Conformational heterogeneity in silica: homogeneous and inhomogeneous linewidths of Oxygen Deficient Centres

Michele D’Amico

*Ph.D Thesis*

(S.S.D FIS/07)

Palermo, Febbraio 2009

Supervisore: Prof. Maurizio Leone
Coordinatore: Prof. Antonio Cupane
(…) It has been usual to speak of the colour so exhibited as displayed by reflection. As however the cause now appears to be so very different from ordinary reflection, it seems objectionable to continue to use that term without qualification, and I shall accordingly speak of the phenomenon as dispersive reflection*. (…) 

*I confess I do not like this term. I am almost inclined to coin a word, and call the appearance fluorescence, from fluor-spar, as the analogous term opalescence was derived from the name of a mineral.

George Gabriel Stokes

“On the change of refrangibility of light”

Phil. Trans. of the Royal Society of London 142, (1852), 463
Contents

Abstract 1

1 Silica and Oxygen Deficient Centres 3
  1.1 Silica ................................................................. 3
  1.2 Oxygen Deficient Centres .......................................... 6
    1.2.1 ODC(II): isoelectronic defects ............................... 7
    1.2.2 ODC(II): the structural model ............................... 9
  1.3 Estimation of the heterogeneity .................................. 11
  1.4 Heterogeneity of ODC(II) in silica .............................. 16

2 Theoretical description of point defects in a solid matrix 19
  2.1 Configurational coordinates model .............................. 20
  2.2 Absorption and luminescence processes ......................... 24

3 Experimental equipment and materials 31
  3.1 Experimental equipment: time resolved luminescence ............ 31
    3.1.1 Excitation source: tunable laser ......................... 31
    3.1.2 Detection system: the CCD camera ......................... 34
    3.1.3 Low temperature equipment ................................. 36
    3.1.4 Methods .................................................... 37
  3.2 Materials ....................................................... 38

4 Luminescence activities of point defects in crystals and glasses:
  quantification of heterogeneity 43
  4.1 Modeling the heterogeneity in silica .......................... 43
  4.2 Fluorescence in silica and in crystalline lithium fluoride .... 46
    4.2.1 Experimental results ..................................... 46
Abstract

From ages sapphire, ruby, quartz and other crystals were chosen for great beauty of their colour, and were used as precious objects to decorate jewels, rings and so on. Trickly, the secret of crystals beauty resides also in their imperfections. Indeed, a perfect crystal is in general transparent to the visible light and it becomes coloured only for the presence of impurity atoms or other matrix defects. The study of these optical properties was, and remains today, one of the most fascinating subjects of the physics of solid state. To add more interest to this matter it is important to remember the recent growth of solid state lasing based on doped crystal as active medium.

On the other side, amorphous materials were used in the past for their simple shape adaptability and for their natural abundance. In particular, the glass of silicon dioxide (silica) was used in a diffuse way to produces bottles, glasses, bowls and so on and it was early discovered the possibility of colouring the glass, doping it with various impurities as iron, copper, lead to create, for example, very beautiful coloured windows. Nowadays, the presence of impurities, and more in general of point defects in silicon dioxide, is a fundamental issue in technological and scientific fields. Indeed, silica is a wide used base material for lenses, optical fibres, filters and transistors where defects can compromise (or optimize) their performances. From viewpoint of solid state physics the study of physical properties of silica as model of amorphous materials is an interesting issue since several decades, leaving until now still unresolved and debated questions.

Summing up, the physics of colour centre in solids is a fascinating matter of great interest and this PhD research work has the aim of studying more in detail the effect of heterogeneity on the optical properties of colour centres in a solid amorphous matrix. Indeed, until now the concept of heterogeneity has been investigated only from a general point of view, and the real spectral extent to the optical activity of colour centres in a glass was not evidenced. In this work, using a particular experimental approach to the problem and doing physical hypotheses on the effects of different defects’ environments of the glass matrix, we obtain for the first time a numerical estimation of inhomogeneous and homogeneous widths for a particular kind of point defects in silica, the Oxygen Deficient Centers of second type, or briefly ODC(II).
The content of this work is so organized:

• The main general features of silica, point defects and the optical activity of the ODC(II) are briefly reviewed in chapter 1. Attention is focused on the state of the art of the current knowledge on heterogeneity and its effects on point defects.

• In chapter 2 the basic theoretical background of the physics of colour centres in a crystal is presented.

• In chapter 3 we describe the experimental equipment used in our time resolved luminescence setup, the samples chosen for our analysis and the methods used to extract information from experimental data.

• In chapter 4 we introduce our main hypothesis to model the effects of an amorphous glass matrix. Experimental results found on two peculiar luminescence bands of ODC(II) in comparison with defects in crystalline materials are also shown.

• In chapter 5 we describe an experimental investigation of the isoelectronic series of silicon, germanium and tin ODC(II) point defects. The model developed in chapter 4 is applied to find out the effect of the central atom on the degree of inhomogeneity experienced by these defects.

• In chapter 6 we study the inhomogeneous and homogeneous features of induced ODC(II) in comparison with as-grown point defects by analyzing it in the frame of the theoretical model of chapter 4. In particular, are described results on electron induced Si-ODC(II) and on neutron and γ-rays induced defects, in the first and in the second section, respectively.

• In chapter 7 we extend our study on time resolved luminescence of Ge-ODC(II) taking into account the effect of different excitation energies on the related absorption band.

• The final chapter is dedicated to resuming the conclusions of our results and to discuss about perspectives.

Experimental results found during the PhD course and presented in this thesis have been published (or accepted for publication) on scientific journals specialized on solid state physics. A complete list is reported at the end of this work in the Scientific Activity section.
Chapter 1
Silica and Oxygen Deficient Centres

In this chapter we briefly introduce the properties of amorphous silicon dioxide (silica) and we review a particular class of related point defects, due to an oxygen deficiency of the material. Attention is also paid on the issue of heterogeneity in solid matrix and in particular we discuss if and how point defects can be considered as a probe of conformational heterogeneity in silica.

1.1 Silica

Silicon dioxide (SiO$_2$) can be found in two variants, quartz and silica which are the most abundant crystalline and amorphous forms, respectively. Quartz and silica show the same stoichiometry and the same geometrical arrangement as the inner and fundamental structure: a geometrical tetrahedron constituted by a silicon atom (in the centre) linked to four oxygen atoms (in the four corners) by strong covalent bonds. The crystalline material is formed when different tetrahedra share a corner respecting translational and symmetrical rules (quartz). The amorphous form, instead, is created when there is a non-regular positioning of tetrahedra with angles and bond lengths distributed throughout the material (silica). The thermodynamics of the creation process of silicon dioxide guides the formation of amorphous or crystalline forms; indeed, when the system is left free to relax from the high temperature melt of the constituents (silicon and oxygen atoms) with a slow cooling rate, an almost perfect packing with minimum distances and thus maximum den-
1. Silica and Oxygen Deficient Centres

Silica (2.65 g/cm$^3$) is possible and crystalline quartz is formed. On the other hand, when the melt is cooled rapidly the system is frozen at the “liquid” distribution of tetrahedra proper of the high temperature, and amorphous silica with lower density (2.20 g/cm$^3$) is obtained. Two main methods of production of silica exist: fusion of natural quartz powders or synthetic creation from oxidation of SiCl$_4$ vapors in flame.

Each kind of commercial silica can be inserted in a traditional classification which discriminates it for method of synthesis and impurity content.

