitters was generated. Each emitter was then surrounded by a finite number \( N \) of defects uniformly distributed inside the sphere of the radius \( R_1 \) (sphere is for 3D case; for 2D the disk of the same radius was used). In a way similar to Davies [14, 15] and Kador [38], an “exclusion volume” was introduced, i.e. defects were not allowed closer than a certain distance \( R_0 \) to the emitter. Figure 3.4 illustrates this configuration.

The lower limit for \( R_0 \) is 1-10 of lattice constants. From these two parameters, \( R_1 \) and \( R_0 \), the radius \( R_1 \) does not affect the results of the simulations as long as it is large enough and the “crystal” contains at least 10 defects. This reflects the insensitivity of the problem to the boundary conditions. The \( R_0 \) however proves to be an essential tuning parameter which affects the shape of the inhomogeneous spectra.

For each member of the generated ensemble the components of the total strain tensor at the emitter’s site were calculated: \( \epsilon_{ij} = \epsilon_{ij}(r_1) + \epsilon_{ij}(r_2) + \cdots + \epsilon_{ij}(r_N) \). The shift of the emission line for a given emitter was calculated as \( \Delta = a_{ij} \epsilon_{ij} \); \( a_{ij} \) represents the coefficients that couple strain to the electronic states of emitters. Several types of matrices \( a_{ij} \), corresponding to different symmetries of the optical center, were considered in [14]. In principle, matrices \( a_{ij} \) can be found from uniaxial stress measurements [40]. The simulations showed that for ZPL shape the exact values of \( a_{ij} \) are of lesser importance than the symmetry of the matrix \( a_{ij} \). The histogram, like the one shown in Figure 3.5, represents the spectral shifts from all elements of the ensemble and defines the inhomogeneous line shape.

Numerical calculations have been performed under the following assumptions:

1. Low concentrations of the defects.
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Figure 3.5: Results for numerical simulations of the process of inhomogeneous broadening due to point defects in 3D. The line-shape produced is invariably symmetric, Lorentzian for this case in agreement with the results of work [56].

Figure 3.6: The point-like defects considered as the sources of inhomogeneous broadening: (a) point defect of a positive strength; (b) point defect of a negative strength; (c) point-dipole; and (d) point bi-dipole.

2. Linear elasticity of the medium.

3. Linear perturbation of the strain.

These assumptions are similar to those used in the statistical theory of the inhomogeneous broadening [56].

3.2.2 Types of Defect Structure

The defects considered are “point-like” in the following sense: the size of a defect is one or two lattice spacing in all dimensions (as illustrated in Figure 3.6). A large substitutional atom or a vacancy represents point defect with the strain field falling off as $1/r^3$ [56]. A pair vacancy-large substitutional atom constitutes a point dipole. As has been shown earlier, such a structure has an orientation and the strain field falls off as $1/r^4$. Finally, the bi-dipole is a point-like defect made of two vacancies on both sides of a large substitutional atom; its strain field falls off as $1/r^5$. 
3.3 Experiment

Xe-related centers were created in diamond by the ion implantation of 180 keV Xe\(^{+}\) ions into a (001) crystallographic plane of a single crystal high purity CVD diamond. After that 1 hour annealing at \(T = 1400^\circ\text{C}\) in high vacuum has been performed. The sample was placed in an optical cryostat. The photoluminescence was excited with Spectra-Physics Ar/Kr gas laser with \(\lambda_{\text{exc}} = 514.5\) nm. Signal was collected by confocal microscope and spectra were measured using Jobin-Yvon T64000 spectrograph in a single stage configura-
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Figure 3.8: For the case of 2D distributed point defects the line shape becomes sensitive to the symmetry of the emitter. It can be no longer symmetric as is the case of the triclinic emitter. The coupling matrices used in simulations are given in the insets and reflect the symmetry of the emitter [40].

\[
\begin{pmatrix}
1.0 & 2.0 & 2.0 \\
2.0 & 1.0 & 2.0 \\
2.0 & 2.0 & 1.0
\end{pmatrix}
\]

\[
\begin{pmatrix}
3.3 & -9.4 & -3.9 \\
-9.4 & -2.1 & 9.7 \\
-3.9 & 9.7 & 7.4
\end{pmatrix}
\]

Figure 3.9: At low concentration of defects the inhomogeneous broadening is determined almost exclusively by the first and the second nearest defect (numerical calculations for the trigonal center and dipoles in 2D).
3.4 Results and Discussion

The first most apparent difference between 2D and 3D distribution of defects is seen in the inhomogeneous line shapes produced: for the 3D case the line shape is invariably symmetric, being Lorentzian for the...
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Figure 3.11: The calculated inhomogeneously broadened line fits closely to the experimental if the defects have the bi-dipole structure and are distributed in a plane. For the shown fit, the radius of the “exclusion” sphere is $R_0 = 2.3$ nm.

Second, when studying the dependence of the full width at half maximum as the function of concentration, one observes a law of scaling: $\text{FWHM} \propto \rho^{n/D}$ (discussed in C.0.9), where $n$ is the power in the strain field fall-off (as in $1/r^n$) and $D$ is the dimension of the problem. This law is valid for low concentrations of defects and has been obtained by Stoneham for the point defects ($n = 3$) in three dimensions ($D = 3$) [56]. Moreover, all parameters of the line-shape, such as its width, asymmetry, kurtosis, etc. scale according to the power law $\propto \rho^{n/D}$; however, the shape of the line stays the same.

The third essential result of interest is that at low concentrations of defects ($\rho R_0^3 \ll 1$), the line shape is determined nearly exclusively by the two nearest defects as illustrated in Figure 3.9. This is the nearest-neighbor approximation discussed in C.0.8.

Assuming the distribution of the point-like defects to be planar and their structure dipole or bi-dipole, one can achieve a good fit to the observed data by adjusting the radius of the “exclusion” sphere, see Figure 3.11. The only known bi-dipole defects in the sample are V-Xe-V, so likely the inhomogeneous broadening of 811.7 nm zero-phonon line at the implantation dose $5 \cdot 10^{12}$ ions cm$^2$ is determined by elastic interaction between Xe centers. Since dipole defects in 2D also allow the fit, there is a possibility of unidentified dipole defects distributed in the layer of Xe centers and causing the observed behavior. It should be noted that for
3.5 Conclusion

As has been shown, when analyzing the inhomogeneous broadening from narrow lines one has to pay attention to the following factors:

1. The distribution geometry of the defects responsible for the broadening.

2. The internal structure of point-like defects.

These factors may manifest themselves either in the asymmetric line-shapes or in the heavy, non-Lorentzian tails. Furthermore, the FWHM as the function of the concentration scales according to the law $\text{FWHM} \propto \rho^{n/D}$ and reveals the difference in the geometries and/or the types of the point-like defect. The experimentally observed change of the line-shape of the 811.7 nm ZPL from Xe-related centers can be now understood in the following way: at the implantation dose $1.1 \cdot 10^{11}$ ions cm$^{-2}$ the inter-Xe-centers elastic interaction is very weak and the line shape is Lorentzian. The latter fact is likely due to the point defects produced during the implantation and not fully annealed. They diffuse noticeably at the annealing temperature and became distributed in 3D. When the implantation dose increases the number of V-Xe-V centers increases as well. These defects are distributed in 2D and their contribution into the total broadening grows faster than that of point defects in the bulk and dominates at higher implantation doses. Thus the unusual ZPL shape observed at the dose $5 \cdot 10^{12}$ ions cm$^{-2}$ reflects 2D distribution of the V-Xe-V defects.
Chapter 4

Homogeneous Broadening of ZPL

4.1 Introduction

As was mentioned in the section 1.1, optically active defects in diamond are currently objects of active research. Various impurities are introduced into single crystal diamonds, poly-crystalline diamond films, nano-diamonds and nano-films with purpose to create a reliable and efficient “artificial atom” that can be used as a solid-state single-photon emitter. Among hundreds of defects some stand out as particularly promising candidates: nitrogen-vacancy, silicon-vacancy, chromium-related center, and xenon-related center to name but a few. The photoluminescence spectra of these optically active centers feature rather narrow emission lines in near- and infrared parts of spectrum, where diamond itself is transparent. It has become possible to create and address a single emitting center in diamond, thus getting closer to the goal of making a source of single-photons on demand. The latter is an essential component of the quantum communication network.

Any optically active defect in crystal is a coupled system “defect+host lattice”. The interaction of optically active defects with host lattice determines not only the temperature independent inhomogeneous broadening of zero-phonon lines (ZPL), as discussed in Chapter 3, but also temperature-dependent behavior of the shape of ZPL which is identical for all emitters in the crystal. The latter is known as homogeneous broadening (or thermal broadening) and will be present even in a pure, homogeneous crystal; it provides important information about defect-lattice coupling mechanism.

To observe homogeneously broadened line-shape one needs to minimize the effects of inhomogeneous broadening. To do that on can satisfy any of the following conditions:

1. Use crystal of very high purity.
2. Observe a small-sized ensemble (1-10 emitters).

3. Access a single emitter (either spatially or spectrally).

4. Work at temperatures when homogeneous broadening dominates over inhomogeneous broadening.

The last condition is often the easiest to satisfy. Collecting photo-luminescence signal from an ensemble of emitters at high enough temperatures (specific to particular defects) one observes the shape of zero-phonon line mostly due to homogeneous defect-lattice interaction. The change of the line-shape parameters with temperature reveals the details of the mechanism of the emitter-lattice interaction. It is therefore necessary to study homogeneous broadening to understand how optically active defect is affected by the crystal lattice.

The problem of homogeneous broadening has been addressed by many authors over the past 60 years. Systems studied varied from a trapped electron coupled to the normal modes of the lattice [41] to a large molecule, distorting and modifying the host lattice to create quasi-localized vibrational states [33]. In many cases, when the optical transition in question happens between two electronic states, emitter can be modeled as a two-level system (TLS). The host lattice represents what can be called a “bath”. In general the quantum mechanical Hamiltonian of the interacting emitter-lattice system can be written as

$$\hat{H} = \hat{H}_{TLS} + \hat{H}_{BATH} + \hat{H}_{INT}. \quad (4.1)$$

In the basis of TLS states $|1\rangle$ and $|2\rangle$ the first term takes the form $\hat{H}_{TLS} = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2|$. 

The interaction between emitters and the lattice (“bath”) leads to two distinct processes: 1) pure dephasing and 2) population relaxation in the ensemble of the emitters. To illustrate the difference between them consider a pure ensemble of two-level systems all of which are in the same initial quantum state $|\Psi_0\rangle = \alpha|1\rangle + \beta|2\rangle$. Density matrix for such an ensemble is then $\hat{\rho}_0 = |\Psi_0\rangle\langle \Psi_0| = |\alpha|^2|1\rangle\langle 1| + |\beta|^2|2\rangle\langle 2| + \alpha\beta^*|1\rangle\langle 2| + \alpha^*\beta|2\rangle\langle 1|$. When interaction between the emitters and the lattice leads to the loss of fixed phase relation between states $|1\rangle$ and $|2\rangle$, the purity of the state $|\Psi_1\rangle$ is destroyed. The off-diagonal terms in the density matrix disappear and the ensemble evolves into a mixture of emitters in the ground and excited state: $\hat{\rho} = |\alpha|^2|1\rangle\langle 1| + |\beta|^2|2\rangle\langle 2|$. When $|\alpha|^2 = \text{const}$ and $|\beta|^2 = \text{const}$ this de-phasing process conserves the population of both states and is called pure dephasing. The other type of $|\Psi\rangle$ state evolution involves relaxation of population, leading for example to the radiative transitions $|2\rangle \rightarrow |1\rangle$. As discussed in [55], the pure-dephasing may be a dominant contributor to the shapes of zero-phonon lines in both absorption and emission spectra.
4.1. INTRODUCTION

The general form for the interaction Hamiltonian $\hat{H}_{INT}$, following [55], can be written as

$$\hat{H}_{INT} = \Delta_1 |1\rangle \langle 1| + \Delta_2 |2\rangle \langle 2| + \Delta_{12} |1\rangle \langle 2| + \Delta_{21} |2\rangle \langle 1|,$$

(4.2)

where diagonal terms correspond to the pure dephasing processes, while off-diagonal are responsible for the population relaxation. All $\Delta$’s are operators acting on the “bath” states.

The diagonal terms in (4.2) effectively produce a time-dependent modulation of the emitters energy levels: $E_1 \rightarrow E_1 + \Delta E_1(t)$ and $E_2 \rightarrow E_2 + \Delta E_2(t)$. This extra-broadening of the levels’ width results in the increase of the width of emission/absorption line.

The lattice (“bath”) is usually modeled with a set of harmonic oscillators, describing either extended optical and acoustic phonons or vibrational states localized near optically active defect:

$$\hat{H}_{BATH} = \sum_{i=1}^{N} \hbar \omega_i (\hat{a}_{i}^\dagger \hat{a}_{i} + \frac{1}{2}).$$

(4.3)

Localized vibrational states may in turn be coupled to the rest of the undistorted lattice and transfer their energy into regular phonons, thus bearing name of quasi-local or pseudo-local modes (QLMs or PLMs).

In the study of pure-dephasing problem, the off-diagonal terms in (4.2) are omitted. The “bath” operators $\Delta_{k}$ are often assumed to depend on the normal mode coordinates $\hat{q}_{i} \propto \hat{a}_{i}^\dagger + \hat{a}_{i}$ and can be expanded into series (assuming small-amplitude oscillation around some equilibrium positions):

$$\Delta_{k} = \Delta E_{k} + \sum_{n=1}^{N} c_{kn} \hat{q}_{n} + \sum_{n,m=1}^{N} d_{knm} \hat{q}_{n} \hat{q}_{m} + O(3)$$

(4.4)

The multitude of models described in literature can be classified based on the following factors:

1. Type and number of modes in the “bath” (e.g. phonons or pseudo-local modes).
2. Frequency spectrum of the modes (e.g. acoustic or optical phonons).
3. Coupling strength (e.g. linear or quadratic in $\hat{q}$ operators).
4. Interaction treatment (e.g. perturbative method or non-perturbative).

Below a brief overview of major models will be given. Before that a final approximation which is often made will be discussed.

Firstly, the terms in the interaction Hamiltonian (4.2) linear in phonon operators $\hat{q} \propto \hat{a}_{i}^\dagger + \hat{a}_{i}$ do not produce such temperature-dependent effects as shift and/or broadening of the zero-phonon line [34]. In some cases such terms are simply neglected. Secondly, the remaining quadratic terms are simplified under
the assumption that quadratic coupling parameters $d_{knm}$ in (4.4) are of the form: $d_{1nm} = U h_n h_m$ and $d_{2nm} = (U + W) h_n h_m$. It allows to reduce the summation in (4.4) by introducing a single collective coordinate for the “bath” motion:

$$\hat{\phi} = \sum_{k=1}^{\infty} h_k \hat{q}_k,$$

(4.5)

then

$$\hat{\Delta}_1 = \Delta E_1 + U \hat{\phi}^2$$

(4.6)

$$\hat{\Delta}_2 = \Delta E_2 + (U + W) \hat{\phi}^2$$

(4.7)

Thus, the total model Hamiltonian of a two level system coupled to a crystal lattice is written in the following way:

$$\hat{H} = (E_1 + \Delta E_1)|1\rangle \langle 1| + (E_2 + \Delta E_2)|2\rangle \langle 2| +$$

$$+ \sum_{k=1}^{N} \hbar \omega_k (\hat{a}_k^\dagger \hat{a}_k + \frac{1}{2}) +$$

$$+ \hat{\phi}^2 [U|1\rangle \langle 1| + (U + W)|2\rangle \langle 2|].$$

(4.8)

A large number of models for thermal broadening of zero-phonon lines is based on the Hamiltonian (4.8).

McCumber and Sturge [48], for example, used quadratic coupling approximation and calculated line-width and shift parameters using perturbation up to the second order in coupling strength. The theory developed by McCumber in [46, 47], although considers a quite general form of the model Hamiltonian, yields Fourier transform for the emission/absorption spectrum $I(t) = FT[I(\omega)]$ under the approximation of linear coupling. When non-linear coupling is considered it is done using second-order perturbation theory, valid for weak coupling limit. Strong coupling limit is also considered, but similar to [41], the results obtained are the moments of the line-shape, not the shape of zero-phonon line itself.

In the works by Osad’ko (see [53, 51] and references therein) the problem is solved for quadratic coupling without limitation of perturbation theory. The main results, valid for all temperatures, are the thermal broadening and shift of the zero-phonon line. Predicted line-shape of the latter is Lorentzian. These results are in good agreement with later works by Skinner and Hsu [55, 34]. Works [53] and [55] also contain reviews of a number of experimental works. It is worth noting that most works focus on explaining the observed change of widths of spectral lines with temperature. As will be shown in the present work it is not always sufficient and the fit of actual line-shape may be required.

The shape of the zero-phonon line for the emitter interacting with quasi-local modes has been studied at all temperatures in the work by Dykman and Krivoglaz [24]. Important feature of their model is non-
symmetric line-shape, exhibiting a fine structure of zero-phonon line for certain values of the parameters of the quasi-local mode. The expressions for spectral distribution of zero-phonon line intensity can be used in numerical calculations, but are limited to cases of weak electron-phonon coupling, when perturbation theory is applicable.

Non-perturbative treatment of quadratic coupling has been also presented in the works of Hizhnyakov [32, 33]. Based on the Hamiltonian of the type (4.2), he obtains the Fourier transform of the spectral shape of zero-phonon line of a two-level system interacting with a single pseudo-local mode. Similar to the case of Dykman and Krivoglaz the line-shape possesses an asymmetry which increases with temperature and exhibits a fine structure for high-Q (i.e. long-lived) pseudo-local modes. Such model, as shown further in this work, is capable of explaining the behavior of 811.7 nm zero-phonon line observed in photoluminescence spectra of Xe-related centers in diamond. Although in [32] the model is valid only for temperatures lower than certain “critical” temperature, it has been extended to all temperatures in [33]. It must be noted that [33] contains expressions with several errors (see Appendix D for the analysis) and can not be used for actual calculations of the zero-phonon lines. However, the author was available for private communication and provided corrected expressions which are used later in this work.

This concludes the overview of most relevant models and approximations used in the theories of thermal broadening of zero-phonon lines due to electron-phonon coupling.

4.2 Theoretical Background

As has been discussed above, a number of models has been proposed to explain temperature dependent behavior of zero-phonon lines of optical defects in crystals. The model chosen for this work was the only one meeting the following criteria: 1) must predict broadening of the zero-phonon line; 2) must yield expression for non-symmetric line-shape; 3) asymmetry must grow with temperature; 4) must cover sufficient temperatures range. As and additional, but not critical, requirement the following may be added: 5) should include the case of pseudo-local vibrations. The reason for this requirement can be seen, for example, in the work [23], where the calculations of vibrational density of states for Xe-related center in diamond predict three pseudo-local modes. The model proposed by Hizhnyakov in [33] satisfied the above mentioned criteria. In addition, the author was available for private correspondence for which I want to express my gratitude. Below, we briefly outline this model, for details see [32] and [33].

The justification for this model can be given as follows. Diamond lattice is tightly packed, with the nearest neighbor distance 0.15 nm. Also, most impurity atoms are larger and heavier than carbon (e.g. N, Si, Cr, Xe have Van der Waals radii 0.16 nm, 0.21 nm, 0.20 nm, 0.22 nm respectively). Therefore one
should expect that the lattice in the vicinity of an impurity is distorted. Such distortion may affect the vibrational motion of lattice. Namely, carbon atoms neighboring an impurity won’t be able to participate in a collective motion of whole lattice. Instead, a vibrational mode (or several modes) spatially localized near impurity may appear. This mode, called pseudo-local mode, interacts both with the impurity and the rest of the lattice. One can therefore consider the following model of a large impurity in diamond lattice: quasi-molecule composed of “impurity atom+neighboring carbon atoms” coupled to the undistorted part of the lattice, see Fig 4.1.

The model Hamiltonian for the system “impurity+PLM”, considered in [33] can be written in the following form (see Fig. 4.2):

\[ \hat{H} = (E_1 + \hat{H}_1)|1\rangle\langle 1| + (E_2 + \hat{H}_2)|2\rangle\langle 2|, \quad E_2 - E_1 = \hbar \omega_0, \quad \text{(4.9)} \]

where

\[ \hat{H}_1 = \sum_j \omega_1 j \hat{a}_1^\dagger \hat{a}_1 + \frac{1}{2}, \quad \text{(4.10)} \]

and

\[ \hat{H}_2 = \sum_k \omega_2 k \hat{a}_2^\dagger \hat{a}_2 + \frac{1}{2}, \quad \text{(4.11)} \]
are Hamiltonians for the vibration motion of the lattice for the lower \(|1\rangle\) and upper \(|2\rangle\) states, respectively. It should be noted, that in the Hamiltonian (4.9) the term coupling the TLS to the vacuum state of radiation is omitted. This coupling, responsible for the spontaneous emission [12], will lead to the Lorentzian lineshape with the natural linewidth \(\gamma_0\) in the emission spectrum. It must be convolved with the line-shape due to the interactions of two-level system and the pseudo-local mode. The difference between the Hamiltonians

\[
H_{TLS} - H_{PLM} = \sum_j \omega_{1j} (a_1^\dagger a_1 + \frac{1}{2}) + \Delta \left( \frac{1}{2} + \sum_{j,k} c_j c_k a_{1j}^\dagger a_{1k} \right), \quad \Delta \equiv \omega_2 - \omega_1.
\]

As has been shown by many authors, the linear term in (4.12) can not cause temperature dependent broadening. Thus, focusing on the quadratic coupling, one can re-write the Hamiltonian \(\hat{H}_2\) following way:

\[
\hat{H}_2 = \sum_j \omega_{1j} (a_1^\dagger a_1 + \frac{1}{2}) + \Delta \left( \frac{1}{2} + \sum_{j,k} c_j c_k a_{1j}^\dagger a_{1k} \right), \quad \Delta \equiv \omega_2 - \omega_1.
\]

Here, \(\omega_1\) and \(\omega_2\) are mean frequencies of the vibrations for lower and upper electronic states, respectively. It is also assumed that \(\Delta \ll \omega_1\) [33].

As shown in [41], the emission spectrum of an optically active impurity may be written as the Fourier
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transform

\[ I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t - \frac{\gamma_0}{2}|t|} \cdot F(t), \quad (4.14) \]

where \( \gamma_0 \) is the natural width, and \( F(t) \) is given by

\[ F(t) = \frac{\text{Tr}[e^{-\beta H_1}e^{-itH_2}]}{\text{Tr}[e^{-\beta H_1}]} \quad (4.15) \]

The main result of the work [33] is the expression for \( F(t) \) for the case of impurity interacting with a single pseudo-local mode of frequency \( \omega \) and the width \( \Gamma \) (\( \Gamma, \Delta \ll \omega \)):

\[ F(t) = \exp \left[ it\Delta(\bar{n} + 1/2) - it\frac{\Delta(\bar{n} + 1)\alpha}{1 + \alpha} + i\frac{\Delta(\bar{n} + 1)}{\lambda(1 + \alpha)} \ln \left( 1 + \alpha - \alpha e^{\lambda t} \right) \right], \quad (4.16) \]

where

\[ \alpha \equiv \frac{\bar{n}\Delta}{i\lambda}, \quad \lambda \equiv \Gamma - \frac{i\Delta}{2} + \sqrt{\Gamma^2 - \Delta^2 - i\Delta(2\bar{n} + 1)}, \quad \text{and} \quad \bar{n} = \left( e^{-\frac{\hbar\omega}{k_BT}} - 1 \right)^{-1}. \quad (4.17) \]

This expression was used in the present work. In the following sections the fit of experimental data is given and corresponding parameters of the pseudo-local mode are found.

4.3 Experiment

Sample studied was type IIa single-crystal CVD diamond (by Element 6), grown along (001) crystallographic plane. It has been implanted with Xe\(^+\) ions having energy \( E_{\text{Xe}} = 180 \) keV. Subsequent annealing at \( T=1400^\circ\text{C} \) has been applied for one hour to remove implantation-induced damage and facilitate Xe-related center formation. Photoluminescence spectra from Xe-centers has been excited using Spectra-Physics Ar\(^+\)/Kr\(^+\) laser with \( \lambda = 514.5 \) nm. Jobin-Yvon T64000 system with confocal microscope has been used to collect spectra from the sample, placed in Cryo-Vac cryostat, at temperatures \( T = 10 \) K - 300 K. As shown in Figure 4.3, below \( T = 25 \) K the linewidth/lineshape of 811 nm ZPL is determined by instrumental and inhomogeneous broadening mechanisms. At higher temperatures one observes the changes in the lineshape: broadening, increase of the red asymmetry, and overall red shift of the line’s center of mass. The full width at half maximum (FWHM) grows as the temperature increases (see Figure 4.5). The temperature dependence of FWHM, combined with actual lineshapes provides rather strong restrictions on possible broadening mechanism(s). Theoretical model, described above, was used to fit the experimental data.
4.3. EXPERIMENT

Figure 4.3: Photoluminescence spectra of Xe-implanted high purity diamond at various temperatures. Narrow zero-phonon line (ZPL) at 811.6 nm is observed at low temperatures. At higher temperatures a weak phonon sideband appears, together with the second (ZPL) near 794 nm (290 cm$^{-1}$). The inset demonstrates the temperature dependence of the full width at half maximum (FWHM) of 811.7 nm zero-phonon line. Below $T < 30$ K the inhomogeneous broadening determines the FWHM. At temperature higher than 30 K homogeneous broadening dominates. These two mechanisms are discussed later in this work.

Figure 4.4: Photoluminescence spectra from Xe-related centers in diamond at temperatures $T=15$ K, 65 K, and 120 K. The observed line-shape changes are: line width and asymmetry into longer wavelength side of the spectrum increase.
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Figure 4.5: Log-Log plot of Full Width at Half Maximum of 811.7 nm zero-phonon line at various temperatures. At $T \leq 60$ K, spectra from implantation doses $1.1 \cdot 10^{11}$ cm$^{-2}$ and $5.0 \cdot 10^{12}$ cm$^{-2}$ differ not only in FWHM, but in line-shapes. This can be attributed to the effects of inhomogeneous broadening as explained in Chapter 3.

4.4 Fitting Procedure for Single Mode Model

The multi-step process of fitting the theoretical model to experimental data can be illustrated by a Figure 4.6. In the beginning the initial ranges of parameters (frequency $\omega_1$, shift $\Delta = \omega_2 - \omega_1$ and decay rate $\Gamma$) have been estimated via tentative fits of the line-widths temperature dependence. Starting volume in the space of parameters $\{\omega, \Delta, \Gamma\}$ contained about 10 000 points with $\omega \in [50, 150]$ cm$^{-1}$, $\Delta \in [10, 50]$ cm$^{-1}$, and $\Gamma \in [2, 96]$ cm$^{-1}$.

First step was to compare for each set of parameters $\{\omega_i, \Delta_i, \Gamma_i\}$ the line-widths at various temperatures as predicted by the model versus the experimental data. The results narrowed down the volume of parameters to several clusters, totaling the number of set of parameters about 100, with $\omega \in [90, 130]$ cm$^{-1}$, $\Delta \in [10, 50]$ cm$^{-1}$, and $\Gamma \in [5, 50]$ cm$^{-1}$. Figure 4.7 demonstrates four different sets of parameters which produce satisfactory fit of the low-temperature part of experimental data. Deviation from experiment at temperatures over 100K is not unexpected, since at these temperatures the approximation of isolated two electronic levels breaks down, as manifested in the appearance and growth of a narrow peak near 794 nm (see Figure 4.12). The intensity of this peak grows like a Boltzmann factor $I_{794} \propto e^{-290\text{cm}^{-1}/T}$ which suggest thermal processes populating some level 290 cm$^{-1}$ higher than 811 nm electronic state.

The second step of the fitting process consisted in fitting the experimental line-shapes measured at various
4.5 Vibrational Structure of The Phonon Sideband

As shown in Figure 4.8, the photoluminescence spectrum measured at $T = 80$ K features a zero-phonon line (centered at 0 cm$^{-1}$) and weak peaks in Stokes (red) and anti-Stokes (blue) part of the spectrum. The peaks’ intensities are about $10^{-3} - 10^{-4}$ of the ZPL. Analysis shows that prominent peaks in Stokes part (96 cm$^{-1}$, 113 cm$^{-1}$, 128 cm$^{-1}$, 133 cm$^{-1}$, and 147 cm$^{-1}$) as well as less prominent peaks in anti-Stokes part (89 cm$^{-1}$, 100 cm$^{-1}$, 115 cm$^{-1}$, 127 cm$^{-1}$, 137 cm$^{-1}$, and 149 cm$^{-1}$) are too narrow to be identified with a
CHAPTER 4. HOMOGENEOUS BROADENING OF ZPL

Figure 4.7: Line-width of the zero-phonon line as the function of temperature: Comparison between the measured (circles) and calculated (solid line) values. Using only line-width does not allow one to uniquely determine the parameters of the pseudo-local mode. The framed set of parameters has been identified in low-temperature photoluminescence spectra.
Results and Discussion

It has been shown that interaction of Xe-related center in diamond with the crystal lattice can be understood within a model describing electron-phonon coupling quadratic in the lattice atoms displacement. A single pseudo-local model, as presented in [33], is sufficient to explain the observed asymmetric line shape at temperatures below 100 K. At higher temperatures there is a disagreement between the predicted and observed line widths, as well as line shapes. These temperatures are high enough for an additional electronic transition to become active. This is confirmed by the appearance and quick growth of anti-Stokes peak at 794 nm (290 cm$^{-1}$, Figure 4.12). Therefore the assumption of an ideal two-level system starts to break down and extra broadening of the zero-phonon line can occur. Such a broadening due to the phonon-assisted population and de-population of the third level positioned about 290 cm$^{-1}$ above the excited level may be attributed for example to Orbach mechanism [5].

In short, Orbach processes occur in a three-level system shown in the left part of the Figure 4.11. The spacing $\delta$ between levels 1 and 2 is much smaller than the separation $\Delta$ between 2 and 3. When direct...
Figure 4.8: Photoluminescence spectra of Xe-implanted high purity diamond at $T=80$ K. Stokes and Anti-Stokes parts of the tail are zoomed in to demonstrate the candidate peaks for pseudo-local mode.

Figure 4.9: Fit of anti-Stokes part of the photoluminescence spectrum suggests an existence of a broad peak, a likely candidate for a pseudo-local mode.
4.6. RESULTS AND DISCUSSION

Figure 4.10: Fit of the shape of zero-phonon line using a single pseudo-local mode. The calculated line-shape is convoluted with a Lorentzian to account for an additional temperature-dependent broadening which is negligible at low temperatures but contributes substantially at higher temperatures, when two-level system approximation breaks down.
transitions between levels 1 and 2 are forbidden, the phonon-assisted transitions to the upper-most level 3 lead to the additional relaxation channel with the rate

$$\tau^{-1} = \frac{Be^{-\Delta kT}}{2}(1 + e^{-\delta kT})$$  \hspace{1cm} (4.18)

In the limit of $\delta \to 0$ and for the observed position of the level 3 $\Delta = 290 \text{ cm}^{-1}$ one recovers the additional Orbach broadening term $\Delta E = Ae^{-290/kT}$.

Indeed, combining two mechanisms: a single pseudo-local mode with the parameters $\omega = 122 \text{ cm}^{-1}$, $\Delta = 46 \text{ cm}^{-1}$, and $\Gamma = 30 \text{ cm}^{-1}$ and additional broadening due to Orbach process of the type $\Delta E = Ae^{-290/T}$ it is possible to describe the observed widths of zero-phonon line in the whole temperature range $T = 30-300 \text{ K}$. See Figure 4.13 for the illustration.

Another type of processes that are possible at higher temperatures are direct phonon-assisted transitions (see [5]) which lead to the extra relaxation rate proportional to $\coth\left(\frac{290}{kT}\right)$. This type of broadening has a different behavior: it contributes a constant term to the broadening at low temperatures and grows linearly with temperature at higher temperatures. It is difficult to fit experimental data with such type of temperature dependence. In addition, already discussed two mechanisms, pseudo-local mode and indirect Orbach processes, are sufficient.
4.6. RESULTS AND DISCUSSION

Figure 4.12: Additional peak $\approx 794$ nm (290 cm$^{-1}$ above the energy level responsible for the 811 nm zero-phonon line) appears in the photoluminescence spectra of Xe-related centers in diamond. It indicates that a simple two-level model is no longer adequate at temperatures $T > 100$ K. One needs to consider additional broadening mechanisms at these temperatures.

Figure 4.13: A simple sum of two line-widths, one due to the quadratic interaction with pseudo-local mode and the other one due to Orbach processes, allows to describe the experimentally observed temperature-dependent behavior of the full width at half maximum for the temperature range 30-300 K.
4.7 Conclusion

Spectroscopy studies of Xe-related center in diamond show that there exists a strong interaction between electronic degrees of freedom of this center and the vibrational motion of the host lattice. This interaction is manifested in temperature dependent line-shapes of 811.7 nm zero-phonon line, observed in the photoluminescence spectra. The fact that the interaction is strong is confirmed by the need for a quadratic electron-phonon coupling with pseudo-local vibrational modes of the lattice. The appearance of pseudo-local vibrational mode is likely due to a large mass of Xe ion and a tightly packed diamond lattice which gets distorted by a foreign impurity ion.

A model that describes coupling between electronic and vibrational degrees of freedom of impurity has been considered. It non-perturbatively accounts for coupling quadratic in vibrational coordinates and yields satisfactory agreement with experimental data at temperatures $T = 30$-$100$ K. It should be noted, that with an additional broadening mechanism (Orbach processes) it’s been possible to achieve satisfactory fits of the actual line-shapes for a wide range of temperatures ($T = 30$ - $300$ K). The results of fitting can be summarized as follows: Xe atom distorts the lattice, creating a localized mode with frequency $120 \pm 5$ cm$^{-1}$. Electronic degrees of freedom of Xe-related center are coupled to these vibrations, which in turn are coupled to the rest of the lattice with the decay rate $\Gamma = 30 \pm 5$ cm$^{-1}$. An important consequence of quadratic electron-phonon coupling is the localized change of the lattice stiffness and the decrease of the frequency of the pseudo-local mode from $170 \pm 5$ cm$^{-1}$ to $120 \pm 5$ cm$^{-1}$ when the Xe-related center transitions from the ground to the excited electronic state. These interactions lead to the gradual increase of the width and asymmetry of 811.7 nm zero-phonon line with increasing temperature. Such behavior is observed in photoluminescence spectra from Xe-related centers in diamond. To fully explain the observed line-widths at temperatures higher than 100 K, one needs to extend the simple two-level model and include an additional relaxation channel, related to the phonon-assisted transitions to the third excited state. Such state is observed as a prominent peak at 794 nm (290 cm$^{-1}$ above 811.7 nm level) in photoluminescence spectra at $T > 100$ K.

Two main questions remain open in this problem: 1) Can the predicted $170 \pm 5$ cm$^{-1}$ Stokes component of the pseudo-local mode be observed in the photoluminescence spectra? and 2) What is the cause of an extra-asymmetry observed in the 811.7 nm zero-phonon lines in the temperature range $T = 120$ – $300$ cm$^{-1}$? Answering these questions will require an extension of the models considered above and may be a recommendation for a future work.
Chapter 5

Optical Saturation in Polarized Photoluminescence

5.1 Introduction

Optically active defects in solids are essentially quantum systems. However, when studying light absorption and emission from such systems it is often convenient and adequate to describe them using a classical model of a dipole. Namely, when a two-level system transitions from the excited to the ground state emitting a photon with the energy $\hbar \omega$, the emission of the electromagnetic field can be attributed to a dipole moment $\mathbf{D}$, either of electric or magnetic nature, experiencing harmonic oscillations with the frequency $\omega$. Optically active defects possess a structure with certain spatial symmetry and therefore may define a specific direction in the crystal lattice (given by a unit vector $\mathbf{d}$). For example, according to the works [3, 6], Xe-related defect in diamond has a trigonal symmetry with the 3-fold symmetry axis aligned with the $\langle 111 \rangle$ crystallographic direction. When the dipole moment $\mathbf{D}$, responsible for either absorption or emission, is aligned with the direction of the defect ($\mathbf{D} \parallel \mathbf{d}$), the absorption or emission is said to be of Z-type or $\pi$-type. Z-type (=\pi-type) emission is linearly polarized. Whenever the absorption or emission happens due to the oscillations of two mutually orthogonal dipoles oscillating in the plane perpendicular to the direction of the defect $\mathbf{d}$, the transition is called XY-type (or $\sigma$-type). Emission due to XY-type (=\sigma-type) transitions is elliptically polarized.

The anisotropy of the emitter, manifested in the distinct polarization pattern of the emitted radiation, can be used to study the spatial symmetry of the associated defect. Such a technique, based on the measurements of the polarized luminescence, has been successfully applied to study properties of optical defects in various
Figure 5.1: (a, b): Classical electric/magnetic dipole oscillating either along a specified direction (z-axis) or rotating in the plane perpendicular to it (xy-plane) produces linearly or elliptically polarized light, respectively. Absorption of the incident radiation polarized perpendicular to $D$ is not possible. Thus both cases describe a purely anisotropic emitter in contrast to (c), when one can speak about some degree of isotropy of the emitter, defined further in the work.

The core idea of this method can be illustrated with the Figure 5.2.

A crystalline sample is excited with linearly polarized laser radiation, coming in the direction specified by a vector $\mathbf{k}$. Crystal contains optically active defects aligned along vectors $\mathbf{d}_i$ and conforming to the host crystal symmetry. Due to the latter, there are several physically equivalent orientations of these anisotropic defects. Collecting a luminescence signal from an ensemble of such emitters, while varying orientations of the sample or the laser polarization, it is possible to establish the symmetry of the defects in crystal and the nature of the emission. For example, for a cubic crystal it may be possible to say a) whether defects are oriented along $\langle 100 \rangle$, $\langle 110 \rangle$, or $\langle 111 \rangle$ directions of the crystal; b) whether absorption/emission was due to the dipole transition of Z or XY type; c) whether the absorbing/emitting dipole is of electric or magnetic nature.

To achieve this, one may study the azimuthal profiles of the detected intensity of the photoluminescence signal from the sample $I(\theta)$, where $\theta$ is the angle of rotation of the sample around the specified axis. When the orientation of the analyzer, given by a unit vector $\mathbf{A}$ (see Figure 5.2), is parallel to the polarization of the incident laser radiation $\mathbf{L}$, the detected signal is called co-polarized and denoted $S_{||}$. If $\mathbf{A}$ is perpendicular to $\mathbf{L}$ the detected signal, called cross-polarized, is denoted $S_\perp$. The degree of polarization of the emitted radiation can be measured by the following quantity:

$$P \equiv \frac{S_{||} - S_\perp}{S_{||} + S_\perp}, \quad P \in [0, 1],$$

(5.1)
Figure 5.2: Schematic of experimental setup for polarized luminescence measurements. A group of optically active defects oriented along physically equivalent crystallographic axes is excited by a laser beam along the direction $k$. The polarization of the laser beam is given by a vector $L$. Signal is collected in the direction $n$, through an analyzer $A$. Rotating either the sample or the polarization of the laser beam one observes the change in the detected intensity of the photoluminescence signal.

where $P = 1$ implies linearly polarized radiation, and $P(\theta) = 0$ for non-polarized radiation. All three quantities: $S_{\parallel}(\theta)$, $S_{\perp}(\theta)$, and $P(\theta)$ are of interest in the measurements of polarized photoluminescence. Several variations of the measurement scheme outlined in Figure 5.2 are possible: 1) a sample is rotated while keeping everything else fixed; 2) excitation polarization is rotated with the rest of the set up fixed; and 3) orientation of the analyzer is rotated and everything else is fixed. Depending on the experimental set up either of these schemes can be used.

The results of polarization measurements in work [6] suggest that Xe-related center possesses a trigonal symmetry with the orientation of the defect along ⟨111⟩ direction. Also, 811.7 nm zero-phonon line is due to electric XY-Z type transition, while 794 nm line is due to electric XY-XY type transition. However, these results do not completely agree with predicted expressions for the degree of polarization $P(\theta)$. Namely, although the polarization of 811.7 nm and 794 nm peaks corresponds most closely to ⟨111⟩ orientation of this defect, the degree of polarization is less than expected, being approximately half of the theoretical value. This may be due to several effects unaccounted in [6] and analyzed further in this work (e.g. optical saturation as discussed below).