- **Type I (Natural dry)**: produced from natural quartz powder, fused with an electric arc in an inert atmosphere. This type of silica features a relatively low (of the order of $\sim 10$ parts per million (ppm) in weight) concentrations of Si-OH impurities (dry silica). Usually it also contains more of 1 ppm of extrinsic impurities, due to the original content in the quartz.

- **Type II (Natural wet)**: the properties are similar to natural dry but the fusion in a $H_2/O_2$ flame causes a higher concentration of Si-OH groups (100 ppm) than in dry silica.

- **Type III (Synthetic wet)**: synthesized by oxidation of SiCl$_4$ in a $H_2/O_2$ flame. This technique gives silica materials with high content of Si–OH and very low presence of impurities.

- **Type IV (Synthetic dry)**: this kind is produced from SiCl$_4$ compound oxidized in a water-free-plasma so as to obtain low concentration of Si-OH. This silica, usually, shows high concentrations of chlorine ([Cl] $\sim 100$ ppm).

Adding to these traditional methods other techniques were recently developed: vapor axial deposition, sputtering, chemical deposition and Sol-Gel synthesis [1, 2]. In particular, this last technique ensures a precise control of dopants in silica and high reproducibility of production process, although it is not used for commercial applications [3–5]. The synthesis of undoped sol-gel silica starts from an aqueous solution of alkoxides like silicon tetramethoxide (TMOS) and silicon tetraethoxide (TEOS). This solution of colloidal solid particles after condensation reaches the gel phase with a network of colloids which span the entire volume. This highly porous gel state is characterized by considerable quantity of solvent inside the pores [4]. Two methods for extracting the solvent are available: i) the sample is kept at room temperature to dry slowly (evaporation) and the material so obtained (xerogel) shows a density close to silica and a macroscopic dimension smaller with respect to the initial
one. ii) In the second method, the gel is heated at high temperature, greater than critical temperature of the solvent, to extract it without boiling until a very porous system (aerogel) with lower density with respect to initial gel state is obtained. A final thermal treatment is done to eliminate the porousness (densification) and to obtain a glassy silica sample. In a xerogel it is done by increasing the temperature up to 900-1000 °C slowly so as to avoid the boiling of the residual solvent and possible consequent cracking of sample; in an aerogel (virtually solvent free) the temperature can reaches higher values in less time. If doped silica is required it is possible to incorporate dopant atoms in the initial aqueous solution, or by mixing the undoped solution with another one obtained by alkoxides of the impurity atoms.

Anyway, independently on the production method and on the type of silica, imperfections of the matrix can grow and they are usually called point defects, because they are localized at most on few tetrahedra. Although quartz and silica have the same short range order as corner sharing SiO$_4$ tetrahedra, the glassy state, besides introducing isotropy and inhomogeneity, provides new structural degrees of freedom that allow the formation of defects peculiar to the amorphous form. In this thesis we perform measurements mainly on Type I and IV silica, since our aim is the study of a particular class of point defects which form mainly on dry materials.

Silica is a fundamental technological material, because of its optical and electrical properties in its wide uses as optical component, as insulators in Metal Oxide Semiconductor transistor, and for guiding or processing light signals (optical fibre and Bragg grating) [1, 2, 6]. It was also hypothesized, and currently investigated, the use of silica glass as container for nuclear waste. Indeed, SiO$_2$ and relate compounds has good mechanical strength and thermal shock resistance and it is possible the growth of glasses at low temperature (1000 °C), thanks to Sol-Gel method of synthesis [7–9]. More in particular, the silica aerogels are widely recognised as precursor materials which can be converted into vitreous silica by short duration treatment at low temperature. The large pore volume of the silica aerogel is used as a sponge to incorporate chemical species [10].

In all these fields, normal creation processes of fusion from quartz and/or chemical synthesis and, moreover, ultraviolet (UV), electrons, neutrons or γ-ray irradiation can create point defects inside the matrix, which affect positively, or make worse, the optical or electric features of silica. For these reasons the study of properties of point defects in irradiated and in as-grown silica is a fundamental technological issue [1, 2]. Moreover, from the general point of view of solid state physics, the comparison be-
tween the properties of colour centres grown during the production steps in an out
of equilibrium condition (freezing from a melt state) and the same kind as defects
induced by irradiation process is an argument of considerable interest, especially con-
cerning the understanding of generation mechanisms, that is the distinction between
two main generation processes of defects: i) taking place in random matrix positions,
ii) occurring preferentially at precursor sites (e.g. strained bonds, presence of near
impurities, other point defects) [6, 11].

Summing up, the physics of colour centres embedded in an amorphous matrix is
a fundamental scientific problem which poses several unanswered questions, which
can be resumed as follows [1, 2, 6, 12, 13]:

- Identification of structural models and characterization of spectroscopic fea-
tures of colour centres, especially those defects which contribute to absorption
in the ultraviolet region (5–8 eV);

- Understanding the radiation hardness of crystalline and amorphous SiO$_2$
  in
correlation also with formation and stability (thermal or temporal) of defects;

- Comprehension of the influence of heterogeneity of glassy state in formation of
defects and modifying their spectroscopic properties;

- Finding out the role of small molecules (hydrogen, water, oxygen, chlorine and
  fluorine) in changing the physical properties both when they are linked to the
matrix and when they are diffusing.

This Thesis tries to partially overwhelm the lack of knowledge in the third point
of this list, that is the effect of conformational heterogeneity in shaping the features
of point defects in silica.

1.2 Oxygen Deficient Centres

The defects due to a local sub-stoichiometry of oxygen in the material are named
Oxygen Deficient Centres (ODC) and they are responsible of the index of refraction
change under ultraviolet (UV) light exposure, which is used to create optical Bragg
gratings in silica fibres [2, 13, 14].! The intrinsic ODCs (thus do not due to impurity
atoms in the material) are mainly three: the ODC(I), the E’-centre and the ODC(II).

The ODC(I) is a diamagnetic defect associated with an absorption band centred
at $\sim$7.6 eV (named $E$-band). Strong experimental results corroborate the neutral
relaxed oxygen vacancy (covalent bond between two silicon atoms) as geometrical structure of ODC(I) [15].

The E’-centre is a paramagnetic defect experimental detected by an absorption band centred at $\sim 5.8$ eV and an EPR signal associated with an electron in a $sp^3$ orbital of a silicon atom linked to three oxygen atoms [16]. From the viewpoint of heterogeneity in silica the EPR signal of E’-centre is important because its lineshape was successfully described by simulation only using an inhomogeneous broadening of the g-factor and the hyperfine interactions. These distributions take into account the effect of the dispersion of geometrical features in silica [17].

The last point defect related to oxygen deficiency is the ODC(II), whose heterogeneous properties are the main subject of this PhD thesis. It is a peculiar defect of the amorphous phase of SiO$_2$ and it has never been observed in the crystalline form$^1$ [2, 18], thus being an interesting model system to investigate the characteristic properties of defects in disordered materials with respect to crystalline ones.

### 1.2.1 ODC(II): isoelectronic defects

The ODC(II) exists both as an intrinsic defect related to silicon atom (Si-ODC(II)) and in other two extrinsic varieties related to the impurity content of germanium (Ge-ODC(II)) and tin (Sn-ODC(II)) atoms. Si, Ge and Sn-ODCs(II), due to their isoelectronic outer valence shell ($ns^2 np^2$ with $n=3$, 4 and 5 respectively), feature similar optical activities (e.g. emission and absorption bands) whereas other parameters (e.g. ISC rates and decay lifetimes) progressively vary along the isoelectronic series, reflecting the different atomic numbers.

Specifically, ODCs(II) are responsible of an intense optical activity in the Vis-UV range: the silicon variant of ODC(II) mainly gives rise to a broad nearly-gaussian optical absorption (OA) band centred at $\sim 5.0$ eV, assigned to the transition between the ground electronic singlet state ($S_0$) and the first excited singlet ($S_1$) one (see figure 1.1). This absorption excites a fast (lifetime in the ns range) emission band centred at $\sim 4.4$ eV, assigned to the inverse $S_1 \rightarrow S_0$ transition [18, 19]. In general a fast luminescence related to a dipole and spin allowed transition is indicated with the term fluorescence. Due to spin-orbit coupling of $S_1$ with the first excited triplet state ($T_1$), at $T>150$ K, it is possible also to populate the $T_1$ state from $S_1$ by

$^1$The signal of intrinsic ODC(II) has been observed in quartz heavily irradiated with neutrons or ions. In this case the presence of defects is associated with the amorphous zones created by bombardment which result embedded in the crystalline material.
1. Silica and Oxygen Deficient Centres

Figure 1.1: General scheme of main electronic levels for oxygen deficient centres of the second type. With solid arrows are indicate the radiative transition in absorption and luminescence. With dashed arrow is indicates the ISC non-radiative transition.

a phonon assisted process named inter-system crossing (ISC) as indicated with a dashed arrow in figure 1.1. The subsequent radiative decay from $T_1$ towards $S_0$ gives rise to an additional PL emission centred at $\sim 2.7$ eV. The lifetime of this band is slow (in the range of ms) due to the forbidden spin selection rules for the $T_1\rightarrow S_0$ transition [18, 20]. In general, a slow luminescence related to a forbidden transition is indicated with the term phosphorescence.

The corresponding bands for Ge-ODC(II) are centred at $\sim 5.1$ eV (OA), the fluorescence at $\sim 4.3$ eV and the phosphorescence at $\sim 3.1$ eV (active at $T>100$ K) [1, 18, 21, 22]. In particular, these defects are currently associated with the variation of refraction index in fibre Bragg gratings after UV writing [1]. Finally, for Sn-ODC(II) the absorption, fluorescence and phosphorescence are centred respectively at $\sim 4.9$, $\sim 4.2$ and $\sim 3.1$ eV (ISC active at $T>50$ K)[23].

For extrinsic defects on germanium and tin it is also possible to populate the $T_1$ state directly from the ground state $S_0$ by exciting with photons of $\sim 3.7$ eV energy. Because of different spin multiplicity of the involved electronic states, this process features a very low absorption cross section and bypasses the ISC channel giving rise to the same $3.1$ eV phosphorescence band independently from the temperature of the sample and with the same lifetime as the $S_0 \rightarrow S_1 \sim T_1 \rightarrow S_0$ process [18, 24]. For Si-ODC(II) the direct excitation of triplet band is very difficult to observe because of a very low absorption cross section according to the phosphorescence lifetime which is
1.2. Oxygen Deficient Centres

Table 1.1: Main UV transitions for isoelectronic ODC(II) defects: energy difference for optical absorption, subsequent singlet and triplet luminescence and related lifetimes.

<table>
<thead>
<tr>
<th>ODC(II)</th>
<th>$S_0 \rightarrow S_1$ [eV]</th>
<th>$S_1 \rightarrow S_0$ [eV]</th>
<th>$\tau_S$ [ns]</th>
<th>$S_0 \rightarrow T_1$ [eV]</th>
<th>$T_1 \rightarrow S_0$ [eV]</th>
<th>$\tau_T$ [$\mu$s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>5.02</td>
<td>4.45</td>
<td>4</td>
<td>3.3</td>
<td>2.75</td>
<td>10000</td>
</tr>
<tr>
<td>Ge</td>
<td>5.17</td>
<td>4.35</td>
<td>8</td>
<td>3.7</td>
<td>3.15</td>
<td>100</td>
</tr>
<tr>
<td>Sn</td>
<td>4.95</td>
<td>4.25</td>
<td>9</td>
<td>3.7</td>
<td>3.10</td>
<td>10</td>
</tr>
</tbody>
</table>

two order of magnitude greater than the germanium ODC(II). Only in few works this directly excited phosphorescence band was observed (for example in [25]). Table 1.1 resumes the absorption energy positions, luminescence ones and relative lifetimes for all optical activities in the isoelectronic ODC(II) series.

1.2.2 ODC(II): the structural model

The most accepted structural model for ODC(II) defects consists in a twofold coordinated atom (=X••), where X can be either a Si, a Ge or a Sn atom, and the symbol •• represents an electron lone pair localized on the X atom [2, 18, 19, 26, 27]. Towards the two fold coordinated model exists several experimental evidences:

- the luminescence polarization data are consistent with a local symmetry being $C_{2v}$, that is, using the well known group theory notation, a symmetry for rotation of a $\pi$ angle around a vertical principal axis and for reflection about a vertical plane passing through this axis [18];

- based on the EPR analysis (the hydrogen hyperfine splitting and the g-factor) of sample prepared by isotopic substitution of $^{28}$Si with $^{29}$Si, the H(I) centre was identified [28, 29] as a dangling bond silicon atom linked to two oxygen and a hydrogen atoms. Experimental results [18, 28, 29] have shown a direct correlation between the decreasing of the optical activity of intrinsic ODC(II) and the increasing of the EPR signal of this paramagnetic H(I) centres. It was concluded that the diamagnetic precursors of the surface H(I) centres are two fold coordinated silicon atoms following to the reaction with atomic hydrogen (see figure below) and thus corroborating the model of ODC(II) as a divalent
1. Silica and Oxygen Deficient Centres

- another proof for the divalent atom model was given by the study of the phosphorescence related to the $T_1 \rightarrow S_0$ transition in the isoelectronic ODC(II) series. Indeed, the associated decay time depends on the spin-orbit coupling between first singlet and triplet electronic excited orbitals. The coupling strength increases with the atomic number $Z$ of the constituent atoms, a phenomenon known as the heavy atom effect [30], because only heavy atoms (largest $Z$ number) significantly contribute to spin-orbit coupling. For ODCs(II), thought in the isoelectronic two-fold-coordinated model, only Si, Ge and Sn atoms are important and a quantitative relation between the atomic spin-orbit coupling constants $\xi$ of the valence $p$ orbitals, and the luminescence radiative lifetime $\tau$ can be obtained [18, 31]:

$$\frac{1}{\tau} \propto E^3 \xi^2$$  \hspace{1cm} (1.1)

where $E$ is the energy difference between $T_1$ and $S_0$ levels. The agreement of Eq. (1.1) with experimental data is very good [31] strongly confirming the divalent model.

However, the structure of Si-ODC(II) is still debated at the moment [2, 18, 32], because it has been proposed an alternative model of this defect as an unrelaxed neutral oxygen vacancy between two silicon atoms ($\equiv$Si-Si$\equiv$)\(^2\) [33, 34] which explains experimental results on the correlation between ODC(II) and $E'$-centres. Indeed, in oxygen deficient silica samples where the OA band of ODC(II) is more intense, it was evidenced the formation of higher concentrations of $E'$-centres under $\gamma$-irradiation than in stoichiometries silica sample (with normal oxygen concentration) where it was measured a ten times less intense 5.8 eV band [35]. Moreover, there are other works [33, 36] which show a bleaching of ODC(II) and a contemporary increase of paramagnetic $E'$-centres, indicating that the former can be thought as precursors of the latter and so pointing towards the oxygen vacancy model.