Although the representation of an emitter with a classical dipole is useful in many cases, it can not account for an important optical effect called saturation which is observed in absorption processes [16]. For
a simple two-level system saturation can be understood as a condition when excitation rate from the ground to the upper state is much faster than the downward relaxation rate due to spontaneous emission. Under such conditions the populations of both levels are stationary and equal, leading to the effective absence of absorption. This may happen when the power $P$ of the excitation radiation is high as compared to a certain value, called saturation power $P_S$.

When the sample is excited with a Gaussian laser beam through an objective of a microscope, high optical saturation levels are easily achieved [19]. A special care must be taken in the analysis of the azimuthal dependence of the luminescence signal in this case. However, when accounted for, high optical saturation levels for Gaussian beams may reveal more details about the absorption-emission process as compared to working in the low-saturation regime.

For the illustration of the optical saturation in photoluminescence from Xe-related defects in diamond see the Chapter 2 and Figure 2.7b showing a typical saturation curve.

### 5.2 Theoretical Background

For a single defect with a dipole moment $\mathbf{D}$ (it will stand for either electric dipole moment $\mathbf{p}$ or magnetic dipole moment $\mathbf{m}$) the signal from the detector, according to the Figure 5.2, will be given by the product of absorption and emission probabilities:

$$ S \propto P_{\text{abs}} \cdot P_{\text{emit}} \propto (\mathbf{V} \cdot \mathbf{D})^2 (\mathbf{E}_{\text{em}} \cdot \mathbf{A})^2 $$

(5.2)

Here $\mathbf{V}$ is either the vector of the incoming electric field $\mathbf{E}$ for the absorption by the electric dipole $\mathbf{D} = \mathbf{p}$ or $\mathbf{V}$ is the magnetic field vector $\mathbf{H}$ if the absorption is due to the magnetic dipole moment $\mathbf{D} = \mathbf{m}$; $\mathbf{E}_{\text{em}}$ is the electric field of the emitted radiation; $\mathbf{A}$ specifies the orientation of the analyzer. Using the expressions for the electric field due to electric/magnetic dipole [36], the emission probability factor can be re-written as $P_{\text{emit}} \propto (\mathbf{D} \cdot \mathbf{a})^2$, where $\mathbf{a} = \mathbf{A} - \mathbf{n}(\mathbf{A} \cdot \mathbf{n})$ for the electric dipole emission or $\mathbf{a} = [\mathbf{n} \times \mathbf{A}]$ for the magnetic dipole emission.

The signal from an ensemble of independent emitters will be given by the sum of contribution from each emitter:

$$ S(k, L, n, A, \theta) = \sum_{i=1}^{N} S_i = \sum_{i=1}^{N} (\mathbf{D}_i \mathbf{V})^2 (\mathbf{D}_i \mathbf{a})^2. $$

(5.3)

Here $\theta$ is a vector describing the orientation of the sample. The set of vectors $\mathbf{k}$, $\mathbf{L}$, $\mathbf{n}$, $\mathbf{A}$, and $\theta$ completely specifies the excitation-observation conditions. For a non-uniform excitation using Gaussian laser beam with
the total power $P_t$ the expression for the collected signal takes the form:

$$S \propto \sum_{i=1}^{M} (D^{(j)}a)^2 \ln \left( 1 + b \cdot P_t \cdot (D^{(j)}V)^2 \right). \quad (5.4)$$

The summation in this formula is over $M$ physically equivalent crystallographic directions. Note that under the excitation with certain polarization $\mathbf{L}$ these directions become no longer equivalent. One can go from low to high saturation expressions for the collected signal simply by changing the absorption part $(D^{(j)}V)^2 \rightarrow \ln \left( 1 + b \cdot P_t \cdot (D^{(j)}V)^2 \right)/bP_t$.

A particular excitation-observation geometry, illustrated in the Figure 5.3 is considered below. It is relevant to the experiments discussed in the next section. The geometry is backscattering ($\mathbf{n} = -\mathbf{k}$), with two orientations of laser polarization: 1) co-polarized, $\mathbf{L} = \mathbf{A} = \mathbf{j}$; 2) cross-polarized, $\mathbf{L} = \mathbf{i} \perp \mathbf{A} = \mathbf{j}$. The laser beam is incident perpendicular to the (001) plane of the diamond crystal. The photoluminescence signal is collected from an ensemble of optically active defects as the sample is rotated around the axis $z$.

Assuming that a) optical transitions are due to an electric dipole, b) the signal is collected within a small solid angle $d\Omega$, c) optical defects are purely anisotropic, and c) either the intensity of the laser beam is low or the excitation of the sample is uniform, one can easily recover the behavior of the photoluminescence intensity $S$ and/or the polarization $P$ of the luminescence as the function of the rotational angle of the sample $\theta$. See Table 5.1 for formulas and Figures 5.7 and 5.8 for azimuthal plots of corresponding signal. These results are well known and have been used to analyze the site symmetry of various optically active defects in diamond [8, 6]. Figures 5.7 and 5.8 show two azimuthal plots for two cases: no-saturation (darker, blue curve) and high-saturation (lighter, red curve). The no-saturation calculations are in agreement with previously published results [8, 6] obtained for purely electric dipole. Results of similar calculations for magnetic dipole transitions as well as for mixed electric-magnetic and magnetic-electric transitions are given in the Appendix ??.

### 5.2.1 Effects of High Numerical Aperture

So far it’s been assumed that the detector receives a signal from one direction within a small solid angle $d\Omega$ directed along $\mathbf{n}$. Under realistic experimental conditions, the signal collected comes from a range of angles, as indicated in the Figure 5.4. To take this into account one must consider the surface density of power $P_\theta(\chi, \phi)$ explicitly dependent on the directional angles $\chi$ and $\phi$. Total collected signal is then given by

$$P_\theta = \int_0^{2\pi} \int_0^{\chi_{\text{max}}} P_\theta(\chi, \phi) \sin \chi \sin \phi d\chi d\phi. \quad (5.5)$$
Figure 5.3: Schematic of the experimental setup for measuring the dependence of the photoluminescence (PL) signal as the function of the samples rotation angle $\theta$ around the axis $z$. In a set up with a confocal microscope the collected radiation propagates in the direction $n = -k$ opposite to the excitation direction. Laser polarization can be rotated with a half-wave plate to allow measurements of co- and cross-polarized signal. Both excitation and signal collected are going through a (001) crystallographic plane of the diamond sample. Xe-related defects are oriented along the four diagonals of the diamond’s unit cube.
Table 5.1: Calculated azimuthal profiles of PL signal $S_{\theta}$ and polarization $P_{\theta}$ for different groups of centers in diamond lattice. Results have been derived for electric dipole transitions in the absence of optical saturation effects. Backscattering geometry shown in Figure 5.3 is assumed.

Figure 5.4: Objective is collecting a signal from all directions within an angle $\chi_{\text{max}}$. Therefore the angle between the analyzer direction $A$ and the direction of the emitted signal $n$ varies. This may affect the observed signal $S(\theta)$ and change the measured degree of polarization. In this picture, no lens is assumed between the emitter and the detector and the signal goes directly to the detector. This is a worst-case scenario, when the wavefront is curved most.
CHAPTER 5. OPTICAL SATURATION IN POLARIZED PHOTOLUMINESCENCE

Figure 5.5: Ratio $P(\theta, \Omega)/P(\theta, d\Omega)$ of the measured degree of polarization of luminescence (finite solid angle – $P(\theta, \Omega)$) to the expected ($P(\theta, d\Omega)$ – small solid angle approximation) as the function of the numerical aperture of the objective.

To obtain $P_\theta(\chi, \phi)$ it is sufficient to substitute the following components of the directional vector $\mathbf{n} = \{\sin \chi \cos \phi, \sin \chi \sin \phi, \cos \phi\}$ into the expressions for $\mathbf{a}$ in (5.3).

Let us consider a concrete experimental set, similar to the back-scattering one shown in the Figure 5.3. Analyzer will be parallel to $y$ axis of the laboratory reference frame and the laser beam will be propagating in the positive $z$-direction. Two orientations of the laser polarization are considered: co-polarized, when $\mathbf{L} = \mathbf{j} \parallel \mathbf{A}$ and cross-polarized, $\mathbf{L} = \mathbf{i} \perp \mathbf{A}$. Luminescence signal is collected in the positive $z$ direction, i.e. $\mathbf{n} = \mathbf{k}$ and therefore $\mathbf{a} \equiv \mathbf{A} \perp \mathbf{n} = \mathbf{j}$. Sample, containing optical centers, is rotated around $z$ axis by a varying angle $\theta$. Electric dipole is assumed for absorption and emission.

To account in the equation (5.3) for the finite numerical aperture of the objective, we first need to calculate

\[
(d_\theta \cdot \mathbf{a}) = (d_\theta \cdot \mathbf{A}) - (d_\theta \cdot \mathbf{n})(\mathbf{A} \cdot \mathbf{n}) = (d_\theta \cdot \mathbf{j}) - (d_\theta \cdot \mathbf{n})(\mathbf{j} \cdot \mathbf{n}),
\]

which, using the components of $d_\theta, \mathbf{A}$ and $\mathbf{n}$, can be written as

\[
(d_\theta \cdot \mathbf{a}) = d_{\theta y} - \sin \chi \sin \phi \left( d_{\theta x} \sin \chi \cos \phi + d_{\theta y} \sin \chi \sin \phi + d_{\theta z} \cos \chi \right).
\]

The last expression leads to

\[
\int_0^{2\pi} \int_0^{\chi_{max}} (d_\theta \cdot \mathbf{a})^2 \sin \chi d\chi d\phi = \frac{\pi}{960} \left[ 128(d_{\theta x}^2 + 8d_{\theta y}^2 + d_{\theta z}^2) - 30(5d_{\theta x}^2 + 31d_{\theta y}^2 + 4d_{\theta z}^2) \cos(\chi_{max}) + 
5(5d_{\theta x}^2 - 17d_{\theta y}^2 - 4d_{\theta z}^2) \cos(3\chi_{max}) - 3(d_{\theta x}^2 + 3d_{\theta y}^2 - 4d_{\theta z}^2) \cos(5\chi_{max}) \right].
\]
5.2. THEORETICAL BACKGROUND

It can be simplified slightly, using the fact that $d_x^2 + d_y^2 + d_z^2 = 1$:

\[
\int_0^{2\pi} \int_0^{\chi_{\text{max}}} (\mathbf{d}_\theta \cdot \mathbf{a})^2 \sin \chi d\chi d\phi = \frac{\pi}{960} \left[ 128 + 896d_{\theta y}^2 - 30(4 + d_{\theta x}^2 + 27d_{\theta y}^2) \cos(\chi_{\text{max}}) - (20 - 45d_{\theta x}^2 + 65d_{\theta y}^2) \cos(3\chi_{\text{max}}) + (12 - 15d_{\theta x}^2 - 21d_{\theta y}^2) \cos(5\chi_{\text{max}}) \right].
\]

(5.9)

In a similar way one finds that

\[
\int_0^{2\pi} \int_0^{\chi_{\text{max}}} \mathbf{a}^2 \sin \chi d\chi d\phi = \frac{\pi}{12} \left[ 16 - 15 \cos(\chi_{\text{max}}) - \cos(3\chi_{\text{max}}) \right]
\]

(5.10)

Thus, the emission factor $P_{\text{em}}(\theta)$ in the expression for the total collected signal $S(\theta) = P_{\text{abs}}(\theta)P_{\text{em}}(\theta)$ may take either of the following two values:

\[
P_{\text{em}}^{(1)}(\theta, \chi_{\text{max}}) = \frac{\pi}{960} \left[ 128 + 896d_{\theta y}^2 - 30(4 + d_{\theta x}^2 + 27d_{\theta y}^2) \cos(\chi_{\text{max}}) - (20 - 45d_{\theta x}^2 + 65d_{\theta y}^2) \cos(3\chi_{\text{max}}) + (12 - 15d_{\theta x}^2 - 21d_{\theta y}^2) \cos(5\chi_{\text{max}}) \right] - \text{for Z-type transition},
\]

(5.11)

and

\[
P_{\text{em}}^{(2)}(\theta, \chi_{\text{max}}) = \frac{\pi}{12} \left[ 16 - 15 \cos(\chi_{\text{max}}) - \cos(3\chi_{\text{max}}) \right] - P_{\text{em}}^{(1)}(\theta, \chi_{\text{max}}) - \text{for XY-type transition.}
\]

(5.12)

It is useful to examine the expressions for the $P_{\text{em}}^{(1)}$ and $P_{\text{em}}^{(2)}$ in the limit of small collecting angle $\chi_{\text{max}} \ll 1$:

\[
P_{\text{em}}^{(1)} \approx \pi \chi_{\text{max}}^2 d_{\theta y}^2 + \frac{\pi \chi_{\text{max}}^4}{12} (3 - 3d_{\theta x}^2 - 10d_{\theta y}^2),
\]

(5.13)

and

\[
P_{\text{em}}^{(2)} \approx \pi \chi_{\text{max}}^2 (1 - d_{\theta y}^2) - \frac{\chi_{\text{max}}^4 \pi}{12} (71 - 3d_{\theta x}^2 - 10d_{\theta y}^2).
\]

(5.14)

If one keeps the terms up to the order $\chi_{\text{max}}^2$ then the signal behaves according to the expressions shown in the Table 5.2. From these expression a limit corresponding to a small solid angle of observation is recovered and the azimuthal dependence take on the forms given in the Table 5.1.

Comparison of the full expression for the collected signal $P_{\text{em}}(\theta)$ with the small-aperture limit shows that for the collection angles with numerical aperture N.A. < 0.5 the small solid angle approximation is valid. Effects of higher numerical apertures are still not very prominent as illustrated in Figure 5.5. It must be
Table 5.2: Small aperture limit of general expressions for the co- and cross-polarized signal collected in the backscattering geometry shown in Figure 5.3. A single emitting defect is considered. From these one recovers all the expressions given in the Table 5.1 for three groups of defects in diamond cubic lattice.

Table 5.2: Small aperture limit of general expressions for the co- and cross-polarized signal collected in the backscattering geometry shown in Figure 5.3. A single emitting defect is considered. From these one recovers all the expressions given in the Table 5.1 for three groups of defects in diamond cubic lattice.

<table>
<thead>
<tr>
<th>Abs–Em</th>
<th>Cross, ⊥ $S_\theta$</th>
<th>Co, ∥ $S_\theta$</th>
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</thead>
<tbody>
<tr>
<td>Z-Z</td>
<td>$d_\theta^2 d_{\theta y}^2$</td>
<td>$d_\theta^2 d_{\theta y}^2$</td>
</tr>
<tr>
<td>XY-XY</td>
<td>$(1 - d_{\theta x}^2)(1 - d_{\theta y}^2)$</td>
<td>$(1 - d_{\theta y}^2)(1 - d_{\theta y}^2)$</td>
</tr>
<tr>
<td>Z-XY</td>
<td>$d_{\theta x}^2 (1 - d_{\theta y}^2)$</td>
<td>$d_{\theta y}^2 (1 - d_{\theta y}^2)$</td>
</tr>
<tr>
<td>XY-Z</td>
<td>$(1 - d_{\theta x}^2) d_{\theta y}^2$</td>
<td>$(1 - d_{\theta y}^2) d_{\theta y}^2$</td>
</tr>
</tbody>
</table>

noted that the analysis has been carried out for the “worst-case” scenario, when the collected signal results from a spherical wave incident on the detector. The presence of lenses, which modify the wave-front of the incoming radiation, reduces the effects of the aperture even more.

5.2.2 Isotropy of Emitter

Next we turn to the analysis of the assumption that the emitter can be modeled as a simple electric or magnetic dipole. A dipole is perfectly anisotropic in a sense that it does not absorb radiation if the field vector $V$ is perpendicular to the dipole vector $D$ (see above for the definition of $V$ and $D$). If the absorption and emission in the direction perpendicular to the dipole moment is allowed, one may talk about the degree of isotropy. The latter may be described by a factor $\beta$, defined as the ratio of probability to absorb the radiation perpendicular to the dipole and the probability to absorb the radiation “normally”, i.e. along the dipole vector $D$:

$$\beta \equiv \frac{\Gamma_{\perp}}{\Gamma_{\parallel}}, \quad \beta \in [0, 1] \quad (5.15)$$

The effect of isotropy is to decrease the observed degree of polarization $P$ of luminescence [28]. The ratio of the polarization of luminescence from isotropic emitters $P_{\beta}$ to the polarization $P_0$ of purely anisotropic ones depends on the isotropy factor $\beta$ rather strongly. For Z-Z type of transitions and the backscattering geometry, described above and shown in the Figure 5.3, these ratios are summarized in the Table 5.3.

The effects of isotropy are close for all three groups of centers, as illustrated in the Figure 5.6. It can be seen from Figure 5.6 that for $\beta \approx 0.1$ the degree of polarization drops to almost half of its maximal value. It should be noted that the decrease of the degree of polarization $P_{\beta}/P_0$ does not depend on the rotational angle of the sample $\theta$, as long the effects of optical saturation are negligible. When optical saturation becomes high, the polarization curves $P_{\beta}(\theta)$ become modulated and the expressions given in the Table 5.3 are no longer valid. We now turn to the analysis of the optical saturation effects.
5.2. THEORETICAL BACKGROUND

Table 5.3: Effect of isotropy of defects on the degree of polarization of the photoluminescence. Degrees of polarization have been calculated for the electric dipole experiencing Z-Z ($\pi - \pi$) type of transition in the backscattering geometry shown in the Figure 5.3. No optical saturation and a small solid angle approximations have been assumed. Results for ⟨100⟩ and for ⟨110⟩ are in agreement with work [28]. The ⟨111⟩ case has not been considered before. See Figure 5.6 for the plots of the given formulas.

<table>
<thead>
<tr>
<th></th>
<th>⟨100⟩</th>
<th>⟨110⟩</th>
<th>⟨111⟩</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{P_\beta}{P_0}$</td>
<td>$\frac{(1 - \beta)^2}{1 + 2\beta + 3\beta^2}$</td>
<td>$\frac{3(1 - \beta)^2}{3 + 10\beta + 11\beta^2}$</td>
<td>$\frac{(1 - \beta)^2}{(1 + 2\beta)^2}$</td>
</tr>
</tbody>
</table>

Figure 5.6: The ratio of the polarization of luminescence from isotropic emitters $P_\beta$ to the polarization $P_0$ of purely anisotropic ones as the function of the isotropy factor $\beta$. Results are for the backscattering geometry described earlier. The transition type is Z-Z ($\pi - \pi$) and optical saturation is not accounted for. Red is for ⟨100⟩, green is for ⟨110⟩, and blue is for ⟨111⟩.
5.2.3 Optical Saturation Effects

The general formula for the signal from an ensemble of $N$ emitters

$$S = \sum_{i=1}^{N} P_{abs}^{i} P_{em}^{i}$$

(5.16)

can be re-written as the average over the $M$ crystallographically equivalent groups of defects:

$$S = \frac{1}{M} \sum_{j=1}^{M} P_{abs}^{j} P_{em}^{j},$$

(5.17)

which can be extended to account for optical saturation effects. For a simple case of constant surface power density (Flat-Top excitation) one obtains:

$$S = \frac{1}{M} \sum_{j=1}^{M} P_{abs}^{j} P_{em}^{j} \left(1 + \gamma P_{abs}^{j}\right)$$

– Flat-Top uniform excitation,

(5.18)

while for the more realistic case of a Gaussian Beam, with the power density given by $I = I_{0}e^{-r^{2}/w^{2}}$ (total power $P_{t} = \pi w^{2}I_{0}$), the expression for the total signal from an ensemble of emitters has the following form:

$$S = \frac{1}{M} \sum_{j=1}^{M} P_{em}^{j} \frac{\ln\left(1 + \gamma P_{abs}^{j}\right)}{\gamma}$$

– Gaussian-Beam non-uniform excitation.

(5.19)

Here $\gamma$ is the parameter describing the level of optical saturation, it is proportional to the total power of the incident beam, $\gamma \equiv P_{t}/P_{S}$, $P_{S}$ being a saturation power, roughly a value at which the signal $S$ stops to grow linearly with the incident power. Saturation power may depend on experimental parameters, for example excitation wavelength.

The effects of optical saturation for the case of Gaussian-Beam excitation are demonstrated in Figures 5.7-5.9. From these figures one can see that using polarization curves together with co- and cross-polarized azimuthal signals allows one to uniquely identify the orientation group of optically active defects. Measurements at low excitation power (and consequently at low saturation levels) do not allow to distinguish Z-XY from XY-Z types of transitions. Introduction of optical non-linearity in the absorption stage (optical saturation) allows to differentiate between Z-XY and XY-Z transitions for $\langle 110 \rangle$ and $\langle 111 \rangle$ defect groups. For a moderate saturation level $\gamma = 10$ there is a clear difference between azimuthal behavior of co- and cross-polarized signals.