\(^2\)This model should not be confused with the structural model for ODC(I), that is a relaxed oxygen vacancy with a shorter distance between silicon atoms.
On the other hand, to take into account other experimental and theoretical results, was proposed an inter-conversion process between ODC(I) (relaxed-oxygen vacancies) and Si-ODC(II) considering that they share the same amount as oxygen deficiency [18, 37, 38].

The Si-ODC(II) is, in general, related to an oxygen deficiency of the material and can form because of dry atmosphere during the process of synthesis or during the fusion from natural quartz; it is also possible to create the defects by particles or photons irradiation. Irradiation of silica with heavy particles (i.e. neutrons, protons or ions) or fast electrons (β-rays) creates localized damage because these processes release their energy mainly because of electron-hole pairs formation or elastic processes of knock-on with silicon or oxygen atoms of the matrix. The oxygen atoms are the mainly subject of permanent displacements from their normal position: indeed, the breaking of the covalent Si-O bond requires $\sim 5$ eV [39, 40], so that $\sim 10$ eV are needed to shift an oxygen atom (coordination with two silicon atoms), whereas over $\sim 25$ eV are required for a silicon atom (coordination with four oxygen atoms) [6].

Irradiation with high energy photons (i.e. laser ultraviolet light, γ-rays, X-rays) creates, instead, diffuse and homogeneous damages and releases its energy mainly by non-elastic processes: fast electrons energized via Compton effect and/or by direct electronic ionization or excitation [6].

Formation of ODC(II) was observed under high energy ion implantation [41–44], under β-irradiation [45], γ-irradiation [45, 46], or owing to neutron bombardment [47–49]. Moreover, several experimental evidences have suggested that heavy irradiation can affect the structural properties of silica (e.g. increasing of density, variation of vibrational spectra), maybe influencing the inhomogeneous features of the solid as well [6].

### 1.3 Estimation of the heterogeneity

Several experimental evidences have led to a general agreement on the fact that the properties of point defects may be significantly different depending on the crystalline or amorphous structure of the solid they are embedded in [2]. Indeed, in a crystal each member of an ensemble of identical defects experiences the same local environment due to the perfect translational symmetry as the host, and they are each other virtually indistinguishable from the spectroscopical point of view. As a consequence, every property of an ensemble of defects of the same species, as absorption,
1. Silica and Oxygen Deficient Centres

Photoluminescence (PL) lineshapes, as well as decay lifetimes, can be interpreted as properties of a single centre\(^3\), and are referred to these features by the adjective *homogeneous*. The homogeneous absorption linewidth is mainly determined by the electron-phonon interaction and it is related to other important physical properties of the defect, such as the Huang-Rhys factor and the phonon vibrational frequencies [1, 2], as we are going to review in the chapter 2.

On the other hand, defects in an amorphous solid are supposedly characterized by statistical distributions of the spectroscopic properties, since the disorder of the matrix gives rise to site-to-site differences among the environments experienced by each single centres [1, 2, 50]. These geometrical differences are usually described by the expression *conformational heterogeneity*, which is borrowed from the terminology of the study of proteins. Indeed, proteins are systems which have physical characteristics common with other complex systems such as glasses, spin glasses, or neural networks. Their fundamental (primary) structure is formed by strong covalent bonds between constituent atoms, whereas the arrangement in the space is obtained by weak hydrogen and sulfur-sulfur bonds, which link different parts of the primary chain. Complexity arises from the fact that no periodicity condition forces the macromolecule into a unique structure. The hydrogen bonds can assume a variety of positions and a given protein can consequently assume a large number of slightly different overall structures, which are called *conformational substates* [51].

Hence, returning to the silica, the conformational heterogeneity gives a further *inhomogeneous* broadening to the lineshapes of the optical bands which reflects the degree of disorder of the amorphous solid and concurs, together with the homogeneous effects, to determine the overall spectroscopic signature of the colour centre [1, 2, 50].

While this general interpretation scheme is widely accepted in literature, no general approach is currently available to separate the homogeneous and inhomogeneous contributions to the experimentally observed linewidth of an absorption or PL band. Moreover, almost nothing is known on the effect of inhomogeneity on the decay properties of a defect. Many experimental approaches have been proposed to estimate the homogeneous and inhomogeneous contributions to the experimental linewidth of an optically active centre: exciton resonant luminescence, resonant second harmonic scattering, photon echo, site-selective spectroscopy and spectral hole burning [50, 52–55]. However, the issue is still open since none of these techniques is applicable to the

\(^3\)Strictly speaking this is true only for defects in a crystal with one possible atomic configuration for unitary cell, whereas if there are different possibilities the defects can reflect this situation in different optical bands.
whole variety of inhomogeneous physical systems of interest. Below we give a quick review of some of these techniques.

- **Site-selective spectroscopy**
  In amorphous solids, and in silica in particular, site-selective spectroscopy (named also fluorescence line narrowing) has been successfully applied only to defects which allow the direct observation of the zero phonon line (ZPL, for a description see chapter 2) by virtue of a weak coupling with the vibrational modes of the matrix [2, 54]. Indeed, in this case the homogeneous absorption spectrum of a single centre at T=0 K is characterized by a high intensity narrow line (ZPL) and a less intense broad band (phonon sideband) on the high energy side due to creation of phonons of the surrounding matrix. The purely electronic transition ZPL shows a width which is $10^4 - 10^7$ times narrower than the width of the sideband attached to it. The inhomogeneous effect of amorphous systems produces different replicas of this spectrum, whose ZPL are shifted at different energies, giving rise to a broad and less structured absorption spectrum [50]. The luminescence signal, accordingly to the bandwidth of exciting light, reflects the spectral features of this broadened absorption spectrum. Indeed, if a wide width spectral excitation source is used, many different centres are explored and the luminescence signal is unstructured as the global absorption band. If, instead, a laser source is used, only the few resonant centres are stimulated to emit and the emission spectrum is characterized by a narrow line (the ZPL in emission) and the related emission sideband, reflecting only homogeneous features of those excited centres. If the entire broadened absorption band is spanned by different laser wavelengths, the spectral distribution of the various ZPLs gives direct information on the inhomogeneous dispersion of the investigated centres [2, 50].

- **Photon echo**
  The photon echo experiment resembles the spin echo effect in nuclear and electronic magnetic resonance measurement. For instance, suppose an inhomogeneous ensemble of centres which can interact with an external electromagnetic field. Each centre has a different transition energy between interacting levels, caused by glassy matrix or by different sizes and thus it is characterized by a different time evolution after an excitation pulse with respect to the other centres. Because of these different evolution rates we observe a dephasing of
the initial macroscopic polarization induced by the first electromagnetic pulse. After a time $t_0$ from the first pulse, a second identical electromagnetic pulse is sent, in order to reverse perfectly the time evolution of all centres. After a time $2t_0$ all centres restore the initial coherence and thus produce a macroscopic polarization which emits a third pulse named photon echo \cite{56}. The capability of the system to rebuild the coherence is guided by normal dephasing process of each single homogeneous centres. There are two main contribution to homogeneous dephasing process: the intrinsic excited electronic decay time $T_1$ (longitudinal time) and the time phase relaxation $T_2$ (transversal time) due to interaction with phonons excited by thermal motion \cite{50}. When the inter-pulse time $t_0$ is enlarged the ensemble of centres experiences their natural dephasing processes for more time and can not recover the initial coherence because of a sort of memory lacking of their initial state. In the photon echo experiment, thus, is studied the decay of the echo signal intensity as a function of interpulse time. This decay time is linked to homogeneous processes and in particular is inversely proportional to the homogeneous linewidth of each centre. The contribution to the homogeneous width is often dominated by electron-phonon coupling, indeed for a dipole allowed transition the intrinsic lifetime $T_1$ is about $10^{-8}$ s and the related half width is about 0.1 $\mu$eV, which is negligible with respect to the phonon broadening \cite{2, 50}.