Finally, for the more realistic case when both optical saturation and the isotropy of emitters need to be taken into account, one can again study the azimuthal co- and cross-polarized signal together with the
### 5.2. THEORETICAL BACKGROUND

Figure 5.7: Calculated azimuthal dependence of co-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure 5.8: Calculated azimuthal dependence of cross-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure 5.9: Calculated degree of polarization of PL signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to $\text{Z-Z}$, $\text{XY-XY}$, $\text{Z-XY}$, $\text{XY-Z}$ type of the transitions.
polarization curves. Figures 5.10-5.12 illustrate the case. As can be seen, the presence of isotropy leads to the “smoothing-out” of the azimuthal signal curves and increases the effects of saturation. For isotropy larger than 10 percent it becomes very difficult to tell apart XY-Z and Z-XY transition using optical saturation in Gaussian beams.

5.3 Experiment

A high purity single crystal CVD diamond grown along (001) crystallographic plane has been subjected to ion implantation with Xe$^+$ ions, having energy 180 keV. Subsequent high temperature $T = 1400^\circ$C annealing for 1 hour resulted in the formation of Xe-related centers. According to SRIM (www.srim.org), these centers are positioned about 50 nm below the surface of the sample and form a thin ($\approx 16$ nm) layer. Luminescence from the sample at room temperature has been excited using an Ar/Kr gas laser with $\lambda_{exc} = 521$ nm. Signal has been collected in a backscattering geometry using a confocal microscope and JY Horiba T64000 spectrometer with LiN2 cooled CCD. Analyzer has been placed before the entrance slits of the spectrometer. Sample was rotated every 5-10 degrees and the polarized photoluminescence signal has been collected for two polarizations of the laser excitations: 1) co-polarized, when the laser polarization is parallel to the analyzer and 2) cross-polarized, when the laser polarization is perpendicular to the analyzer. Figure 5.13 shows a schematic of the described set up.

5.4 Results and Discussion

Figure 5.14 demonstrates experimental results for the polarization of 811.7 nm zero-phonon line measured at both low ($I=0.12$ mW) and high ($I = 4.8$ mW) intensities of the laser beam. Corresponding saturation levels are $\gamma \approx 0.5$ and $\gamma \approx 10$. The curves agree with Z-XY (or XY-Z) type of transition in groups $\langle 100 \rangle$ or $\langle 111 \rangle$, as can be seen in Figure 5.9.

Looking at co-polarized signal from the sample, as shown in Figure 5.15, one can readily identify the defect group as $\langle 111 \rangle$. Figure 5.16 shows the cross-polarized photoluminescence signal and also agrees with $\langle 111 \rangle$ case (much better than with $\langle 100 \rangle$).

To establish the type of the transition responsible for the 811 nm zero-phonon line, one can repeat the measurements at higher saturation level. As can be seen from Figure 5.7, the changes of the azimuthal dependence of the co-polarized signal for Z-XY and XY-Z transitions are not identical. Namely, the contrast $K$ of the plots, defined as the ratio of the maximum signal to the minimum $K = \frac{S_0}{S_{45}}$, increases for the Z-XY transition and the “petal-like” structure becomes more pronounced. The contrast $K$ for XY-Z decreases and
5.4. RESULTS AND DISCUSSION

Figure 5.10: Calculated azimuthal dependence of co-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure 5.11: Calculated azimuthal dependence of cross-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
5.4. RESULTS AND DISCUSSION

Figure 5.12: Calculated polarization of PL signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure 5.13: Schematics of the experimental set up used to measure polarized photoluminescence. Ar/Kr gas laser is used for excitation at $\lambda = 521$ nm. Laser polarization is controlled with a half-wave plate. The laser beam is focused on the CVD diamond crystal using a confocal microscope. Same microscope is used to collect a photoluminescence signal from the sample and send it to the LiN2-cooled CCD camera of the JY-Horiba T64000 spectrograph in a single-stage configuration and 900 gr/mm gratings. Sample is placed on a rotating table and was rotated around a vertical axis.
5.4. RESULTS AND DISCUSSION

Figure 5.14: Polarization of 811.7 nm PL signal collected from ensemble of Xe-related centers in CVD diamond in backscattering geometry at low saturation level $\gamma_{exp} \approx 0.5$, with the beam power incident on the sample $I = 0.12$ mW and high saturation level $\gamma_{exp} \approx 10$, with the beam power incident on the sample $I = 4.8$ mW on a micron-sized laser spot.
Figure 5.15: Co-polarized PL signal at 811 nm collected from ensemble of Xe-related centers in CVD diamond in backscattering geometry at two saturation levels: $\gamma_{\text{exp}} \approx 0.5$ and $\gamma_{\text{exp}} \approx 10$. 
Figure 5.16: Cross-polarized PL signal at 811 nm PL collected from ensemble of Xe-related centers in CVD diamond in backscattering geometry at low saturation level $\gamma_{\text{exp}} \approx 0.5$ and $\gamma_{\text{exp}} \approx 10$. 

$S_\perp$
the shape approaches a square rotated by 45 degrees.

Azimuthal plots for the high saturated case are also given in the figures 5.15 and 5.16. They demonstrate that co-polarized signal does become slightly less pronounced in agreement with XY-Z type of transition.

The azimuthal plots of the photoluminescence signal and the polarization curves shown in Figures 5.7-5.12 have been calculated with the assumption that both absorption and emission are due to electric dipole transitions. If this assumption is correct, then the conclusions based on experimental data are the following: 1) zero-phonon line at 811.7 nm from Xe-related center must be due to XY-Z type of transitions and 2) the optically active defects must have \langle 111 \rangle orientation in cubic crystal. The latter fact is in agreement with earlier works on Xe-related center [6] and with the theoretical calculations of stability of V-Xe-V configuration [3]. However, there is a possibility that absorption is due to a magnetic dipole and/or the emission is also of magnetic nature. As can be seen from the Figures F.1-F.13 (see Appendix F), it is impossible to distinguish “electric dipole absorption – electric dipole emission” (ED-ED for short) from “magnetic dipole absorption – magnetic dipole emission” (MD-MD for short) in the backscattering geometry described earlier. Also, there is no difference between “electric dipole absorption – magnetic dipole emission” (ED-MD for short) and “magnetic dipole absorption – electric dipole emission” (MD-ED for short). In fact, experimental data, shown in Figures 5.14, 5.15, and 5.16 excludes every possibility except for the following four: 1,2) “electric dipole absorption – electric dipole emission” (ED-ED) or “magnetic dipole absorption – magnetic dipole emission” (MD-MD) in XY-Z type of transition; and 3,4) “electric dipole absorption – magnetic dipole emission” (ED-MD) or “magnetic dipole absorption – electric dipole emission” (MD-ED) in XY-XY type of transition. All four possibilities require defects to have \langle 111 \rangle orientation.

5.4.1 Nature of The Dipole Transition

It has been demonstrated that using the backscattering geometry with the laser light incident perpendicular to the (001) crystallographic plane does not allow to unambiguously identify the nature and the type of transition responsible for 811.7 nm zero-phonon line. One can modify the method by changing the direction of incidence of the laser beam relative to the sample. This way it may be possible to to access other crystallographic planes of the crystal. For example, in Figure 5.3 one may try to incline the sample so that the laser beam is incident perpendicular to (011) plane. The motivation for doing this is the following: by exciting a group of defects from a certain angle it is possible to “single out” one crystallographic direction. This reduces the overall symmetry of the problem and makes polarization measurements more discriminating. See [28] for more details.

One obstacle to successfully apply excitation at various angles to the given crystallographic plane is total
5.4. RESULTS AND DISCUSSION

Figure 5.17: Accessing (011) plane of a single crystal diamond sample grown along (001) plane. Using prism allows one to get to the (011) plane at sufficiently large angle. Rotating the sample around the axis perpendicular to (001) plane it is possible to measure the azimuthal profile of co-polarized photoluminescence signal.

internal reflection. Usually a single crystal sample is grown and/or cut along certain crystallographic planes. Due to high refractive index of the diamond ($n \approx 2.42$) it is impossible to access the other planes with the laser beam coming from air. This can be remedied using a glass prism, as illustrated in the Figure 5.17.

For this inclined backscattering geometry there is a difference between “electric dipole absorption – electric dipole emission” and “magnetic dipole absorption – magnetic dipole emission” in azimuthal profiles of co-polarized photoluminescence signal for XY-Z type of transition at high saturation levels (cross-polarized profiles look similar). The difference is also seen between “electric dipole absorption – magnetic dipole emission” and “magnetic dipole absorption – electric dipole emission” in azimuthal profiles of saturated co-polarized photoluminescence signal for XY-XY type of transition. See Figures 5.18 and 5.19.

The difference in the behavior of co-polarized signal with increasing saturation level can be used to eliminate some of the ambiguity in the nature and type of the transition responsible for 811.7 nm line. One even does not need to measure the whole azimuthal profile. Instead it is sufficient to measure the contrast of the profile $K$ at various excitation powers. Contrast of a profile is defined as the ratio of the maximum signal to the minimum signal. For Figures 5.18 and 5.19 it will be $K = \frac{S(0^\circ)}{S(45^\circ)}$. Indeed, as calculations show in Figures 5.20 and 5.21 there is a clear difference for XY-Z type of transition between purely electric
CHAPTER 5. OPTICAL SATURATION IN POLARIZED PHOTOLUMINESCENCE

Figure 5.18: Co-polarized signal at low (blue, darker) and high (red, lighter) saturations behaves differently with the increasing saturation for purely electric and purely magnetic transitions. The petal structure becomes more pronounced for magnetic dipole case.

Figure 5.19: Co-polarized signal at low (blue, darker) and high (red, lighter) saturations behaves differently with the increasing saturation for electric-magnetic and magnetic-electric transitions. The petal structure becomes slightly more pronounced for magnetic dipole case.
5.5 Conclusion

Measurements of polarized luminescence provide a powerful tool for studying optically defects in crystals. There is one dimension of this approach that is usually overlooked: Using optical saturation to enhance the discriminating power of the polarization measurements. As has been demonstrated, high levels of optical saturation, which are easily achieved in micro-luminescence measurements with Gaussian laser beams, can be properly accounted for and provide additional information about the absorbing/emitting dipoles and consequently about the optically active defects.

Also it has been shown that it is possible to use complimentary geometries for the optical excitation of the defects in crystal without the need to re-cut the surfaces of the sample. This allows one to narrow down the multitude of different possibilities for the absorption (Z, XY, electric dipole of magnetic dipole) and emission (Z, XY, electric dipole of magnetic dipole) type and nature and to identify the orientation of the
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Figure 5.21: Contrast of the azimuthal profile of co-polarized signal for electric-magnetic and magnetic-electric XY-XY transition. Blue curve corresponds to the anisotropic case, red curve is for 10 % isotropy factor.

Figure 5.22: Contrast of the azimuthal profile of co-polarized signal as the function of the excitation power measured in the inclined backscattering geometry.
optically active defects within the host lattice.

The experiments and analysis performed for the model Xe-related center in diamond allowed to confirm the orientation of this defect in diamond lattice as \( \langle 111 \rangle \) and to identify the 811.7 nm zero-phonon line as purely magnetic XY-Z transition.
Chapter 6

Summary and Future Work

6.1 Summary

Spectroscopy studies of Xe-related optically active defect in diamond have been presented in this work. These studies, motivated by previous works on Xe-related center [58, 45, 44, 6, 7], extend the results of those works by revisiting old problems and addressing new ones.

Namely, in Chapter 2 a method for determination of important parameter is developed: conversion efficiency of implanted ions into emitting centers. It is a quantity which characterizes the effectiveness of the whole process of ion implantation, followed by thermal annealing. It has been shown how to properly account for the effects of Gaussian laser beams both in relations between the collected signal and the number of emitters, as well as the in the optical saturation effects. Two methods of micro-luminescence mapping have been described: 1) aperture-free and 2) confocal aperture method. Depending on the experimental set up either of them can be used to estimate the conversion efficiency of any optically active defect. Both methods had been applied to measure the conversion efficiency of Xe$^+$ ions, implanted at 180 keV into high purity CVD diamond and subsequently annealed at 1400$^\circ$ C for 2 hours. The results of two methods are similar and show that approximately 1 out of 3 ions turns into the optically active defect.

Next, in Chapter 3, a problem of inhomogeneously broadened zero-phonon line was studied. The behavior of 811.6 nm zero-phonon line, observed in photoluminescence spectra of Xe-related center in diamond, does not follow the predictions of the classical statistical theory of inhomogeneous broadening [56]. This work demonstrates how to extend the classical theory to account for two main effects of ions implantation: 1) two-dimensional distribution of defects, and 2) complex configuration of defects, such as point dipoles and bi-dipoles (see 3.1). The main results is that the observed change of the spectral shape of the zero-phonon line with the increase of the concentration of Xe-related defects is the manifestation of inter-emitter (Xe-Xe)
interaction through elastic strain in the surrounding medium (diamond).

In the following chapter, the mechanism of temperature-dependent broadening of 811.7 nm zero-phonon line from Xe-related centers is discussed. Given the large mass of Xe, dense packing of the diamond lattice, and the results of previous theoretical calculations [23] a model of pseudo-local vibration coupled to the electronic degrees of freedom of the Xe-related center is analyzed. An important feature of the approach presented in Chapter 4 is the extensive search for the parameters of the pseudo-local vibration. It was based not only on the behavior of the width of the zero-phonon line (ZPL) with temperature, but also on the fit of line-shapes measured at various temperatures. Vibronic structure of the phonon side-band of 811.7 nm ZPL allowed to uniquely identify the parameters of the mode in agreement with independent fit of numerical model developed in [33].

Finally, in the Chapter 5 it has been confirmed that Xe-related optical center has an orientation $\langle111\rangle$ within the diamond lattice. What may be called an improvement over previously used approach is the analysis of several important factors, such as: 1) optical saturation effects for Gaussian excitation beams, 2) finite aperture of the objective, and 3) possible isotropy of the Xe-related emitter. It has been established that the isotropy of the emitter is about 10%. Also, the type of transition, responsible for the 811.7 nm line has been confirmed as $\sigma - \pi$ (=XY-Z). Using polarized photoluminescence technique a new important result has been obtained: transitions in Xe-related center, responsible for the 811.6 nm line are, in fact, of magnetic nature.

The results outlined above not only answer research questions posed in the beginning of the work, but raise new ones, as described in the following section.

### 6.2 Recommendation for Future Work

Considering the under-studied status of Xe-related center in diamond, the list of suggested research problems may be long, following more or less the lines of research of the well-known negatively charged nitrogen-vacancy (NV$^-$) center. Several important questions that need to be addressed in the future studies of Xe-related center are given below. The order of the questions does not reflect their relative importance.

1. The spatial structure(s) of Xe-related center needs to be determined with certainty. Given the varying results of theoretical analysis [3, 30, 23] and the inconclusiveness of existing experiments [7], it is necessary to firmly establish whether this center has the inversion symmetry. EPR measurements are of particular interest considering the magnetic nature of 811.6 nm zero-phonon line.

2. The dose-dependence and implantation-energy dependence of conversion efficiency should be studied. It
is known that at low implantation energies optically active defects are not only less scattered laterally but also positioned close to the surface of the sample. The latter allows more efficient coupling of emitted radiation to waveguides and cavities. In the case of NV\(^-\) center the closeness to the surface decreases the conversion efficiency [52]. It is unknown how strongly this may affect Xe-related defect. Being just 50 nm below the surface and having conversion efficiency about 30% makes it likely that Xe-related center will not suffer significant conversion efficiency degradation at lower implantation energies.

3. The method for manipulating the conversion efficiency may be developed. Additional post-implantation treatment of the diamond sample with high energy electrons or protons can be used to create more vacancies which will be captured by Xe atoms to create more optically active defects. Decreasing the number of emitting centers per unit area may also be beneficial for solving the next problem.

4. There is a need to create and address a single emitting Xe-related defect. It is important to have a single emitter to study its properties as a source of single-photons. High-precision single ion implantation or low dose implantation can be used to create well-isolated Xe-related defects.

5. Electronic structure of Xe-related defects can be further studied. Apart from the work [23], little has been done so far on Xe theoretically. Experimentally, only a simple tentative energy levels scheme has been proposed [44]. Excitation, absorption and EPR spectroscopy can be applied to this center in the way similar to NV\(^-\) center in diamond.

6. Life-time measurements and life-time manipulation through coupling of Xe-related centers to optical micro-cavities can be performed. Coupling to cavities and waveguides is an important aspect of making Xe-related center a part of a “quantum circuit”.

7. To confirm the results of Chapter 3 for the mechanism of inhomogeneous broadening it is possible to study how the width of the 811.7 nm zero-phonon line changes with the implantation dose. If the conclusion made in Chapter 3 are correct then in the limit of low implantation doses one expects the scaling of the spectral width with the implantation dose \(\rho\) as \(\rho^{5/2}\). This is characteristic to point-like bi-dipole defects distributed in a plane.

8. The conclude the study of homogeneous broadening of 811.7 nm zero-phonon line (ZPL) of Xe-related defects in diamond one needs to confirm the existence of the predicted pseudo-local vibrational mode. Namely, a temperature-dependent measurements of the Stokes and anti-Stokes part of the ZPL tails should be made with the focus on the Stokes spectral region 165-175 cm\(^{-1}\) from the ZPL’s center.
9. The dependence of the polarization of photoluminescence from Xe-related centers at various temperatures and excitation wavelengths can be studied to gain more insights into the structure and dynamics of this center. The results for room temperature measurements for 811.6 nm ZPL are discussed in Chapter 5 (for a single excitation wavelength, $\lambda_{\text{exc}} = 521$ nm). Similar measurements can be performed at lower temperatures to avoid the effects of phonon-assisted transition to the higher state seen as the second ZPL at 794 nm. Also, the study of 794 nm ZPL can be made in a way analogous to the more prominent 811.7 nm line. Preliminary results (not reported here) suggest that transition responsible for 794 nm line must be of electronic nature. Given the common excitation channel of both 794 nm and 811.7 nm lines, the latter fact does not agree with the magnetic nature of 811.7 nm line, as established in Chapter 5. More research is needed on this question.
Appendix A

Conversion Efficiency: Mathematical Appendix

A.0.1 Correction Factor $\beta$ For Gaussian Beam

The correction factor $\beta$ is defined as the ratio $\beta \equiv \frac{\overline{X^2}}{\overline{X^2}}$, where $X$ is the signal from a single emitter under given excitation $I(r)$. Therefore one needs to evaluate both averages for a given excitation profiles $I(r)$. In a simple case of non-saturated excitation signal from a single emitter is directly proportional to the excitation power: $X = c\alpha_0 \cdot I$. The coefficient $c$ is assumed to be the same for all centers, $\alpha_0$ corresponds to the absorption coefficient. Since optical centers are uniformly distributed, their probability distribution function (PDF) is constant. Total probability of finding a center inside the circle of the radius $R$ must be 1, so the normalized PDF is:

$$f(x, y) = \frac{1}{\pi R^2} \quad (A.1)$$

For a given random position $(x, y)$ of the emitter in the laser spot the signal is

$$X(x, y) = c\alpha_0 \cdot I_0 e^{-\frac{(x^2+y^2)}{w^2}} = X_1 e^{-\frac{r^2}{w^2}} \quad (A.2)$$

$X_1$ is the maximum signal from an optical center when it is positioned exactly at the center of the laser beam.

Expectation value is then given by

$$\overline{X} = \iint f(x, y)X(x, y)\rho_0 dxdy = \frac{X_1\rho_0}{\pi R^2} \iint e^{-\frac{r^2}{w^2}} dxdy \quad (A.3)$$
Evaluating the integral in polar coordinates one gets
\begin{equation}
\overline{X} = X_1 \rho_0 \frac{w^2}{R^2} \left( 1 - e^{-\frac{2R^2}{w^2}} \right) \tag{A.4}
\end{equation}

Introducing the dimensionless size of the working area \( k \equiv R/w \), the previous expression can be rewritten
\begin{equation}
\overline{X} = X_1 \rho_0 \cdot \frac{1 - e^{-k^2}}{k^2}. \tag{A.5}
\end{equation}

In a similar way one can calculate the average of the square of the signal \( \overline{X^2} \):
\begin{equation}
\overline{X^2} = \int \int f(x,y) \left[ c \alpha_0 \rho_0 \cdot I(x,y) \right]^2 dxdy = \frac{X_1^2 \rho_0^2}{\pi R^2} \int_0^R \int_0^{2\pi} e^{-\frac{2r^2}{w^2}} r dr d\phi, \tag{A.6}
\end{equation}

which yields after integration
\begin{equation}
\overline{X^2} = \frac{X_1^2 \rho_0^2}{2k^2} \left( 1 - e^{-2k^2} \right). \tag{A.7}
\end{equation}

Therefore the parameter \( \beta \) is given by:
\begin{equation}
\beta(k) = \frac{k^2}{2} \cdot \frac{(1 - e^{-2k^2})}{(1 - e^{-k^2})^2} = \frac{k^2}{2} \cdot \coth \left( \frac{k^2}{2} \right). \tag{A.8}
\end{equation}

The presence of optical saturation effects changes the statistics of \( X \) and leads to a different expression for \( \beta \). Denoting intensity dependent absorption coefficient \( \alpha(I) \), the average signal can now be written as
\begin{equation}
\overline{X} = \frac{1}{\pi R^2} \int \int c \alpha(I) \cdot I(x,y) \rho_0 dxdy \tag{A.9}
\end{equation}

In many cases (see [13]) \( \alpha(I) \) can be taken in the form
\begin{equation}
\alpha(I) = \frac{\alpha_0}{1 + I/I_s}, \tag{A.10}
\end{equation}

\( I_s \) being is a saturation intensity.

Thus, for a Gaussian beam and optical saturation effects present one gets
\begin{equation}
\overline{X} = \frac{c \alpha_0 I_0 \rho_0}{R^2} \int_0^R \frac{e^{-r^2/w^2} 2r dr}{1 + \gamma e^{-r^2/w^2}} = \frac{c \alpha_0 I_0 \rho_0}{k^2} \ln \left( \frac{1 + \gamma}{1 + \gamma e^{-k^2}} \right) \tag{A.11}
\end{equation}

Here \( \gamma \equiv I_0/I_s \) is saturation parameter. It is proportional to the total power of the laser beam \( P \) and inversely proportional to the laser spot area: \( \gamma = P/\pi w^2 I_s \).
The average of the squared signal looks a little bit more complicated:

$$\bar{X^2} = \frac{e^2 \alpha_0^2 I_s^2 \rho_0^2}{k^2} \left[ \ln \left( \frac{1 + \gamma}{1 + \gamma e^{-k^2}} \right) - \frac{\gamma(1 - e^{-k^2})}{(1 + \gamma)(1 + \gamma e^{-k^2})} \right]$$

(A.12)

Finally, the expression for $\beta$ in the case of saturation evaluate to

$$\beta(k, \gamma) = k^2 \ln \left( \frac{1 + \gamma}{1 + \gamma e^{-k^2}} \right) - \frac{\gamma(1 - e^{-k^2})}{(1 + \gamma)(1 + \gamma e^{-k^2})} \ln^2 \left( \frac{1 + \gamma}{1 + \gamma e^{-k^2}} \right)$$

(A.13)

### A.0.2 Error Analysis

The expression for the conversion efficiency for the aperture-free case is given by

$$q = \frac{N_{\text{emit}}}{N_{\text{impl}}} = F \cdot \frac{1}{w^2} \cdot \frac{S^2}{\pi \sigma_S^2 \rho_0}$$

(A.14)

with $F(k, \gamma) \equiv \beta/k^2$. The uncertainty in the dimensionless size of the useful area $k = R/w$ leads to the error in the factor $F$. The relative error in $q$ is split into three terms: $\varepsilon_q = \varepsilon_F + 2\varepsilon_w + \varepsilon$; the first term is due to the error in $F$, the second is due to the error in the size of the laser spot, and the third one incorporates experimental errors in implantation dose and signal measurements. The relative error $\varepsilon_F$ can be expressed in terms of the relative error in $k$: $\varepsilon_F = \varepsilon_k k F' / F$, where $F'$ is the partial derivative of $F$ with respect to $k$. The analytic expression for $k F' / F$ is extensive, its calculated dependence on $k$ is shown in Figure A.1. As can be seen, the sensitivity of the relative error $\varepsilon_F$ to the error in $k$ is relatively low when $k > 2$. This was the case for the experiments discussed in Chapter 2. In the experiments the signal-to-noise criterion gave $\varepsilon_k = 6\%$, which implied only 1.2% error in the conversion efficiency. On the other hand, the error in the size of the laser spot $\varepsilon_w$ significantly affects the uncertainty in $q$. In the case of the measurements described in this work $\varepsilon_w = 10\%$, which implied that $\varepsilon_q$ is at least 20%. When confocal aperture is used to set the size of the useful area during mappings the accurate value of $w$ is not required and any errors associated with $w$ are excluded.

### A.0.3 Active Sieve Model

To understand what may affect the conversion efficiency the following simple model can be considered: Implanted ions are randomly distributed inside the sample forming a thin layer some distance below the surface. Their positions are assumed fixed during annealing. In the space above the layer of implanted ions there are vacancies created as the result of ion implantation. There may be vacancies below the ion-implanted
layer, however in high purity crystal the concentration of “induced” vacancies is much higher.

Due to the diffusion during the annealing process the vacancies begin to drift, passing through the plane of implanted ions. Let $j_{in}(t)$ be the surface current density of vacancies coming onto the plane. When a vacancy (V) passes at certain distance from an ions an active complex “V-Ion” is formed. The probability to capture a vacancy is proportional to “cross-section” of ion $\sigma$. The number of ions available for conversion decreases with time. Denoting the number of remaining ions $N_R$ and the number of ions converted into optically active centers as $N_C$ the balance equation may be written in the following way:

$$
\frac{dN_C}{dt} = -N_R \sigma j_{in} = (N_0 - N_C) \sigma j_{in}.
$$

where $N_0$ is the total number of implanted ions. After integration of (A.15) one obtains:

$$
q = \frac{N_C}{N_0} = 1 - e^{-M},
$$

where $M \equiv \sigma \int_0^t j_{in} dt$ is the number of vacancies passed through the area $\sigma$ during the annealing process. Figure A.2 demonstrates the dependence of the conversion efficiency $q$ on $M$. This results suggests that to increase the conversion efficiency it is desirable to increase the concentration of vacancies or the annealing time. Number of vacancies can be increased if one uses higher implantation energies for the ions. As shown in [52], the conversion efficiency as the function of the implantation energy of nitrogen ions exhibits the saturation-like behavior, similar to the Figure A.2.
Figure A.2: Conversion efficiency $q$ strongly depends on the number $M$ of vacancies that pass through a “cross section” area of an implanted ion during annealing.

Some comments can be made on the kinetics of vacancies. When they diffuse, they may encounter interstitial atoms of the host lattice and recombine. This decreases the concentration of the vacancies in time. The concentration also decreases due to the increase of the volume, occupied by vacancies in the process of diffusion. The latter leads to the growth of the characteristic size $L$ of the volume occupied by the vacancies: $L = L_0 + D\sqrt{t}$, where $D$ is the diffusion coefficient. The volume, occupied by the vacancies grows as $V \propto L^3$ and changes in time as $V = V_0(1 + \frac{D}{L_0}\sqrt{t})^3$. Thus, the average concentration of vacancies changes in time according to

$$\rho(t) = \rho_0 \cdot \frac{e^{-\alpha_T t}}{(1 + \delta \sqrt{t})^3},$$

(A.17)

where $\delta \equiv D/L_0$; $\alpha_T$ is the temperature dependent recombination rate; $\rho_0$ is initial average concentration of vacancies.

The surface current density of the vacancies at the plane of implanted ions is then given by

$$j_{in}(t) = \frac{\rho(t)}{2}v_T = \frac{\rho_0}{2}v_T \cdot \frac{e^{-\alpha_T t}}{(1 + \delta \sqrt{t})^3},$$

(A.18)

$v_T$ is the temperature dependent diffusion velocity. One half is due to the fact that vacancies drift randomly and half of them moves from the plane of ions upwards to the sample’s surface.

The total number $M$ of vacancies that will pass through a cross-section area $\sigma$ during the annealing time $t$ can be now written as

$$M(t) = \rho_0 \frac{\sigma v_T}{2} \mu(t),$$

(A.19)
APPENDIX A. CONVERSION EFFICIENCY: MATHEMATICAL APPENDIX

Figure A.3: Effects of diffusion on the total number of vacancies that pass through the layer of ions.

where
\[
\mu \equiv \int_0^t \frac{e^{-\alpha \tau}}{(1 + \delta \sqrt{\tau})^3} d\tau \quad (A.20)
\]

The behavior of the function \(\mu(\tau)\) is shown in Figure A.3 for three levels of diffusion: significant (\(\delta = 1\), red curve); moderate (\(\delta = 0.1\), green curve); low (\(\delta = 0.01\), blue curve). When the diffusion is negligible one can evaluate the integral in (A.20) to get
\[
\mu = \frac{1}{\alpha T} \left(1 - e^{-\alpha \tau t}\right), \quad (A.21)
\]

which implies that long enough annealing will result in the total number of vacancies through the cross-section \(\sigma\)
\[
M = \rho_0 \frac{\sigma v_T}{2 \alpha T}. \quad (A.22)
\]

In any case, \(M\) is proportional to the initial concentration of vacancies \(\rho_0\).

For \(\text{Xe}^+\) ions implanted into diamond crystal SRIM simulations show that the concentration of vacancies is proportional to the ion implantation dose (see Figure A.4). The dependence on the energy of the implanted ions for all parameters shown in Figure A.4 can be approximated with power law \(aE^{0.8}\). Therefore, for \(\text{Xe}\) ions implanted into diamond the conversion efficiency within the model of active sieve takes the form:
\[
q = 1 - e^{-\rho_{\text{Xe}} \frac{\sigma v_T}{2} \mu(t) a E^{0.8}}. \quad (A.23)
\]
Figure A.4: Implantation parameters as the function of energy of implanted ions for Xe into diamond. Calculated using SRIM (www.srim.org).

The conversion efficiency thus is sensitive to the energy of implantation, as well as the implantation does of Xe ions $\rho_{\text{Xe}}$. 
Appendix B

Conversion Efficiency: Computer Program

Below a computer program is given for calculating the correction factor $\beta$ (see section 2.1) for the confocal aperture method. It written in C programming language and can be compiled in any environment with GNU Compiler Collection and GNU Scientific Library installed (GNU/Linux is recommended). To do so, create a Makefile with the following content (some modification may be required if newer version of the libraries are used):

```
aperture : aperture.o
    gcc -L/usr/local/lib -lgsl -lgslcblas -lm -lglib-2.0 -o aperture aperture.o

aperture.o : aperture.c
    gcc -Wall -I/usr/local/include -I/usr/include/glib-2.0 -l/usr/lib/glib-2.0/
               include -c aperture.c
```

Then modify the experimental parameters in the C-code (e.g. the size of the aperture $R$), compile and the program by executing

```
make
./aperture
```

on the command line.

Computer Program:

```c
#include <stdlib.h>
#include <math.h>
#include <sys/time.h> // for enhanced randomness
```
// GNU Scientific Library is used for
// 1. Random Numbers Generation
// 2. Statistical Processing of the Results
// 3. Special Functions (Bessel Functions)
// 4. Monte-Carlo Integration
#include <gsl/gsl_rng.h>
#include <gsl/gsl_randist.h>
#include <gsl/gsl_statistics.h>
#include <gsl/gsl_sf_bessel.h>
#include <gsl/gsl_monte.h>
#include <gsl/gsl_monte_miser.h>

// These Point-Spread Functions can be used:
// 1. Bessel Function
// 2. Flat-Top
// 3. Cone-Like (Party-Hat)
// 4. Parabolic
// 5. Error-Function-shaped

#define r1 3.8317 // first zero of Bessel function J_1
#define norm1 2.6318 // normalization for r1

#define r2 7.0156 // second zero of Bessel function J_1
#define norm2 2.8686

#define r3 10.1735 // 3rd zero
#define norm3 2.9457

#define rX r1 // shortcut to quickly switch between r1, norm1 etc.
#define normX norm1

#define r 0.50 // radius of the diffraction spot as ratio r/R
// R is the working area size
// Simulating 20x20 mapping
#define MAP_SIZE 400

double R = 0.8;
double w = 2.0; // laser spot e-radius
double g = 60; // saturation parameter;
double norm = 0; // normalization factor for the signal from a single emitter

 //* ---------- Monte Carlo Integration Variables--------------*/
size_t dimension = 2;// dimension of the integral in Monte-Carlo
size_t calls = 5000;
double xlower[2] = {0, 0}; // integration boundaries
double xupper[2] = {2* M_PI, 1.1};
gsl_rng *randomizer_MC;
gsl_monte_miser_state *miser_state;

 /**<--- Point Spread Functions. Intensity Distribution Due To Diffraction---*/
double I_Bessel(double rho);
double I_Flattop(double rho);
double I_Partyhat(double rho);
double I_Parabola(double rho);
double I_ErrFuncFamily(double rho);

double Excitation(double *xy); // Excitation of the sample.
double fraction(double *xy);
double f(double *x, size_t dim, void *params);

int main (void)
{
    const gsl_rng_type * T;
    gsl_rng * randomizer;

    // signal from the current point on the map
    double signal = 0;
    // signal from a single emitter in the center of the beam
    double X1 = 0;

    unsigned int i, n;
    double xy[2]; // random position of the emitting center

    // signal from emitter, calculated with diffraction effects
    double S_diffr = 0;
    // signal from emitter, calculated using geometric optics
    double S_geom = 0;

    double delta = 0;
    struct timeval tv;
    long seed;

    size_t Map_Size = MAP_SIZE;
    double SGeom_Set[MAP_SIZE]; // simulated 'mapping' results
    double SDiffr_Set[MAP_SIZE];
    double Delta_Set[MAP_SIZE];
double N_Avg = 5000;

double N_emit; // number of emitting centers in the working area

double N_inside = 0;
// statistical characteristics of mappings

double SGeom_Mean, SGeom_Sigma;
double SDiffr_Mean, SDiffr_Sigma;
double Delta_Mean, Delta_Sigma;
double BetaGeom; // correction factor \( S^2 / \sigma^2 \)
double BetaDiffr;

miser_state = gsl_monte_miser_alloc(dimension);

{
    // setting up randomizer
    gsl_rng_env_setup();
    T = gsl_rng_ranlux389;
    randomizer = gsl_rng_alloc(T); // for generating centers' coordinates
    randomizer_MC = gsl_rng_alloc(T); // for Monte-Carlo integration
    // using current time to seed the random number generator
    gettimeofday(&tv, NULL);
    seed = tv.tv_usec;
    gsl_rng_set(randomizer, seed);
    gettimeofday(&tv, NULL);
    seed = tv.tv_usec;
    gsl_rng_set(randomizer_MC, seed);
}
// randomizer is set up

// warming-up randomizer
xy[0] = gsl_ran_flat(randomizer, -(R+r), +(R+r));
xy[1] = gsl_ran_flat(randomizer, -(R+r), +(R+r));
/* calculating total signal from a single center in the center of the aperture. */
xy[0] = 0.0;
xy[1] = 0.0;
/* We need to increase the size of the aperture for a moment not to lose the signal if \( r > R \) */
R = 2*r;
X1 = fraction(xy);
R = 1.0000; // closing the aperture to it’s initial size
printf("Total signal: \%5.4f\n", X1);

for (n = 0; n < Map_Size; n++)
{
}
S_diffr = 0;
S_geom = 0;
delta = 0;
N_emit = gsl_ran_poisson(randomizer, N_Avg);

// calculating the signals at a given point on the map
for (i = 1; i <= N_emit; i++)
{
    xy[0] = gsl_ran_flat(randomizer, -(R+r), +(R+r));
    xy[1] = gsl_ran_flat(randomizer, -(R+r), +(R+r));
    signal = X1*Excitation(xy); // total signal from the center at this position \{x_i, y_i\}
    if ( (fabs(xy[0]) < R) && (fabs(xy[1]) < R) )
        // the emitter is inside the aperture
        {
            S_geom = S_geom + signal;
            N_inside = N_inside + 1;
            if ( (fabs(xy[0]) < (R-r) ) && (fabs(xy[1]) < (R-r) ) )
                // the center is inside the "core" -- no need to integrate
                {
                    S_diffr = S_diffr + signal;
                }
            else
                {
                    S_diffr = S_diffr + signal*fraction(xy);
                }
        }
    else
        {
            S_diffr = S_diffr + signal*fraction(xy);
        }
}

delta = S_diffr/S_geom;
SGeom_Set[n] = S_geom;
SDiffr_Set[n] = S_diffr;
Delta_Set[n] = delta;
}

{ 
gsl_rng_free(randomizer);
gsl_rng_free(randomizer_MC);
gsl_monte_miser_free(miser_state); }
APPENDIX B. CONVERSION EFFICIENCY: COMPUTER PROGRAM

```c
// Extracting the statistical parameters
SGeom_Mean = gsl_stats_mean(SGeom_Set, 1, MAP_SIZE);
SGeom_Sigma = gsl_stats_sd(SGeom_Set, 1, MAP_SIZE);

SDiffr_Mean = gsl_stats_mean(SDiffr_Set, 1, MAP_SIZE);
SDiffr_Sigma = gsl_stats_sd(SDiffr_Set, 1, MAP_SIZE);

Delta_Mean = gsl_stats_mean(Delta_Set, 1, MAP_SIZE);
Delta_Sigma = gsl_stats_sd(Delta_Set, 1, MAP_SIZE);

BetaGeom = (N_Avg/((1+r)*(1+r)))*SGeom_Sigma*SGeom_Sigma/(SGeom_Mean*SGeom_Mean);
BetaDiffr = N_Avg*SDiffr_Sigma*SDiffr_Sigma/(SDiffr_Mean*SDiffr_Mean);

// Displaying the results
printf("Beta Geometrical: %5.4f\n", BetaGeom);
printf("Beta Diffractional: %5.4f\n", BetaDiffr);
printf("Average Delta: %5.4f\n", Delta_Mean);
printf("Delta STD: %5.4f\n", Delta_Sigma);

return 0;
```

```c
double I_Bessel(double rho)
// Intensity distribution in the Point Spread Function
{
    double result = 0;
    double x = rho*rX/r;
    if (rho < r)
    {
        if (x == 0)
        {
            result = (rX*rX)/(4*normX*r*r);
        }
        else
        {
            result = (rX*rX)/(normX*r*r)*(gsl_sf_bessel_J1(x)/x)*(gsl_sf_bessel_J1(x)/x);
        }
    }
    else
    {
        //... (additional code not included)
    }
    return result;
}
```
double I_Flattop(double rho)
// Normalized flat-top circle function
{
    double result = 0;
    if (rho < r)
        result = 1/(M_PI*r*r);
    else
        result = 0;
    return result;
}

double I_Partyhat(double rho)
{
    double result = 0;
    if (rho < r)
        result = (1 - rho/r)/0.2619; // normalized
    else
        result = 0;
    return result;
}

double I_Parabola(double rho)
{
    double result = 0;
    if (rho < r)
        result = (1 - (rho*rho)/(r*r))/0.3927; // normalized
    else
        result = 0;
    return result;
}

double I_ErrFuncFamily(double rho)
{
    double result = 0;
    double scale = 5; // the bigger the scale --- the closer the flat-top
    if (rho < r)
        result = erf(scale*(r-rho))/0.4981;
    else
        result = 0;
return result;
}

double Excitation(double *xy)
/* Distribution of the intensities of emitting centers due to
the excitation profile and saturation effects*/
{
    return exp( -(xy[0]*xy[0]+xy[1]*xy[1])/(w*w))/(1+g*exp( -(xy[0]*xy[0]+xy[1]*xy[1])/(w*w));
}

double f(double *x, size_t dim, void * params)
// the function being integrated in polar coordinates I(r)*r
// it describes the intensity of the signal from emitter i.e.
// defines Point Spread Function
{
    double result = 0;
    double xj, yj;
    double *xiyi = (double *) params;
    // calculating the coordinates with respect to the aperture
    xj = xyi[0] + x[1]*cos(x[0]);
    yj = xyi[1] + x[1]*sin(x[0]);

    if ( (fabs(xj) < R) && (fabs(yj) < R) )
        result = I_Bessel(x[1]) * x[1];
    else
    {
        result = 0;
    }
    return result;
}

double fraction(double *xy)
// Monte Carlo integrator. Determines the signal from
// a single emitter positioned at (x, y)
{
    gsl_monte_function F = {&f, dimension, (void *)xy};
    double result, error;

    gsl_monte_miser_init(miser_state);
    gsl_monte_miser_integrate(&F, xlower, xupper, dimension, calls, randomizer_MC, miser_state, &result, &error);
    return result;
}
Appendix C

Inhomogeneous Broadening:
Mathematical Appendix

C.0.4 Statistical Theory Of Inhomogeneous Broadening Overview

A problem of an optically active center (emitter) in crystal, whose transition energy $\hbar \omega$ experiences a shift $\hbar \delta \omega$ due to an external perturbation is considered. The position of a perturber (e.g. other defect) relative to the emitter is given by a vector $\mathbf{r}$. The perturber is allowed to have any position inside of a crystal, except too close to the emitter. Thus one may introduce the minimal distance between the perturber and the emitter $R_0$ and also the characteristic size of the crystal $R_1$: $R_0 \leq r \leq R_1$. The shift due to a single perturber is determined by the type of the latter and depends on the relative position $\mathbf{r}$. For example, a general expression for $\delta \omega$ due to elastic strain has the form of an inverse power law multiplied by some angular factor (see section C.0.6):

$$\delta \omega(\mathbf{r}) = S \frac{\psi(\theta, \phi)}{r^n} = \frac{S}{R_0^n} \cdot \frac{\psi(\theta, \phi)}{\xi^n}, \quad n > 0.$$ (C.1)

In this formula $S$ is the strength of the coupling between the emitter and the strained medium. Also the expression has been factorized to introduce a dimensionless shift of the frequency $\Delta_1(\mathbf{r}) \equiv \psi \cdot \xi^{-n}$ due to a single perturber.