- **Spectral hole burning**
  The spectral hole burning (SHB) is an experimental technique performed on an inhomogeneous broadened absorption band related to an ensemble of absorbing guests in a transparent host. Using a tunable and narrow exciting light a homogeneous portion of the global ensemble of absorbing species, is transferred to an excited state because of the resonance with the exciting energy. If during this process, is performed an absorption experiment on the whole system, is found a hole in the normal OA spectrum due to the lack, from the ground state, of the previously excited homogeneous portion \cite{50}. In this way one can obtain important information about the homogeneous parameters of the guest, normally hidden by the inhomogeneous broadening of the system. Different kind of hole burning techniques exist depending on the time spent in the excited state (if more or less of a normal lifetime) or depending on the persistence or not of the burned hole. In general an SHB experiment is performed at low temperature to minimize the broadening due to coupling with phonon
population and to maximize the ratio between the global inhomogeneous width $\sigma_{in}$ and the homogeneous one $\sigma_{ho}$ in order to better separate the hole burned by the laser source [50]. It is very important to note that the width of the hole in the global absorption band is two times larger than the homogeneous width of the removed species. Indeed, the exciting light of energy $E_l$ interacts with those centres which are far at least $\sigma_{ho}$ from $E_l$, and they bring away a $\sigma_{ho}$ portion of their related absorption band [50]. In this condition the absorbing species left in the ground state, when are probed by another external light source, show a $2\sigma_{ho}$ burned hole: the information is revealed by the molecules that are absent from the ensemble which form the initial inhomogeneous distribution. In an SHB experiment, from the energy position of holes, their grow rate, their dependence from temperature and time can be obtained useful information about general host dynamics, for example, dephasing mechanism (local mode coupling, phonon of the host), spectral diffusion, energetic barrier heights. Moreover, it was observed that an hole burning spectrum can be obtained by the cosine Fourier-transform of the photon echo signal [57] and often both techniques are contemporary applied [57, 58]. The hole burning technique is particularly interesting also for its technological implications, namely the promising feature of writing information bits as homogeneous “holes” in a sufficiently broad inhomogeneous optical band, thus creating solid state optical memories with very high bit density, because of the addition of the frequency domain to the spatial one where are usually recorded the information [1, 50]. Finally, the SHB gives the great advantages of the absence of the disturbing scattered light which is present in the site selective spectroscopy.

In particular, the photon echo and hole burning techniques have been used for characterize the homogeneous properties of quantum dots that are crystals of nanometric dimensions embedded in dielectric matrix. In general quantum dots show a distribution of their size and thus an inhomogeneous broadening of their optical activities [59–62]. These two techniques were also used to analyze the homogeneous optical features of trivalent and divalent rare heart ions in doped silica glasses [63–66].
1. Silica and Oxygen Deficient Centres

1.4 Heterogeneity of ODC(II) in silica

In previous papers, have been reported optical measurements on the luminescence of ODC(II), performed at several temperatures both by time-resolved and stationary luminescence techniques [20, 23, 67–71]. In particular, was studied the absorption and related luminescence signals of Ge-ODC(II) [67–70] and Sn-ODC(II) [23] both in natural silica [67, 69] and in Ge or Sn sol-gel silica samples [23, 68, 70]. In stationary measurements as a function of temperature of the singlet and triplet luminescence bands of these ODCs(II), the rate of inter-system crossing ($k_{\text{ISC}}$) shows a non-arrhenius behaviour. This result was understood with the hypothesis of the existence of a distribution of $k_{\text{ISC}}$ related to ODCs(II) in different environments, induced by the intrinsic conformational heterogeneity of silica. Moreover, the non-exponential characteristic decay of the luminescence bands was a further proof of the dispersion of $k_{\text{ISC}}$. These considerations about inhomogeneity experienced by point defects in silica was previously found also for the optical activity of Si-ODC(II), where the presence of different absorption bands after excitation at different laser wavelengths was argued due to slightly different ODC(II) defects [20].

In [71] the authors studied the Si-ODC(II) PL activity of two silica samples (a natural dry silica sample and a neutron irradiated synthetic one) by time resolved phosphorescence. The triplet band of ODC(II) excited passing through the first singlet excited state, when measured as function of emission and excitation energies resulted characterized by a dispersion of lifetimes. This result was also related to the presence of conformational heterogeneity in silica which maps itself in a dispersion of the optical activities.

Although it is clear from these previous works that inhomogeneous effects are responsible of peculiar properties of luminescence of ODC(II) in silica, it does not exist a clear experimental way to discriminate the two contributions (homogeneous and inhomogeneous) to the optical linewidth. Suppose, for instance, that the statistical distribution of geometrical properties of silica matrix maps itself in a simple distribution of the energy position of emission peaks of different defects. From the spectral viewpoint, a PL stationary measurement observes, at the same time, a global luminescence signal related to all defects which were excited by the energy source. In this kind of experiments the only way to discriminate different defects is to excite and study them selectively with a narrow energy tunable source. This is possible only when the overlap between different sub-bands is not great (it is not the case of ODC(II) [2]) or when the system under investigation shows a predominant and
“sharp” feature which allow a discrimination of different sub-bands related to different defects (as shown by another particular point defect in silica, the Non Bridging Oxygen Hole Centre, by using the zero phonon line [18]). From the temporal viewpoint, in general, time-resolved luminescence measurements were performed with the aim of measuring the lifetime of the species of defect, and it was estimated at the peak of the related emission bands [2]. The results of different lifetimes observed at different emission energies were associated with a general effect of heterogeneity, that is to the presence of many defects sharing the same atomic composition but with differences in the structural environment, without attempts to extract other important information from the behaviour of experimental data [71, 72].

It is worth underlining two previous works [24, 69] where was studied the detailed effect of different excitation energy on stationary optical measurements of the ODC(II). It has been evidenced a dependence of the energy position of absorption and emission peaks and it was pointed out a model to fit these behaviours hypothesizing a linear mapping between some spectroscopic parameters and a generic configurational coordinate (or a quadratic relationship for some other parameters). To reflect the inhomogeneous dispersion of silica geometrical features, this coordinate was also supposed gaussian distributed and the related half-width (thought as the inhomogeneous width) resulted to be $\sigma_{in}=66\pm3$ meV, whereas the homogeneous half width of a single Ge-ODC(II) was found to be $\sigma_{ho}=203\pm7$ meV [24]. This approach surely has given for the first time the possibility of a reasonable numerical estimation of an inhomogeneous broadening, but it was based on a distribution of a generic coordinate with no direct physical meaning or general applicability, supposing an ad-hoc linear or quadratic functional links.