It is further assumed that when $N$ perturbers interact with the emitter their contributions to the total shift is additive:

$$\Delta = \Delta_1(\mathbf{r}_1) + \Delta_1(\mathbf{r}_2) + \ldots + \Delta_1(\mathbf{r}_N).$$ (C.2)

Another important assumption is that of statistical independence of individual contributions $\Delta_1(\mathbf{r}_1), \Delta_1(\mathbf{r}_2), \ldots$.
\[\Delta_1(r_N).\] This implies that the positions of the perturbers \(r_1, r_2, \ldots, r_N\) are uncorrelated; it is a reasonable approximation at low concentrations of perturbers. Under these assumptions the total shift \(\Delta\) is the sum of \(N\) independent random variables \(\Delta_1(r)\).

The aforementioned assumptions were used by Stoneham in [56]. The method has been subsequently used by other authors as well (Davies [14, 15], Kador [38]). The line-shape obtained using this method turns out to be Lorentzian with the shift of the peak and the FWHM proportional to the concentration of the defects.

The expression for the line-shape is written in the following way:

\[
I_N(\Delta) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dx e^{-ix\Delta} \cdot \left(1 - \frac{\rho J(x)}{N}\right)^N = F[G_\Delta(x)].
\]  

\(F[\ldots]\) denotes the Fourier transform of the argument. This is the formula for the line-shape determined by \(N\) defects (see (3.17-3.18) in Stoneham). Given the Fourier pre-image \(G_\Delta(x)\), one can calculate the moments of the line-shape (see M. Lax):

\[
M_n = i^n \frac{d^n}{dn} G_\Delta(x) \bigg|_{x=0}.
\]  

(C.4)

The moment of interest is \(M_1\) which would give the position of the peak for a symmetrical line:

\[
M_1 = i \frac{dG_\Delta(0)}{dx} = -i\rho J'(0) \left(1 - \frac{\rho J(0)}{N}\right)^{N-1}.
\]  

(C.5)

For point defects distributed in three dimensions with the shift given by \(\Delta = \frac{S\psi}{r^3}\), the expression for \(J(x)\) has the form (A3.1 Stoneham)

\[
J(x) = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_{R_1}^{R_2} drr^2 \left(1 - e^{-ixS\psi/r^3}\right).
\]  

(C.6)

From this immediately follows that \(J(0) = 0\). Therefore \(M_1 = -i\rho J'(0)\). Differentiation of (C.6) yields:

\[
J'(0) = iS \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \psi(\theta, \phi) \int_{R_1}^{R_2} drr^2 \cdot \frac{1}{r^3}.
\]  

(C.7)

Thus, the first moment can be written in the following way:

\[
M_1 = S\rho \left(\frac{1}{r^3}\right)\langle \psi \rangle.
\]  

(C.8)
Direct integration over the angular variables results in \( \langle \psi \rangle = 0 \) and this means that the line can not be shifted.

### C.0.5 Parameters of the Line-Shape.

Before considering any particular approach for calculating the probability density function \( \mathcal{P} \) for a given spectral shift \( \mathcal{P}(\Delta) \), one can investigate a number of general properties of this distribution. Namely, the four main parameters of the line shape—the shift, the width, the asymmetry, and the weight of the tails—can be evaluated much easier than the line shape itself. This is the central idea of the well known method of moments. Thus we will study how the average shift \( \mu \), the standard deviation \( \sigma \), the asymmetry \( \gamma \), and the kurtosis \( \kappa \) behave when the concentration of perturbers, or the size of the crystal, or other parameters of the model change.

Two distinct cases are feasible. The first takes place when the random variables in (C.2) are identical. That means all perturbers have the same probability to be at a given position \( \mathbf{r} \). When the broadening is due to defects that are different and independent from emitters this condition is satisfied. Inhomogeneous broadening of zero phonon line of Si center in diamond by nitrogen impurities is an example. The other possibility is realized when the emitters also act as perturbers. The terms in the sum C.2 are now not identical and the expression should be rewritten to reflect this. Therefore we write

\[
\Delta = \Delta^{(1)}(\mathbf{r}_1) + \Delta^{(2)}(\mathbf{r}_2) + \ldots + \Delta^{(N)}(\mathbf{r}_N). \tag{C.9}
\]

This expression should be understood in the following way: \( \Delta^{(1)}(\mathbf{r}_1) \) is the shift due to the first nearest perturber, \( \Delta^{(2)}(\mathbf{r}_1) \) is due to the second—and so on. As a result of ion implantation the number of emitters in a fixed volume varies from point to point. In its turn the distance between two neighboring emitters also exhibits fluctuations around the average value \( R_a \) which is determined by the concentration of emitters. Hence the probability density function for \( \Delta^{(1)}(\mathbf{r}_1) \) should be peaked at \( R_a \), and other \( \Delta^{(n)}(\mathbf{r}_n) \) have peaks at \( R_a \cdot n^{1/D} \), \( D \) being the dimension of the model. It is worth stressing that the probability density function for each term in (C.9) is not fixed but changes with concentration.

Each variable \( \Delta_1 \) has a well-behaved probability density function \( p(\Delta_1) \) which is non-zero only inside some interval \([\Delta_{min}, \Delta_{max}]\) and therefore has all moments. According to the central limit theorem, as the number \( N \) of perturbers which contribute into the spectrum increases, the resulting line-shape approaches a Gaussian in the interval \([N\Delta_{min}, N\Delta_{max}]\). It should be noted that this convergence to Gaussian can be slow and on its way from the line shape due to a single perturber \( p(\Delta_1) \) to \( N \) perturbers \( \mathcal{P}(\Delta) \) the observed line may have any reasonable shape. If the convergence is indeed slow, the approximation of dilute perturbers
will not allow the line-shape to become Gaussian. Anyway, one should expect the change of the line-shape when the concentration of perturbers increases even in this linear regime.

Furthermore, for the method of moments it is sufficient to study a single-perturber function \( p(\Delta_1) \) because of the following scaling relationships:

\[
\mu = N\mu_1, \quad \sigma = \sqrt{N}\sigma_1, \quad (C.10)
\]
\[
\gamma = \frac{\gamma_1}{\sqrt{N}}, \quad \kappa = \frac{\kappa_1}{N}. \quad (C.11)
\]

Quick inspection of these formulae confirms the prediction of the central limit theorem: \( \lim_{N \to \infty} \gamma = 0, \lim_{N \to \infty} \kappa = 0 \), i.e. the line becomes symmetric with the kurtosis of the Gaussian. One more thing that is evident from this general consideration – the linewidth increases according to the square law regardless of a specific mechanism of broadening.

### C.0.6 Point Defects in 3D

In the linear approximation the energy shift of the transition in two-level system coupled to the strain in the environment is given by

\[
\hbar \omega - \hbar \omega_0 = \hbar \omega_1 \sum_{i,j=1}^{3} a_{ij} e_{ij}, \quad (C.12)
\]

where \( a_{ij} \) is the matrix of coupling coefficients and \( e_{ij} \) is the strain tensor. For a single point defect of the strength \( S \), positioned at the coordinates \( x_i \) relative to the emitter, the strain tensor \( e_{ij} \) has the form

\[
e_{ij} = \frac{S}{r^3} \left( \delta_{ij} - 3 \frac{x_i x_j}{r^2} \right) = \frac{S}{r^3} \psi_{ij}(\theta, \phi). \quad (C.13)
\]

The shift due to a single point defect can be written as

\[
\omega - \omega_0 = \frac{S\omega_1}{R_0^3} \frac{\psi(a, \theta, \phi)}{\xi^3}. \quad (C.14)
\]

In this formula \( \xi \) denotes the dimensionless distance between the defect and the emitter \( (\xi \equiv r/R_0 \geq 1) \); \( \psi(a, \theta, \phi) \) is the angular part given by

\[
\psi(a, \theta, \phi) = \sum_{i,j=1}^{3} a_{ij} \psi_{ij}(\theta, \phi) \quad (C.15)
\]
The angular part evidently depends on the matrix of the coupling coefficients. More precisely it depends only on the symmetric part of the latter which can be specified by six parameters \( \mathbf{a} = (a_1, a_2, a_3, a_4, a_5, a_6) \):

\[
a_{ij} = \begin{pmatrix}
a_1 & a_4 & a_5 \\
a_4 & a_2 & a_6 \\
a_5 & a_6 & a_3
\end{pmatrix}.
\]

Thus, the line-shape due to a single point defect is determined by the dimensionless part of (C.14):

\[
\Delta_1(r) \equiv \frac{\psi(\mathbf{a}, \theta, \phi)}{\xi^3}
\]

The average shift is zero due to the vanishing angular part:

\[
\langle \psi(\mathbf{a}, \theta, \phi) \rangle = \sum_{i,j=1}^{3} a_{ij} \langle \psi_{ij}(\theta, \phi) \rangle,
\]

\[
\langle \psi_{ij}(\theta, \phi) \rangle = \int_{0}^{\pi} \sin \theta d\theta \int_{0}^{2\pi} d\phi \cdot \psi_{ij}(\theta, \phi) = 0, \quad i, j \in \{1, 2, 3\}.
\]

In this case the expressions for the standard deviation, skewness, and kurtosis are simplified:

\[
\mu_1 = 0, \quad \sigma_1 = \sqrt{\langle \Delta_1^2 \rangle}
\]

\[
\gamma_1 = \frac{\langle \Delta_1^3 \rangle}{\sigma_1^3}, \quad \kappa_1 = \frac{\langle \Delta_1^4 \rangle}{\sigma_1^4} - 3.
\]

Using the normalized probability density function for the radial part \( P(r) \):

\[
P(r) = \frac{3r^2}{R_1^3 - R_0^3},
\]

these can be written in terms of the crystal size and the concentration of defects.

\[
\langle \Delta_1^2 \rangle = \langle \frac{1}{r^6} \rangle \cdot \langle \psi^2 \rangle = \frac{S^2 A_2}{R_0^6(N_1/N_0 - 1)} \cdot \left[ 1 - \frac{N_0}{N_1} \right] = \frac{S^2 A_2}{R_0^6 R_1^3},
\]

\[
\langle \Delta_1^3 \rangle = \langle \frac{1}{r^9} \rangle \cdot \langle \psi^3 \rangle = \frac{S^3 A_3}{2R_0^9(N_1/N_0 - 1)} \cdot \left[ 1 - \left( \frac{N_0}{N_1} \right)^2 \right] = \frac{S^3 A_3}{2R_0^9 R_1^3} \left( \frac{1}{R_0^3} + \frac{1}{R_1^3} \right),
\]
\[\langle \Delta_4^1 \rangle = \langle \psi^4 \rangle = \frac{S^4 B_4}{3 R_0^2 (N_1/N_0 - 1)} \left[ 1 - \left( \frac{N_0}{N_1} \right)^3 \right] = \frac{S^4 A_4}{3 R_0^2 R_1^2} \left( \frac{1}{R_0^2} + \frac{1}{R_0^2 R_1^2} + \frac{1}{R_1^2} \right). \quad (C.22)\]

The number of defects within the crystal is given by \( N = \frac{4}{3} \pi \rho (R_1^3 - R_0^3) \). Combining the latter with the scaling relationships for \( \sigma, \gamma, \kappa \) we’ll obtain the desired expressions:

\[\sigma = S \sqrt{\frac{4 \pi A_2}{3 R_0^2}} \cdot \sqrt{\rho} \cdot \sqrt{1 - \frac{R_0^3}{R_1^3}}. \quad (C.23)\]

The first factor in (C.23) is constant, the second shows that the line-width grows as the square root of the concentration of defects. The last factor shows, that when considering “thermodynamic limit” \( N \to \infty \), \( \rho = \text{const} \) we increase the size of the crystal and the number of defects interacting with the emitter, but the width spectrum saturates rather quickly to it’s maximal value \( \sigma^* \). This suggests, that 99% of the linewidth is due to the defects within a sphere of the radius

\[R_{99\%} = (1 - 0.99^2)^{-1/3} \approx 3.69 R_0 \quad (C.24)\]

Next, the skewness is given by the following expression:

\[\gamma = \sqrt{\frac{3}{\pi}} \cdot \frac{A_3}{4 A_2^{3/2} R_0^{3/2}} \cdot \frac{1}{\sqrt{\rho}} \cdot \frac{1 + R_0^3/R_1^3}{\sqrt{1 - R_0^3/R_1^3}}; \quad (C.25)\]

finally, the kurtosis can be written as

\[\kappa = \frac{A_4}{4 \pi A_2^2 R_0^3} \cdot \frac{1}{\rho} \left( \frac{1 + R_0^3/R_1^3 + R_0^6/R_1^6}{1 - R_0^3/R_1^3} - \frac{9 A_2^2}{A_4} \frac{R_0^3/R_1^3}{(1 - R_0^3/R_1^3)} \right). \quad (C.26)\]

As can be seen in Fig. C.1, the parameters of the line become insensitive to the size of the crystal when the latter is at least 20 times larger that the minimum distance between the defect and the emitter. The limiting values of the parameters are:

\[\sigma^* = S \sqrt{\frac{4 \pi A_2}{3 R_0^3}} \cdot \sqrt{\rho}, \quad (C.27)\]

\[\gamma^* = \sqrt{\frac{3}{\pi}} \cdot \frac{A_3}{4 A_2^{3/2} R_0^{3/2}} \cdot \frac{1}{\sqrt{\rho}}; \quad (C.28)\]

\[\kappa^* = \frac{A_4}{4 \pi A_2^2 R_0^3} \cdot \frac{1}{\rho}. \quad (C.29)\]
Figure C.1: The parameters of the spectrum (width $\sigma$, asymmetry $\gamma$, and kurtosis $\kappa$) approach a limit quite fast as the size of the crystal $r_1$ increases. The kurtosis is given for a particular coupling matrix: $a_1 = 4.59; a_2 = 4.59; a_3 = -4.31; a_4 = -2.63; a_5 = 2.63; a_6 = 10.67$.

The formulae (C.27), (C.28), and (C.29) show that the line shape monotonically approaches a Gaussian with $\gamma \to 0$ and $\kappa \to 0$, while FWHM $\propto \sigma \propto \sqrt{\rho}$.

C.0.7 Point Defects in 2D

Considerations given above also apply for the planar distribution of defects. Setting the angle $\theta = \pi/2$ and averaging the shift $\Delta_1(r)$ one obtains the first result that is different from three dimensional case:

$$\langle \Delta_1 \rangle = \frac{2SB_1}{r_0^3(N_1/N_0 - 1) \cdot \left(1 - \sqrt{\frac{N_0}{N_1}}\right)} \cdot \left(1 - \left(\frac{N_0}{N_1}\right)^2\right). \quad \text{(C.30)}$$

First of all, the average of the angular part $B_1$ in general case is not zero. For three dimensions this would cause a divergence due to the radial factor, but for the planar case the shift $\langle \Delta \rangle = N_1 \langle \Delta_1 \rangle$ approaches a finite limit. The next three averages are:

$$\langle \Delta_1^2 \rangle = \frac{S^2B_2}{2r_0^6(N_1/N_0 - 1)} \cdot \left[1 - \left(\frac{N_0}{N_1}\right)^2\right], \quad \text{(C.31)}$$

$$\langle \Delta_1^3 \rangle = \frac{2S^3B_3}{7r_0^9(N_1/N_0 - 1)} \cdot \left[1 - \left(\frac{N_0}{N_1}\right)^{7/2}\right], \quad \text{(C.32)}$$

$$\langle \Delta_1^4 \rangle = \frac{S^4B_4}{5r_0^{12}(N_1/N_0 - 1)} \cdot \left[1 - \left(\frac{N_0}{N_1}\right)^5\right]. \quad \text{(C.33)}$$
Figure C.2: The probability of finding $N$th neighbour at a distance $r$ is $P = P_1 \cdot P_2$; where $P_1$ is the probability of finding $N - 1$ defects in the volume $V_{N-1}$ and $P_2$ is the probability of finding exactly one defect in the annulus of the thickness $\varepsilon$.

C.0.8 Nearest Neighbour Approximation

2D Case

Assuming the distribution of the defects is Poissonian the probability density of finding $N$th neighbour at the distance $r$ from an emitter is given by the following expression:

$$P(N, r) = C_N \frac{2\pi\rho}{(N - 1)!} e^{N_0 r} e^{-\pi \rho r^2} e^{-\pi \rho r^2 - N_0} N^{N-1}. \quad (C.34)$$

Here $C_N$ is the normalization factor, $\rho$ is the surface density of the defects, and $N_0 \equiv \pi \rho r_0^2$ is the number of defects excluded from the region of the radius $r_0$ around the emitter. This formula can be derived if one considers two disjoint regions $V_{N-1}$ and $V_1$ as shown in Fig. C.2. The probability of finding $N - 1$ defects inside the “volume” $V_{N-1}$ is given by

$$P_1 \propto e^{-\bar{N}} \frac{\tilde{N}^{N-1}}{(N - 1)!}, \quad \bar{N} = \pi \rho (r^2 - r_0^2) = \pi \rho r^2 - N_0, \quad (C.35)$$

while the probability of finding a single defect inside the ring $V_1$ equals

$$P_2 \propto e^{-\bar{N}} \frac{\tilde{N}^1}{1!}, \quad \bar{N} = 2\pi r\varepsilon. \quad (C.36)$$

Expanding the expression for $P_2$ as powers of $\varepsilon$ and keeping only the terms linear in $\varepsilon$ one gets $P_2 = 2\pi r\varepsilon$. The product $P_1 \cdot P_2$ gives the desired probability of two independent events.

Consider now the simplest case of the first nearest neighbour ($N = 1$). The probability density (C.34) then reduces to

$$P(r) \equiv P(1, r) = \frac{2\pi\rho e^{-\pi \rho r^2}}{e^{-N_0} - e^{-N_1}}, \quad (C.37)$$
where $N_1 \equiv \pi \rho r_1^2$ is the total number of defects in the crystal; also the normalization factor $C_1$ has been evaluated.

Having determined the probability density function $P(r)$ we can proceed to calculation of the moments $<\Delta^n>$:

$$<\Delta^n> = S^n A^n <\frac{1}{r^{3n}}>, \quad <A^n> \equiv <\psi(\theta, \phi)>.$$  \hfill (C.38)

The radial average is given by the integral

$$<\frac{1}{r^{3n}}> = \frac{2\pi \rho}{e^{N_0} - e^{-N_1}} \int_{r_0}^{r_1} e^{-\pi \rho r^2} \frac{(\pi \rho)^{3n/2}}{r^{3n-1}} dr = \frac{(\pi \rho)^{3n/2}}{e^{N_0} - e^{-N_1}} \int_{N_0}^{N_1} e^{-t} dt \quad \hfill (C.39)$$

Evaluating the integral for $n \in \{1, 2, 3, 4\}$ one gets:

$$<\Delta> = \frac{2SB_1}{r_0^3} \frac{N_0}{e^{-N_0} - e^{-N_1}} \left[ e^{-N_0} - \sqrt{N_0} \sqrt{N_1} - \sqrt{\pi N_0} \left( \text{Erf}(\sqrt{N_1}) - \text{Erf}(\sqrt{N_0}) \right) \right] \quad \hfill (C.40)$$

Next,

$$<\Delta^2> = \frac{3SB_2}{2r_0^6} \frac{N_0}{e^{-N_0} - e^{-N_1}} \left[ e^{-N_0} (1 - N_0) + \frac{N_0^2}{N_1} e^{-N_1} (1 - \frac{1}{N_1}) + N_0^3 (\text{Ei}(-N_1) - \text{Ei}(-N_0)) \right]. \quad \hfill (C.41)$$

$$<\Delta^3> = \frac{5SB_3}{5r_0^9} \frac{N_0}{e^{-N_0} - e^{-N_1}} \left[ \frac{N_1^{7/2}}{N_1} e^{-N_1} \left( \frac{8}{15} - \frac{1}{15N_1} + \frac{6}{15N_1^2} - \frac{1}{N_1^3} \right) + e^{-N_0} \left( 1 - \frac{6}{15} N_0 + \frac{4}{15} (N_0^2 - \frac{8}{15} N_0^3) \right) \right. + \frac{8}{15} N_0^{7/2} \sqrt{\pi} \left( \text{Erf}(\sqrt{N_1}) - \text{Erf}(\sqrt{N_0}) \right) \left[ e^{-N_0} \left( 1 - \frac{N_0}{4} + \frac{N_0^2}{12} - \frac{N_0^3}{24} + \frac{N_0^4}{24} \right) + \frac{N_0^3}{24} (\text{Ei}(-N_0) - \text{Ei}(-N_1)) \right] \quad \hfill (C.42)$$

$$<\Delta^4> = \frac{7SB_4}{7r_0^{12}} \frac{N_0}{e^{-N_0} - e^{-N_1}} \left[ N_0^5 e^{-N_1} \left( \frac{1}{4N_1} - \frac{1}{12N_1^2} + \frac{1}{24N_1^3} - \frac{1}{24N_1^4} - \frac{1}{N_1^5} \right) + e^{-N_0} \left( 1 - \frac{N_0}{4} + \frac{N_0^2}{12} - \frac{N_0^3}{24} + \frac{N_0^4}{24} \right) + \frac{N_0^3}{24} \left( \text{Ei}(-N_0) - \text{Ei}(-N_1) \right) \right]. \quad \hfill (C.43)$$

Even for a relatively small number of defects $N_1$ in the crystal, say $N_1 \approx 1000$, all the expressions listed above become independent of $N_1$ and can be simplified:

$$<\Delta> = \frac{2SB_1}{r_0^3} N_0 \left[ 1 - e^{N_0} \sqrt{\pi N_0} \left( 1 - \text{Erf}(\sqrt{N_0}) \right) \right], \quad \hfill (C.44)$$
\[
< \Delta^2 > = \frac{S^2 B_2}{2r_0^6} N_0 \cdot \left[ 1 - N_0 - N_0^2 e^{N_0} \text{Ei}(-N_0) \right], \tag{C.45}
\]

\[
< \Delta^3 > = \frac{2S^3 B_3}{7r_0^9} N_0 \left[ 1 - \frac{6}{15} N_0 + \frac{4}{15} N_0^2 - \frac{8}{15} N_0^3 + \right.
\frac{8}{15} N_0^{7/2} e^{N_0} \sqrt{\pi} \left( 1 - \text{Erf}(\sqrt{N_0}) \right) \left. \right], \tag{C.46}
\]

\[
< \Delta^4 > = \frac{S^4 B_4}{5r_0^{12}} N_0 \left[ 1 - \frac{N_0}{4} + \frac{N_0^2}{12} - \frac{N_0^3}{24} + \frac{N_0^4}{24} + \right.
\frac{N_0^5 e^{N_0}}{24} \text{Ei}(-N_0) \right]. \tag{C.47}
\]

### 3D Case

The probability density function for the nearest neighbor in three dimensions has the following form:

\[
P(r) = \frac{4\pi \rho r^2 e^{-\frac{4}{3}\pi r^3}}{e^{-N_0} - e^{-N_1}}. \tag{C.48}
\]

The general form of the radial average is then given by

\[
< \Delta^n > = \frac{S^n A_n N_0^n}{r_0^n (e^{-N_0} - e^{-N_1})} \int_{N_0}^{N_1} e^{-t} dt. \tag{C.49}
\]

\[
< \Delta^2 > = \frac{S^2 A_2}{r_0^6} \cdot \frac{N_0}{e^{-N_0} - e^{-N_1}} \left[ e^{-N_0} - \frac{N_0}{N_1} e^{-N_1} + N_0 \left( \text{Ei}(-N_0) - \text{Ei}(-N_1) \right) \right] \tag{C.50}
\]

\[
< \Delta^3 > = \frac{S^3 A_3}{2r_0^9} \cdot \frac{N_0}{e^{-N_0} - e^{-N_1}} \left[ e^{-N_0} - N_0 e^{-N_0} + \frac{N_0^2}{N_1} e^{-N_1} - \frac{N_0^2}{N_1} e^{-N_1} + \frac{N_0^2}{N_1} \left( \text{Ei}(-N_1) - \text{Ei}(-N_0) \right) \right], \tag{C.51}
\]

\[
< \Delta^4 > = \frac{S^4 A_4}{3r_0^{12}} \cdot \frac{N_0}{e^{-N_0} - e^{-N_1}} \left[ e^{-N_0} \left( 1 - \frac{N_0}{2} + \frac{N_0^2}{2} \right) - \frac{N_0^3}{2N_1} \cdot e^{-N_1} \left( \frac{1}{2} - \frac{1}{2N_1} + \frac{1}{N_1^2} \right) + \right.
\frac{N_0^3}{2} \left( \text{Ei}(-N_0) - \text{Ei}(-N_1) \right) \right] \tag{C.52}
\]
Using the expression for the limiting values of the width, asymmetry, and kurtosis, one obtains:

\[
\frac{\sigma}{\sigma^*} = \sqrt{e^{-N_0} - \frac{N_0}{N_1} e^{-N_1} + N_0 \left( \text{Ei}(-N_0) - \text{Ei}(-N_1) \right) \over e^{-N_0} - e^{-N_1}},
\]

\( (C.53) \)

Figure C.3: The contribution from the first nearest neighbor to the total width of the inhomogenous line.

For a reasonable number of defects inside the crystal (e.g. \( N > 100 \)) this formula simplifies to

\[
\frac{\sigma}{\sigma^*} = \sqrt{1 + N_0 e^{N_0} \text{Ei}(-N_0)}.
\]

\( (C.54) \)

The Fig. C.3 demonstrates that for sufficiently small concentrations, when the number \( N_0 \) of defects excluded from the sphere of the radius \( r_0 \) around the emitter is small, the linewidth is determined by the nearest neighbor only. Similarly,

\[
\frac{\gamma}{\gamma^*} = \frac{1 - N_0 - e^{N_0} N^2_0 \text{Ei}(-N_0)}{(1 + N_0 e^{N_0} \text{Ei}(-N_0))^{3/2}},
\]

\( (C.55) \)

\[
\frac{\kappa}{\kappa^*} = \frac{1 - \frac{N_0}{2} + \frac{N^2_0}{2} + \frac{N^3_0}{3} e^{N_0} \text{Ei}(-N_0)}{(1 + N_0 e^{N_0} \text{Ei}(-N_0))^2},
\]

\( (C.56) \)

C.0.9 Scaling of Line Shape Parameters

The profile of inhomogenously broadened line is determined by the statistical properties of the spectral shift \( \Delta \). For an emitter surrounded by a number \( N \) of point-like defects in linearly elastic medium \( \Delta = \Delta(r_1) + \Delta(r_2) + \ldots + \Delta(r_N) \), see Figure C.4. Each term in this sum has the structure \( \Delta(r_k) = a_{ij} \epsilon_{ij}(r_1) \), where for point-like defects (monopoles, dipoles, or bi-dipoles as discussed in 3.2.2) the strain tensor \( \epsilon_{ij} \) has the form:

\[
\epsilon_{ij} = \frac{\Phi_{ij}(\theta, \phi)}{r^n},
\]

\( (C.57) \)
APPENDIX C. INHOMOGENEOUS BROADENING: MATHEMATICAL APPENDIX

Figure C.4: An emitter (two-level system) surrounded by randomly distributed point defects is coupled to the strain produced by the latter. The emitted photon has the frequency shifted by $\Delta$. The probability function of $\Delta$ is determined by the type of spatial distribution of the defects.

Therefore the total shift of the transition energy $\Delta$ is given by the sum

$$\Delta = \sum_{k=1}^{N} \frac{A(\theta_k, \phi_k)}{r_k^n}, \quad A(\theta, \phi) \equiv a_{ij} \Phi_{ij}(\theta, \phi). \quad (C.58)$$

The distance $r_k$ can be expressed in terms of the average distance between the defects $d$: $r_k = \xi_k d$. For a given density (either surface of bulk) $\rho$ the average distance is $d = \rho^{-1/D}$, where $D$ is the dimension of the problem. The expression for the total shift $\Delta$ (C.58) now can be rewritten

$$\Delta = \rho^{n/D} \sum_{k=1}^{N} \frac{A(\theta_k, \phi_k)}{\xi_k^n}. \quad (C.59)$$

The statistical properties of the total shift $\Delta$ are essentially determined by the sum. At low concentration of defects, when their positions $(\xi_k, \theta_k, \phi_k)$ can be considered uncorrelated, the sum does not change when one increases the density $\rho$. To see that one needs to realized that changing the density amounts to simply changing the scale (like zooming in or out of the picture) without affecting the statistical feature of the sum.

Thus, the shift $\Delta$ and all associated statistical parameters of it’s distribution: standard deviation of the histogram, asymmetry etc. scale with the density as $\rho^{n/D}$ at low concentration of defects.
Appendix D

Homogeneous Broadening:
Mathematical Appendix

In this section a brief analysis of the results of the work [33] is given. It is shown that the expressions for the shape of the zero-phonon line, as given in [33], can not be correct, most likely due to several typos. The corrected expressions have not yet been published, but the author of [33], V. Hizhnyakov, provided them in private correspondence and these corrected expressions are used in section 4.2 of this work.

The model for quadratic electron-phonon coupling, presented in [33], is solved in a non-perturbative manner and yields the expression for the spectral line-shape for absorption and luminescence valid for any temperature. A two-level system coupled to a single pseudo-local mode (PLM) is considered in this model. The frequencies of PLM are $\omega_1$ and $\omega_2$ for the initial and final states, respectively ($\Delta \equiv \omega_2 - \omega_1$). The PLM is coupled to the rest of the crystal and has the width $\Gamma$. According to [33], to obtain the line-shape of the zero-phonon line in the frequency domain $I(\omega)$ one needs to evaluate the Fourier transform of the function

$$F(t)e^{-\gamma_0 |t|} = \exp\left(-\frac{\gamma_0}{2} |t| - i\sigma\Delta(\bar{n} + 1)t + \frac{i\Delta(\bar{n} + 1)}{\lambda(1 + \alpha)} \ln[1 + \alpha - \alpha e^{-\lambda t}]\right),$$  \hspace{1cm} (D.1)

where the following abbreviations are used:

$$\bar{n} = \frac{1}{e^{\beta \omega_1} - 1}, \hspace{0.5cm} \beta = \frac{1}{k_B T}$$  \hspace{1cm} (D.2)

$$\lambda = \Gamma - \frac{i\Delta}{2} + \sqrt{\Gamma^2 - \Delta^2/4 - i\Gamma \Delta (2\bar{n} + 1)} = \Delta \mu$$  \hspace{1cm} (D.3)

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with an obvious definition of $\mu$

$$\mu \equiv \frac{\Gamma}{\Delta} - \frac{i}{2} + \sqrt{\frac{\Gamma^2}{\Delta^2} - \frac{1}{4} - \frac{i}{\Delta}(2\bar{n} + 1)} \quad (D.4)$$

Also,

$$\alpha = \frac{-i\bar{n}\Delta}{\lambda} = \frac{-i\bar{n}}{\mu} \quad (D.5)$$

and

$$\sigma = (\bar{n} + 1)\left(\frac{1}{1 + \alpha - \alpha e^{-\lambda t}} - 1\right) \quad (D.6)$$

The frequency domain line-shape $I(\omega)$ is given by the Fourier transform:

$$I(\omega) = \frac{1}{\pi \hbar} \text{Re} \left[ \int_0^{+\infty} e^{i\omega t} F(t) e^{-\frac{\gamma_0}{2} |t|} dt \right]. \quad (D.7)$$

For the integral to converge the function $F(t)e^{-\frac{\gamma_0}{2} |t|}$ must decrease at positive infinity. To avoid divergent logarithm in (D.1) the real part of $\lambda$ is assumed to be positive. Under this condition the asymptotic behavior of $F(t)e^{-\frac{\gamma_0}{2} |t|}$ is determined by the term

$$-\frac{\gamma_0 t}{2} - \frac{i\sigma \Delta (\bar{n} + 1) t}{1 + \alpha} = -\frac{\gamma_0 t}{2} \left(1 + 2i\sigma \frac{\Delta \bar{n} + 1}{\gamma_0 1 + \alpha}\right) \quad (D.8)$$

Taking into account that

$$\sigma(t \to \infty) \approx -\frac{(\bar{n} + 1)\alpha}{1 + \alpha} \quad (D.9)$$

the condition for the convergence can be written in the following way:

$$\text{Re} \left[ 1 - 2\frac{\Delta (\bar{n} + 1)^2}{\gamma_0 (1 + \alpha)^2} \alpha \right] > 0 \quad (D.10)$$

or, equivalently,

$$(\bar{n} + 1)^2 \text{Re} \left[ \frac{\alpha}{(1 + \alpha)^2} \right] < \frac{1}{2} \cdot \frac{\gamma_0}{\Delta} \quad (D.11)$$

The left side of this inequality is temperature dependent, therefore we have a constraint on the range of temperatures. Using the notation introduced above, the condition for convergence can be written like

$$\bar{n}(\bar{n} + 1)^2 \cdot \text{Re} \left[ \frac{\mu}{(\mu - i\bar{n})^2} \right] < \frac{1}{2} \cdot \frac{\gamma_0}{\Delta} \quad (D.12)$$

For the parameters given in the paper ($\Gamma = 1.0 \text{cm}^{-1}$, $\Delta = 1.5 \text{cm}^{-1}$, $\gamma_0 = 0.2 \div 0.3 \text{cm}^{-1}$, $\omega_1 = 10 \text{cm}^{-1}$)
the convergence condition is not satisfied for temperatures above \(5.8 \div 7.0\) K. The numerical evaluation of integral gives divergent results for the aforementioned temperatures. For the temperatures above 45 K the results are reasonable again in accordance with the Figure D.1.
Appendix E

Optical Saturation in Polarized Luminescence: Mathematical Appendix

The experimental set up discussed here is schematically shown in Figure E.1. For further analysis we will need formulas for the transverse electric and magnetic fields emitted by the laser, electric dipole, and magnetic dipole (see [36]):

\[ 
\mathbf{H} = \sqrt{\frac{\varepsilon_0}{\mu_0}} [\mathbf{k} \times \mathbf{E}] \left( = \frac{1}{c} [\mathbf{k} \times \mathbf{E}] \right) \text{for any transverse EM wave.} \tag{E.1} 
\]

EM radiation from an electric dipole is given by:

\[ 
\mathbf{E}_e = E(r) \left( \mathbf{p} - \mathbf{n}(\mathbf{n} \cdot \mathbf{p}) \right) = E(r) \mathbf{p}^\perp_n, \tag{E.2} 
\]

where \( E(r) = \sqrt{\frac{\mu_0}{\varepsilon_0}} \frac{ck^2e^{ikr}}{4\pi r} \) - spatial part of the electric field amplitude; \( \mathbf{p}^\perp_n \equiv \mathbf{p} - \mathbf{n}(\mathbf{n} \cdot \mathbf{p}) \) is the component of the electric dipole moment perpendicular to the unit vector \( \mathbf{n} \).

Magnetic dipole radiation has the following electric field in the direction \( \mathbf{n} \):

\[ 
\mathbf{E}_m = \frac{E(r)}{c} [\mathbf{m} \times \mathbf{n}], \tag{E.3} 
\]

As for the laser excitation, its polarization is determined by the direction of the electric field and is specified by a unit vector \( \mathbf{L}(\mathbf{L}||\mathbf{E}) \). Therefore, a unit vector in the direction of the incoming magnetic field is given by \( \mathbf{h} = [\mathbf{k} \times \mathbf{L}] \).
Figure E.1: Schematic representation of the experimental setup: optical center, possessing either electric dipole or magnetic dipole moment, is excited by laser radiation, coming in the direction $\mathbf{k}$. Polarization of the laser is specified by a unit vector $\mathbf{L}||\mathbf{E}$. Electromagnetic radiation emitted by the optical center is observed in the direction given by the unit vector $\mathbf{n}$. Detector D measures the incoming electric field. Analyzer is placed before the detector D and it lets through only the component of the electric field that is parallel to a unit vector $\mathbf{A}$. 
Measuring polarized luminescence from an optical center is a two-step process: First there is an absorption, then there is an emission. The power of EM radiation incident on the detector D is therefore proportional to either

$$P \propto (E_{\text{in}} \cdot p)^2 \cdot (E_{\text{out}} \cdot A)^2$$

electric dipole absorption \hspace{1cm} (E.4)

or

$$P \propto (H_{\text{in}} \cdot m)^2 \cdot (E_{\text{out}} \cdot A)^2$$

magnetic dipole absorption \hspace{1cm} (E.5)

When optical saturation effects in absorption are taken into account, the first factor in (E.4) and (E.5) should be replaced by a non-linear function $S((E_{\text{in}} \cdot p)^2)$ or $S((H_{\text{in}} \cdot m)^2)$. It should be noted that in (E.4) and (E.5) we have not specified the type of the emitted field $E_{\text{out}}$ (electric dipole or magnetic dipole). Using the unit vector $L$, which specifies the laser polarization, (E.4) and (E.5) can be rewritten in the following way

$$P \propto (L \cdot p)^2 \cdot (E_{\text{out}} \cdot A)^2$$

electric dipole absorption \hspace{1cm} (E.6)

$$P \propto ([k \times L] \cdot m)^2 \cdot (E_{\text{out}} \cdot A)^2$$

magnetic dipole absorption \hspace{1cm} (E.7)

Finally, when collecting a signal from a group of $N$ independent centers, the total signal collected will be given by the sum $P_\theta = \sum_{i=1}^{N} P_\theta^i$ of contribution from each center, assuming there are no coherent phenomena among the members of the group.