In this PhD thesis we use an approach based on a new theoretical model which analyze experimental data acquired by time-resolved luminescence. From the theoretical viewpoint the main idea is modeling the dispersion of geometrical characteristics in silica by a gaussian distribution of one homogeneous property of point defects. For different reasons which will appear clear ahead, the zero phonon line turns out to be the most suitable homogeneous parameter to be distributed (see section 4.1). Moreover, our model lies on a basic physical parameters that controls luminescence processes: the spontaneous Einstein emission coefficient. Indeed, it shows a third power emission energy dependence which implies that different defects emitting at different energies are expected to show different luminescence lifetimes. In the following sections we refer to the dispersion of lifetimes in a luminescence band and, as
we will show, to a spectral shift of the first moment of the band, with the expression *luminescence spectral dispersion*.

The strong idea is to tentatively discriminate different sub-bands within an inhomogeneous ensemble of silica defects, not from the spectral side, but on temporal side. It is also worth noting that our analysis will cover a wide range of characteristic lifetimes of the luminescence: from nanosecond to microsecond, over three order of magnitudes (for a detailed description of the model see chapters 2 and 4).

From the experimental viewpoint our method requires the capability of recording the time evolution of an entire luminescence band and it was possible only using an instrument with a pulsed exciting source (for a detailed instrumental description see chapter 3). As we will see in the next chapters this approach results successfully in fitting and understanding experimental data, and moreover in extracting very important physical parameters related to ODC(II) point defects in silica: first of all the inhomogeneous half width, then the homogeneous one, the Huang-Rhys factor, the frequency of “effective” vibrational mode and the oscillator strength. Last but not least, it is very important to observe that our results will be strongly corroborated by experimental data on defects in crystalline materials which do not show the lifetime dispersion mentioned above, as correctly expected by our theoretical model.
Chapter 2

Theoretical description of point defects in a solid matrix

In this chapter we briefly review the standard theoretical description of the optical properties of a point defect in a crystal [1, 2, 12], in order to adapt it later to the case of amorphous systems. We will explain in detail only that parts useful to better get insight to the experimental results shown in the next chapters.

A crystal material is formed by a regular repetition of a fundamental unit (unitary cell) respecting translation symmetry rules. The unitary cell can be constituted by one or more atoms in fixed position which are linked by different kinds of forces (ionic, covalent or both) which determine the strength of the crystal to external physical actions. With point defects in general it is meant to the breaking of the crystalline symmetry caused by imperfection in the normal arrangement of one or few close cells: lacking of one normal atom, presence of impurities atoms in interstitial positions or in substitutional ones, dangling bonds, series of close vacancies, self trapped holes are all examples of point defects. Several experimental techniques have been used to characterize the different point defects in crystalline matrix: infrared and Raman spectroscopy for vibrational features, electron paramagnetic resonance measurements for paramagnetic defects, absorption in vacuum-UV to study the properties of the electron absorption edges and optical absorption in visible and ultraviolet (UV) range, and/or related luminescence activities especially for diamagnetic defects. In particular, when the point defects insert their own electronic levels in the forbidden energy gap between valence and conduction bands of the host crystalline material, this latter results coloured because it can now usually interact with visi-
2. Theoretical description of point defects in a solid matrix

ble light. For this reason, the expression “colour centres” is used to indicate these imperfections of the matrix.

2.1 Configurational coordinates model

One common way to describe the optical activity of a point defect is to treat it as a molecular system interacting with the vibrational modes of the surrounding matrix. The Hamiltonian of such a system can be written, neglecting spin terms, as the sum of kinetics energy $K$ of nuclei ($n$) and electrons ($e$) and potential energy of all possible charge pairs in the electrostatic interaction $V^e$ between them, as expressed by Eq. (2.1):

$$H = K_n + K_e + V^e_{e-e} + V^e_{e-n} + V^e_{n-n}. \quad (2.1)$$

Because of the heavier rest mass of nuclei with respect to electrons it is possible to consider the motion of both of them approximately independent (Born-Oppenheimer approximation) [2, 73]. It means that the motion of electrons is relatively faster than nuclei’s one and the electronic cloud reorganizes quickly itself after a slow displacements of the nuclei: the nuclear position affects the electrons energy only as a parameter. From the point of view of nuclei this electronic energy, depending in a parametric way from their position, appears as a global electrostatic potential which is the mean of kinetic and potential energies related to electrons $<K_e+V^e_{e-e}+V^e_{e-n}>$. With these assumptions the system is characterized by a quantum wave function $\Psi(R, r)$ which depends separately on the position of nuclei ($R$) and electrons ($r$) and thus can be factorized in:

$$\Psi(R, r) \simeq \Phi(R) \cdot \chi(R, r). \quad (2.2)$$

Then, the Schrödinger equation which describes the wave functions of the system can be separated in two parts, related to electronic wavefunction $\chi(R, r)$ and nuclear one $\Phi(R)$:

$$[K_e + V^e_{e-e} + V^e_{e-n}] \chi(R, r) = E(R) \chi(R, r) \quad (2.3)$$

$$[K_n + V^e_{n-n} + E(R)] \Phi(R) = \varepsilon \Phi(R)$$

We can write the nuclear positions as function of the equilibrium position $R_0$ and a displacements $u$ as $R = R_0 + u$ [2, 73]. In the following discussion we will use the
2.1. Configurational coordinates model

description named *configurational coordinates model* where the nuclear displacement $u$ after a linear transformation is expressed in term of configurational coordinates $Q_{\mu}$. For complex systems the generic coordinate $Q_{\mu}$ is a normal coordinate related to the normal mode labeled with $\mu$. In the following, the defect is assumed to be described by a single configurational coordinate $Q$, that is the system is coupled with a single related vibrational mode. Considering the weak dependence of electronic motion from nuclear displacements it is possible to substitute the coordinate $Q$ in the electron wave function $\chi$ with the average value $Q_0$ (*Condon approximation*), and solve separately the *Schrödinger* equation for electrons [2, 73].

We can also expand the global potential energy $V_{\text{conf}} = V_{\text{e-n}} + < K_{\text{e-e}} > + V_{\text{e-e}}^e - n$ in Taylor series and keep only terms up to the second order. In these hypotheses $V_{\text{conf}}$ results to have harmonic oscillator form characterized by a typical frequency $\omega_p$ thought as an opportuneley defined “mean” frequency of all real modes coupled to the observed experimentally electronic transition [1]. In this scheme, the system thought in a fixed electronic state can be found in one of the different vibrational levels whose corresponding energies are equal spaced by an energy $\hbar \omega_p$. We remark again that the coupling with a single frequency should be regarded as a simplified, though effective, representation of the much more complicated picture of electron-phonon coupling. Also, it is worth noting that in this scheme one cannot distinguish between a single mode with a strong coupling and several degenerate modes with weaker coupling.

Figure 2.1 resumes all ideas exposed above: for the electronic ground state the parabolic potential for the nuclei is indicated, it is centred at the equilibrium position $Q_0$ of minimum potential energy; the equal spaced discrete harmonic levels are also displayed.

Let us consider an *optical absorption* (OA) transition of suitable energy $E_{\text{Abs}}$ provided by external photons\(^1\) to obtain the transition of one electron of the point defects from its ground ($g$) state to the first excited ($e$) state\(^2\): the time scale of

\(^{1}\)The physical description of the optical absorption process is discussed below in section 2.2.