**E.0.10 Electric Dipole Absorption – Electric Dipole Emission**

When EM radiation from the optical center is due to the change in the electric dipole moment, the detected signal is proportional to

$$P \propto (L \cdot p)^2 \cdot (E_e \cdot A)^2.$$  \hspace{1cm} (E.8)

Using (E.2), we can write

$$E_e \cdot A \propto p_n^\perp \cdot A_p^\perp = p_n^\perp \cdot A_n^\perp = (p \cdot A) - (p \cdot n)(n \cdot A) = (A_n^\perp)_p^\|.$$  \hspace{1cm} (E.9)

Thus, the detected signal is proportional to

$$P \propto \left[ L_p^\| \right]^2 \cdot \left[ \left( A_n^\perp \right)_p^\| \right]^2.$$  \hspace{1cm} (E.10)
The orientation of the optical center is represented by a unit vector $d$, which is determined by the center’s axis of highest symmetry. When the orientation of the electric dipole moment is parallel to the orientation of the optical center, then corresponding emission is called $Z$ (or $\pi$) type and the emitted EM-wave is linearly polarized along the vector $d$. The other type of emission, called $XY$ (or $\sigma$), occurs when there are two dipole moments in the plane perpendicular to $d$ and they are 90 degrees phase shifted, yielding a circular polarized light. With this in mind we can consider four different situations:

1. **absorption $Z$ – emission $Z$**
   
   Since $p$ is parallel to $d$ both for emission and absorption we can rewrite the detected signal as
   \[
   P \propto L_{d}^\parallel \cdot (A_{n}^\perp)^{\parallel}_{d}^2. \tag{E.11}
   \]

2. **absorption $XY$ – emission $XY$**
   
   \[
   P \propto L_{d}^\perp \cdot (A_{n}^\perp)^{\perp}_{d}^2. \tag{E.12}
   \]

3. **absorption $Z$ – emission $XY$**
   
   \[
   P \propto L_{d}^\parallel \cdot (A_{n}^\perp)^{\perp}_{d}^2. \tag{E.13}
   \]

4. **absorption $XY$ – emission $Z$**
   
   \[
   P \propto L_{d}^\perp \cdot (A_{n}^\parallel)^{\parallel}_{d}^2. \tag{E.14}
   \]

Given a unit vector $d$, an arbitrary vector $V = \{V_x, V_y, V_z\}$ can be resolved into two mutually orthogonal components:

\[
V = V_{d}^\parallel + V_{d}^\perp. \tag{E.15}
\]
where

\[ V_d^\parallel = \mathbf{d}(\mathbf{d} \cdot \mathbf{V}) \] – parallel to \( \mathbf{d} \),

(E.16)

and

\[ V_d^\perp = \mathbf{V} - V_d^\parallel = \mathbf{V} - \mathbf{d}(\mathbf{d} \cdot \mathbf{V}) \] – perpendicular to \( \mathbf{d} \).

(E.17)

From the above expressions follows that

\[ [V_d^\parallel]^2 = (\mathbf{d} \cdot \mathbf{V})^2, \] 

(E.18)

and

\[ [V_d^\perp]^2 = V^2 - (\mathbf{d} \cdot \mathbf{V})^2. \]

(E.19)

The unit vector \( \mathbf{d} \), specifying the orientation of the defect, has the following components in the fixed (laboratory) coordinate system (see Figure E.1): \( \mathbf{d} = \{d_x, d_y, d_z\} \). When rotated by an angle \( \theta \) around the vertical axis, e.g. due to the rotation of the sample containing the optical center, its components become \( \mathbf{d}_\theta = \{d_x \cos \theta - d_y \sin \theta, d_x \sin \theta + d_y \cos \theta, d_z\} \). With this in mind we can summarize the signal from the detector as the function of sample’s rotation angle \( \theta \) in the table given below (\( \mathbf{a} \equiv \mathbf{A}_n^\perp \)):

<table>
<thead>
<tr>
<th>Abs–Em</th>
<th>( P_\theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-Z</td>
<td>( (\mathbf{d}<em>\theta \cdot \mathbf{L})^2(\mathbf{d}</em>\theta \cdot \mathbf{a})^2 )</td>
</tr>
<tr>
<td>XY-XY</td>
<td>((1 - (\mathbf{d}<em>\theta \cdot \mathbf{L})^2)(\mathbf{a}^2 - (\mathbf{d}</em>\theta \cdot \mathbf{a})^2))</td>
</tr>
<tr>
<td>Z-XY</td>
<td>((\mathbf{d}<em>\theta \cdot \mathbf{L})^2(\mathbf{a}^2 - (\mathbf{d}</em>\theta \cdot \mathbf{a})^2))</td>
</tr>
<tr>
<td>XY-Z</td>
<td>((1 - (\mathbf{d}<em>\theta \cdot \mathbf{L})^2)(\mathbf{d}</em>\theta \cdot \mathbf{a})^2)</td>
</tr>
</tbody>
</table>

In general, signal from the detector \( P_\theta \) as the function of the sample’s rotation angle \( \theta \) is then given by

<table>
<thead>
<tr>
<th>Abs–Em</th>
<th>Cross, \perp ( P_\theta )</th>
<th>Co, \parallel ( P_\theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-Z</td>
<td>( d_{\theta x}^2 I_{em}^{(1)}(\mathbf{d}, \theta) )</td>
<td>( d_{\theta y}^2 I_{em}^{(1)}(\mathbf{d}, \theta) )</td>
</tr>
<tr>
<td>XY-XY</td>
<td>((1 - d_{\theta x}^2) I_{em}^{(2)}(\mathbf{d}, \theta) ) ((1 - d_{\theta y}^2) I_{em}^{(2)}(\mathbf{d}, \theta) )</td>
<td></td>
</tr>
<tr>
<td>Z-XY</td>
<td>( d_{\theta x}^2 I_{em}^{(1)}(\mathbf{d}, \theta) )</td>
<td>( d_{\theta y}^2 I_{em}^{(1)}(\mathbf{d}, \theta) )</td>
</tr>
<tr>
<td>XY-Z</td>
<td>((1 - d_{\theta x}^2) I_{em}^{(1)}(\mathbf{d}, \theta) ) ((1 - d_{\theta y}^2) I_{em}^{(1)}(\mathbf{d}, \theta) )</td>
<td></td>
</tr>
</tbody>
</table>

As a side-note, when optical saturation effects are considered, the first factor in the table is replaced by some non-linear function of that factor. For example, instead of \( d_{\theta x}^2 I_{em}^{(1)}(\theta) \) one gets \( S\left(d_{\theta x}^2\right) I_{em}^{(1)}(\theta) \) for Z-Z transition.
So far an optical center has been modeled as a perfect dipole. As such it never absorbs radiation polarized in the direction perpendicular to the dipole moment. This is a case of perfectly anisotropic emitter. A slight imperfection can be modeled in the framework of classical dipole moments as follows: optical center is allowed to possess an additional, smaller in magnitude, dipole moment, \( \mathbf{p}' \), perpendicular to the main dipole moment, \( \mathbf{p} \). This will allow the absorption of radiation polarized perpendicular to the main dipole moment \( \mathbf{p} \). Quantitatively, the degree of isotropy can be described by the parameter \( \beta \), defined as the ratio of the probability to absorb the radiation perpendicular to the main dipole moment, \( \mathbf{p} \) to the probability to absorb the radiation parallel to \( \mathbf{p} \):

\[
\beta = \frac{\Gamma_{\perp}}{\Gamma_{\parallel}}, \quad \beta \in [0, 1]
\]  

(E.20)

Obviously, the dipole moment \( \mathbf{p}' \) will affect the emitted radiation. The signal on the detector will be proportional to

\[
I \propto \left[ \mathbf{L} \cdot (\mathbf{p} + \mathbf{p}') \right]^2 \cdot \left[ \mathbf{A} \cdot (\mathbf{E}_e + \mathbf{E}'_e) \right]^2 , \quad \mathbf{p}' \perp \mathbf{p} \text{ and } p'^2 = \beta p^2
\]  

(E.21)

Since \( \mathbf{p}' \perp \mathbf{p} \) and \( p'^2 = \beta p^2 \), for any vector \( \mathbf{V} \) the following relations hold:

\[
\left[ \mathbf{V} \cdot (\mathbf{p} + \mathbf{p}') \right]^2 = (\mathbf{V} \cdot \mathbf{p})^2 + \beta [V^2 - (\mathbf{V} \cdot \mathbf{p})^2] + 2(\mathbf{V} \cdot \mathbf{p})(\mathbf{V} \cdot \mathbf{p}').
\]  

(E.22)

When time evolution of the dipole vectors \( \mathbf{p} \) and \( \mathbf{p}' \) are not correlated, the last term in the previous expression disappears after a time averaging and it can be recast into the following form:

\[
\left[ \mathbf{V} \cdot (\mathbf{p} + \mathbf{p}') \right]^2 = (1 - \beta)(\mathbf{V} \cdot \mathbf{p})^2 + \beta V^2
\]  

(E.23)

Since the electric field radiated by an electric dipole \( \mathbf{p} \) in the direction \( \mathbf{n} \) is given by \( \mathbf{E} \propto \mathbf{p} - \mathbf{n}(\mathbf{p} \cdot \mathbf{n}) \), we can finally write the signal received by the detector \( I \) taking into account possible isotropy factor \( \beta \):

\[
I_\beta = \left[ (1 - \beta)(\mathbf{L} \cdot \mathbf{p})^2 + \beta \right] \cdot \left[ (1 - \beta)(\mathbf{a} \cdot \mathbf{p})^2 + a^2 \beta \right], \quad \mathbf{a} = \mathbf{A}_n \perp
\]  

(E.24)

It is reasonable to assume that in experiment when a small solid angle approximation can be made the analyzer is perpendicular to the direction of observation, i.e. \( \mathbf{A} \perp \mathbf{n} \) and therefore \( \mathbf{a} = \mathbf{A}, a^2 = A^2 = 1 \). This leads to a simplified expression for the signal from a single isotropic emitter with the main electric dipole moment \( \mathbf{p} \):

\[
I_\beta = \left[ (1 - \beta)(\mathbf{L} \cdot \mathbf{p})^2 + \beta \right] \cdot \left[ (1 - \beta)(\mathbf{A} \cdot \mathbf{p})^2 + \beta \right].
\]  

(E.25)
we can write

\[ L = \operatorname{When measuring polarized luminescence from emitters, two polarizations of the incident laser radiation are\]

arrives at:

\[ I_\beta = (1 - \beta)^2 I_0 + \beta (1 - \beta) F + \beta^2, \quad \text{(E.26)} \]

where \( I_0 \equiv (\mathbf{L} \cdot \mathbf{p})^2 \cdot (\mathbf{A} \cdot \mathbf{p})^2 \) is the signal from a purely anisotropic emitter \((\beta = 0)\); \( F \equiv (\mathbf{L} \cdot \mathbf{p})^2 + (\mathbf{A} \cdot \mathbf{p})^2 \).

When measuring polarized luminescence from emitters, two polarizations of the incident laser radiation are of interest: co-polarized, when \( \mathbf{L} \parallel \mathbf{A} \), and cross-polarized, when \( \mathbf{L} \perp \mathbf{A} \). For these special orientations of \( \mathbf{L} \) we can write

\[ I_\beta^\parallel = (1 - \beta)^2 (\mathbf{A} \cdot \mathbf{p})^4 + 2\beta (1 - \beta) (\mathbf{A} \cdot \mathbf{p})^2 + \beta^2 = (1 - \beta)^2 I_0^\parallel + \beta (1 - \beta) F^\parallel + \beta^2, \quad \text{(E.27)} \]

and

\[ I_\beta^\perp = (1 - \beta)^2 \left( (\mathbf{A} \cdot \mathbf{p})^2 - (\mathbf{A} \cdot \mathbf{p})^4 \right) + \beta = (1 - \beta)^2 I_0^\perp + \beta (1 - \beta) F^\perp + \beta^2, \quad I^\perp = F^\parallel / 2 - I_0^\parallel, \quad F^\perp = 1. \quad \text{(E.28)} \]

To get the last expression we used the fact that \( (\mathbf{L} \cdot \mathbf{p})^2 + (\mathbf{A} \cdot \mathbf{p})^2 = 1 \) for \( \mathbf{L} \perp \mathbf{A} \) and the unit vector \( \mathbf{p} \).

The expressions for the co- and cross-polarized signal, as given above, are valid for a single emitter. When a group of \( N \) such emitters is given with varying orientations, one has to sum over all emitters:

\[ I_\beta = \sum_{i=1}^{N} I^{(i)}_\beta. \quad \text{(E.29)} \]

For completeness the expressions for \( I_\beta^\parallel + I_\beta^\perp \) and \( I_\beta^\parallel - I_\beta^\perp \), used in calculating the polarization \( P_\theta = (I_\beta^\parallel - I_\beta^\perp) / (I_\beta^\parallel + I_\beta^\perp) \) are given below:

\[ I_\beta^\parallel + I_\beta^\perp = (1 + \beta)[\beta + (1 - \beta) \cdot (\mathbf{A} \cdot \mathbf{p})^2] = (1 + \beta) \left[ \beta + (1 - \beta) \cdot \frac{F^\parallel}{2} \right], \quad \text{(E.30)} \]

\[ I_\beta^\parallel - I_\beta^\perp = 2(1 - \beta)^2 (\mathbf{A} \cdot \mathbf{p})^4 - [3\beta^2 - 4\beta + 1] (\mathbf{A} \cdot \mathbf{p})^2 - \beta (1 - \beta). \quad \text{(E.31)} \]

or

\[ I_\beta^\parallel - I_\beta^\perp = 2(1 - \beta)^2 I_0^\parallel - [3\beta^2 - 4\beta + 1] \cdot \frac{F^\parallel}{2} - \beta (1 - \beta). \quad \text{(E.32)} \]

We further consider three groups of optical centers, with their orientations conforming to the symmetry of the cubic lattice and given by the following unit vectors:

1. \( \mathbf{d}^{100} = \{1, 0, 0\}, \mathbf{d}^{010} = \{0, 1, 0\}, \mathbf{d}^{001} = \{0, 0, 1\} \).

2. \( \mathbf{d}^{110} = \frac{1}{\sqrt{2}} \{1, 1, 0\}, \mathbf{d}^{101} = \frac{1}{\sqrt{2}} \{1, 0, 1\}, \mathbf{d}^{011} = \frac{1}{\sqrt{2}} \{0, 1, 1\}, \mathbf{d}^{11-10} = \frac{1}{\sqrt{2}} \{1, -1, 0\}, \mathbf{d}^{01-1} = \frac{1}{\sqrt{2}} \{0, 1, -1\}, \)
\[ d^{10-1} = \frac{1}{\sqrt{3}} \{1, 0, -1\}. \]

3. \( d^{111} = \frac{1}{\sqrt{3}} \{1, 1, 1\}, d^{-11-1} = \frac{1}{\sqrt{3}} \{-1, -1, 1\}, d^{1-1-1} = \frac{1}{\sqrt{3}} \{-1, 1, -1\}. \]

When rotated around \( z \)-axis, the \( x \) and \( y \) components mix and vector components take form given in the Table E.1

Within each group all directions are equivalent and the total detected signal \( I_\theta \) is the sum of contribution from all optical centers. For example, for the first group the resulting signal is given in the Table E.2. Those expressions can be cast into a different form, see Table E.3. In a similar way we obtain the total collected signal for the second and third group of defects, Tables E.4 and E.5.

The effect of the isotropy of the emitters on the collected signal can be expressed using the modified version of the formula 5.3

\[
S_\beta = \sum_{i=1}^{N} [(1 - \beta)(D_i V)^2 + \beta] \cdot [(1 - \beta)(D_i a)^2 + \beta],
\]

where the first factor corresponds to the absorption, and the second corresponds to the emission probability.

For Z-type absorption/emission the probability \((DV)^2\) is replaced with \(\beta + (1 - \beta)(DV)^2\), while for XY-type transitions it is \(1 - (1 - \beta)(DV)^2\).
$$d_\theta = \begin{bmatrix} d_{\theta x} \\ d_{\theta y} \\ d_{\theta z} \end{bmatrix}$$

Table E.1: Components of the rotated defect vectors $d$ for various group of centers.
TABLE E.2: SIGNAL FROM $\langle 100 \rangle$ GROUP OF CENTERS.

<table>
<thead>
<tr>
<th>Abs–Em</th>
<th>Cross, $\perp P_0$</th>
<th>Co, $\parallel P_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z-Z$</td>
<td>$2 \cos^2 \theta \sin^2 \theta$</td>
<td>$\sin^4 \theta + \cos^4 \theta$</td>
</tr>
<tr>
<td>$XY-XY$</td>
<td>$1 + 2 \sin^4 \theta \cos^2 \theta$</td>
<td>$1 + \cos^4 \theta + \sin^4 \theta$</td>
</tr>
<tr>
<td>$Z-XY$</td>
<td>$\cos^4 \theta + \sin^4 \theta$</td>
<td>$2 \cos^2 \theta \sin^2 \theta$</td>
</tr>
<tr>
<td>$XY-Z$</td>
<td>$\cos^4 \theta + \sin^4 \theta$</td>
<td>$2 \sin^2 \theta \cos^2 \theta$</td>
</tr>
</tbody>
</table>

Table E.3: Signal from $\langle 100 \rangle$ group of centers. Version II

<table>
<thead>
<tr>
<th>Abs–Em</th>
<th>Cross, $\perp P_0$</th>
<th>Co, $\parallel P_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z-Z$</td>
<td>$\frac{1}{4}(1 - \cos 4\theta)$</td>
<td>$\frac{1}{4}(3 + \cos 4\theta)$</td>
</tr>
<tr>
<td>$XY-XY$</td>
<td>$\frac{1}{4}(5 - \cos 4\theta)$</td>
<td>$\frac{1}{4}(7 + \cos 4\theta)$</td>
</tr>
<tr>
<td>$Z-XY$</td>
<td>$\frac{1}{4}(3 + \cos 4\theta)$</td>
<td>$\frac{1}{4}(1 - \cos 4\theta)$</td>
</tr>
<tr>
<td>$XY-Z$</td>
<td>$\frac{1}{4}(3 + \cos 4\theta)$</td>
<td>$\frac{1}{4}(1 - \cos 4\theta)$</td>
</tr>
</tbody>
</table>

Table E.4: Signal from $\langle 110 \rangle$ group of centers

<table>
<thead>
<tr>
<th>Abs–Em</th>
<th>Cross, $\perp P_0$</th>
<th>Co, $\parallel P_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z-Z$</td>
<td>$\frac{1}{16}(3 + \cos 4\theta)$</td>
<td>$\frac{1}{16}(3 - \cos 4\theta)$</td>
</tr>
<tr>
<td>$XY-XY$</td>
<td>$\frac{1}{16}(19 + \cos 4\theta)$</td>
<td>$\frac{1}{16}(25 - \cos 4\theta)$</td>
</tr>
<tr>
<td>$Z-XY$</td>
<td>$\frac{1}{16}(13 - \cos 4\theta)$</td>
<td>$\frac{1}{16}(7 + \cos 4\theta)$</td>
</tr>
<tr>
<td>$XY-Z$</td>
<td>$\frac{1}{16}(13 - \cos 4\theta)$</td>
<td>$\frac{1}{16}(7 + \cos 4\theta)$</td>
</tr>
</tbody>
</table>

Table E.5: Signal from $\langle 111 \rangle$ group of centers
Appendix F

Optical Saturation in Polarized Luminescence: Azimuthal Plots

F.0.12 MD-MD

In this section azimuthal plots for the photoluminescence signal in backscattering geometry, shown in the Figure 5.13, are given for the magnetic dipole absorption and magnetic dipole emission case (MD-MD).
### Figure F.1: Calculated azimuthal dependence of co-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.2: Calculated azimuthal dependence of cross-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.3: Calculated degree of polarization of PL signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $<100>$, $<110>$, $<111>$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.4: Calculated azimuthal dependence of co-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.5: Calculated azimuthal dependence of cross-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.6: Calculated polarization of PL signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
F.0.13 ED-MD

In this section azimuthal plots for the photoluminescence signal in backscattering geometry, shown in the Figure 5.13, are given for the electric dipole absorption and magnetic dipole emission case (ED-MD).
Figure F.7: Calculated azimuthal dependence of co-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.8: Calculated azimuthal dependence of **cross-polarized** photoluminescence signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.9: Calculated **degree of polarization** of PL signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.10: Calculated azimuthal dependence of co-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.11: Calculated azimuthal dependence of cross-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.12: Calculated polarization of PL signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
F.0.14 MD-ED

In this section azimuthal plots for the photoluminescence signal in backscattering geometry, shown in the Figure 5.13, are given for the magnetic dipole absorption and electric dipole emission case (MD-ED).
APPENDIX F. OPTICAL SATURATION IN POLARIZED LUMINESCENCE: AZIMUTHAL PLOTS

Figure F.13: Calculated azimuthal dependence of co-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.14: Calculated azimuthal dependence of cross-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.15: Calculated degree of polarization of PL signal collected in backscattering geometry. Gaussian beam excitation is assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.16: Calculated azimuthal dependence of co-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
APPENDIX F. OPTICAL SATURATION IN POLARIZED LUMINESCENCE: AZIMUTHAL PLOTS

Figure F.17: Calculated azimuthal dependence of cross-polarized photoluminescence signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
Figure F.18: Calculated polarization of PL signal collected in backscattering geometry. Gaussian beam excitation and 10 percent isotropy are assumed. Blue (darker) curves correspond to the case of no optical saturation, red (lighter) is for optical saturation $\gamma = 10$. Columns left to right correspond to $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ defect group. Rows top to bottom correspond to Z-Z, XY-XY, Z-XY, XY-Z type of the transitions.
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Bibliography