\(^{2}\)Strictly speaking the excited electronic states are “apparent” until the system remains in the ground state. They form the complete set of electronic states resulting from the theoretical analysis of the Hamiltonian of the system and only the ground state is occupied and thus “real”. After the absorption of one photon the system is changed because of different electron distribution and thus the complete set of electronic states is now different. The actual occupied excited state of the system is then “real” and the other one (together with the “new” ground state) turn out to be “apparent” [73].
2. Theoretical description of point defects in a solid matrix

**Figure 2.1:** Configurational coordinate diagram for the description of optical transition in a molecular system or point defects in a solid matrix.
this process is one thousand times faster than the typical time scale of nuclear displacement [74]. This consideration is at the base of classical Franck-Condon principle which considers possible only those transitions which are vertical in the configurational diagram represented in figure 2.1, i.e. the nuclei substantially do not move during the electron up-transition. From quantum-mechanical viewpoint the nuclear harmonic oscillator wave functions related to each excited discrete vibrational level show higher probability densities on the turning points (those point identified by the intersection between the vibrational levels and the electronic potential). Considering that the probability density for the ground vibrational level results higher in the centre of potential, the transition probabilities between vibrational levels, which are proportional to the overlap of nuclear wave function, turn out to be maximum for vertical transitions (quantum Franck-Condon principle).

In the new excited electronic state the nuclei find itself in a non-equilibrium position and the system looses its exceeding energy $S$ by a relaxation process of the nuclei towards the new equilibrium coordinate $Q'_0 = Q_0 + \Delta Q$. In the approximation of linear phonon coupling the relation between the lost energy $S$ and the coordinate change $\Delta Q$ is assumed linear and it turns out that the vibrational frequency of the nuclear harmonic potential in the $(e)$ state is the same $\hbar \omega_p$ as the $(g)$ state.

In general, different paths to return towards the ground state are possible, i.e. interaction with phonon population (non-radiative decay), mixing with other electronic levels or emission of photons of proper energy $E_{em}$ (radiative decay). Here we are going to discuss this last process, named photoluminescence (PL), which, as the OA process, is almost instantaneous in the timescale of nuclear motion. The luminescence process is also characterized by its lifetime which can be thought, for a statistical ensemble of identical point defects, as the mean time spent in the excited state before the decay. When the system falls down to the ground state, as shown in figure 2.1, further nuclear relaxations are needed to return to the coordinate $Q_0$, with consequent energy exchange with the coupled phonons population. In the linear phonon coupling approximation the shape of the two parabolic curves is the same and the lost vibrational energy is still $S$.

Resuming the global excitation-emission path, from the viewpoint of interaction with an external electromagnetic field, it has been observed an absorption of photons of energy $E_{Abs}$ and subsequent emission of photons of energy $E_{em} = E_{Abs} - 2S$: this energy difference $2S$ is called Stokes shift [2, 12]. Another important parameter is the number of matrix phonons involved in the absorption (or photoluminescence)
transition $H = S/h\omega_p$ which is named Huang-Rhys factor [2, 12].

### 2.2 Absorption and luminescence processes

The typical energy difference involved in the interaction between the external electromagnetic field and the point defects is a few electronvolts (eV) which correspond to a frequency of electromagnetic wave which lies in the visible or ultraviolet range. This frequency allows to consider the system as punctual with respect to the related wavelength and thus to use the dipole approximation [74]. Within this approximation the transition rate $W$ of a single absorption process is proportional to the square of the matrix element of the electric dipole moment operator between $(g)$ and $(e)$ electronic states:

$$W \simeq |<\Psi_e(Q, r)| e \cdot r |\Psi_g(Q, r)>|^2 = |<\Phi_e(Q)| \Phi_g(Q)>|^2 \cdot |<\chi_e(Q_0 + \Delta Q, r)| e \cdot r |\chi_g(Q_0, r)>|^2 = |M|^2 \cdot |D|^2$$  \tag{2.4}

where we have used the Born-Oppenheimer wave functions as described by Eq. (2.2). In general, we have to compute the total transition rate $W_{tot}$ for all possible vibronic transitions between $(g)$ and $(e)$ electronic states. Numbering these vibrational levels, respectively, with the subscripts $j$ and $k$ we obtain:

$$W_{tot} \simeq |D|^2 \sum_{j,k} |M_{jk}|^2$$  \tag{2.5}

where the first term $|D|^2$ is related only to the electronic wave functions and is proportional to the intensity of the optical absorption, while the second one is related to the overlap of nuclear wave functions (Franck-Condon factor) between $(g)$ and $(e)$ electronic states. Because of their orthonormalization rule the sum on all vibronic transition gives an unitary term, thus affecting only the shape of the absorption band. With the hypothesis of system at zero Kelvin degrees, only transitions from the $j = 0$ ground level are possible and the Franck-Condon factors can be calculated as overlap integrals between harmonic oscillator wave functions, resulting expressed by a Poisson distribution [2]:

$$|M_{0k}|^2 = e^{-H \frac{H^k}{k!}}$$  \tag{2.6}
2.2. Absorption and luminescence processes

where $H$ is the Huang-Ryhs factor previously defined. In figure 2.2 are shown the values of the normalized transition rates $|M_{0k}|^2$ as a function of the excited vibrational levels $k$ and for different $H$ values: it is worth noting that small values of $H$ give a strongly asymmetric shape because of the presence of the transition towards the excited electronic state with $k=0$ (zero phonon line, ZPL) which imposes itself, at an energy $E_0$, over the rest of the discrete spectrum. When $H$ increases the rate of transition related to the ZPL decrease and the shape becomes more symmetric, because of the increasing of transition rates for other $k$. For large $H$ the ZPL is practically absent and the entire discrete shape can be well fitted by a gaussian bell curve centred at $k \simeq H$ and a $\sigma \propto \sqrt{H}$ half-width.

Suppose now, an ensemble of point defects belonging to the same species, in a concentration $\rho$ inside the material and consider an electromagnetic wave of energy $E$ and intensity $I_0$ which, going through the material, interacts with each point defects. At the end of the material of thickness $d$ the intensity of the wave will be reduced because of absorption processes and it results:

$$I(E, d) = I_0 e^{-\alpha(E)d}. \quad (2.7)$$

The parameter $\alpha(E)$ is known as the absorption coefficient and it depends from the energy of the incoming light because only electromagnetic waves of proper wavelength can promote the point defects to their excited electronic state. The absorption
2. Theoretical description of point defects in a solid matrix

Coefficient it can be measured by performing a simple absorption spectrum [2] and it is related to the concentration $\rho$ of point defects by the relation (2.8):

$$\alpha(E) = \rho \cdot \Omega(E)$$

(2.8)

where $\Omega(E)$ is the absorption cross section related to a single point defect, calculated as follow [1, 2]:

$$\Omega(E) = \frac{1}{n} \left( \frac{E_{\text{eff}}}{E_{\text{ext}}} \right)^2 \frac{4\pi^2}{3\hbar c g_l} |D|^2 \sum_k |M_{0k}|^2 E \cdot \delta[E - (E_0 + k\hbar\omega_p)]$$

(2.9)

where we have used the transition rate as in Eq. (2.5), the summation is carried out over the all possible vibronic transitions and $\delta$ indicates a Dirac delta function (indicates with the bars in figure 2.2). In the expression (2.9) the term $\frac{1}{n} \left( \frac{E_{\text{eff}}}{E_{\text{ext}}} \right)^2$ is named effective field correction and accounts for the polarization effect induced by the external field on the solid [2, 12]. We have assumed also that the refraction index $n$ is constant in the electromagnetic range investigated and we have indicated with $g_l$ the degeneracy of the lower electronic state. We can group all constants in Eq. (2.9) in a term given by: $\beta = \frac{1}{n} \left( \frac{E_{\text{eff}}}{E_{\text{ext}}} \right)^2 \frac{4\pi^2}{3\hbar c g_l} |D|^2$ to obtain a simpler expression for $\Omega(E)$:

$$\Omega(E) = \beta \sum_k |M_{0k}|^2 E \cdot \delta[E - (E_0 + k\hbar\omega_p)].$$

(2.10)

Given a population of identical defects, the envelop of the $\delta$ functions in Eq. (2.10) describes their characteristic homogeneous absorption lineshape, with (aside from the effect of the factor $E$) a $E_{\text{Abs}} = E_0 + H\hbar\omega_p$ first moment and a $\sigma_{\text{ho}} = \sqrt{H\hbar\omega_p}$ half-width, related to the full width at half maximum (FWHM) as: FWHM $\approx 2.35 \sigma_{\text{ho}}$.

One important dimensionless parameter for the absorption process, is the oscillator strength $f$ which is defined as [2]:

$$f = \frac{2m_e}{3\hbar^2 e^2 g_l} E_{\text{Abs}} |D|^2$$

(2.11)

where $m_e$ and $e$ are respectively the mass and the charge of an electron and $\hbar$ is the Planck’s constant. This parameter $f$ indicate the “strength” of the electronic transition and results proportional to the absorption cross section $\Omega(E)$ integrated over all energies [2]:

$$\int \frac{\Omega(E)}{E} dE = \beta \cdot f.$$
2.2. Absorption and luminescence processes

If the parameter $f$ is known, using expression (2.12) and measuring the dependence of $\alpha(E)$ on energy (absorption spectrum), it is possible to obtain the concentration $\rho$ of the defects in the material:

$$\rho = \frac{1}{\beta f} \int \frac{\alpha(E)}{E} dE. \quad (2.13)$$

After relaxation towards the bottom of excited electronic state, the system can return back to the ground state by spontaneous photon emission. As already told, the hypothesis of linear electron-phonon coupling implies that the two potential wells (ground and excited), and thus also the respective nuclear wave functions $\Phi(Q)$ are the same. From symmetry considerations, then the following relation between the pair integrals overlap between these nuclear functions holds:

$$M_{0k} = M_{j0}. \quad (2.14)$$

Giving a look to the configurational coordinate diagram in figure 2.1 we can observe that the vibronic transition $0 \rightarrow k$ in absorption and the inverse one $j \rightarrow 0$ in luminescence are symmetric with respect to the zero phonon line $E_0$ (vibronic transition $0 \leftrightarrow 0$). Thus, it exists a relation between absorption and luminescence band shapes; moreover the transition rates of the two processes are related as well. For the absorption the transition rate is proportional to $|M_{0k}|^2$ and to the energy through the oscillator strength $f$. The rate of luminescence ($1/\tau$) is equal to the spontaneous Einstein emission coefficient ($A$) which, in a medium with refraction index $n$, is related to the stimulated Einstein emission coefficient ($B$) by the following relation:\footnote{It is important to remember that the Einstein relations were obtained for a simple two-levels system [75] in equilibrium with a generic field described by an ensemble of harmonic oscillators. However, proper quantum mechanical analysis produces the same relation 2.15 and predict automatically the existence of spontaneous emission [73, 74].}

$$A = \frac{n^3}{\pi^2 c^3 \hbar^2} \cdot E^3 \cdot B. \quad (2.15)$$

Applying the relation (2.15) to all possible vibronic transition between the two electronic states is possible to write:

$$1/\tau = \gamma \sum_k |M_{0k}|^2 (E_0 - k\hbar\omega_p)^3 \quad (2.16)$$

where $\gamma = \frac{n^2}{\pi^2 c^2 \hbar^2} g_{\nu} \beta$. The cubic dependence appearing in the above expression is a direct consequence of the relation between Einstein coefficients for absorption and
2. Theoretical description of point defects in a solid matrix

spontaneous emission. The PL radiative lifetime $\tau$ can be then linked to the absorption profile using the Eq. (2.10), obtaining the so called Forster’s equation [2, 76]:

$$\frac{1}{\tau} = \frac{r^2}{\pi^2 c^2 \hbar^3} \frac{g_i}{g_u} \int (2E_0 - E)^3 \frac{\Omega(E)}{E} dE$$  \hspace{1cm} (2.17)

where $g_u$ is the degeneracy of the upper electronic state.

Returning to the spectral side, given that the Einstein coefficient $B$ is directly proportional to $|M_{0j}|^2$, using relations (2.14) and (2.15) and remembering the consideration about the ZPL symmetry, we can finally write the following relationship of mirror symmetry which links the absorption $\Omega(E)$ and luminescence $L(E)$ band shapes of a single point defect [2]:

$$\frac{L(E)}{E^3} \propto \frac{\Omega(2E_0 - E)}{2E_0 - E}.$$  \hspace{1cm} (2.18)

Using this equation and Eq. (2.10) we can obtain:

$$L(E) \propto \beta \sum_k |M_{0k}|^2 E^3 e^{-t/\tau} \cdot \delta[E - (E_0 - k\hbar\omega_p)]$$  \hspace{1cm} (2.19)

which represents the homogeneous emission lineshape, with (aside from the effect of the factor $E^3$) a $E_{em} = E_0 - H\hbar\omega_p$ first moment and a $\sigma_{ho}$ half-width. Expression (2.19) does not take into account the dependence from the excitation energy within the absorption band.

Eq. (2.16) can be often approximated using $k \sim H$, thus obtaining:

$$1/\tau = \gamma(E_0 - S)^3.$$  \hspace{1cm} (2.20)

This expression shows that the decay rate is proportional to $\gamma$ and approximately to the third power of the first moment of the emission band, $E_{em} = E_0 - S$.

Summing up, the global expression for the luminescence of a population of identical point defects in a solid matrix as a function of the spectral position $E$ and time $t$ after an exciting light pulse (homogeneous shape) is:

$$L(E, t) \propto \gamma \sum_k |M_{0k}|^2 E^3 e^{-t/\tau} \cdot \delta[E - (E_0 - k\hbar\omega_p)].$$  \hspace{1cm} (2.21)

This expression assumes that non radiative channels from the excited state are absent, because in that case the lifetime $\tau$ should be rewritten as $\tau = (A + k_{nr})^{-1}$, where $k_{nr}$ indicates the rate of non-radiative processes possibly present.
From the experimental viewpoint, luminescence signals can be detected by stationary measurements or by time resolved ones. In the first case the luminescent system is illuminated by a light which excites continuously the active centers. A stationary state is reached where the observed emission spectrum reflects the spectral features of the global excited system without regard of their temporal dynamics. Time resolved luminescence, instead, add temporal information to the spectral one, using pulsed excitation light and temporal discrimination of related emission spectra.

As we see from Eq. (2.21), the shape and kinetics of the homogeneous luminescence band are completely characterized by four parameters: $E_0$ (the ZPL position), $\hbar \omega_p$ (the phonon energy), $\gamma$ (proportional to $|D|^2$) and $H$ (the Huang-Rhys factor). $H$ and $\hbar \omega_p$ can be expressed in terms of the half Stokes shift $S$ and of the homogeneous half-width $\sigma_{ho}$: $\hbar \omega_p = \frac{\sigma_{ho}^2}{S}$ and $H = \frac{S^2}{\sigma_{ho}^2}$. In this way, expression (2.21) can be alternatively regarded as depending on the four parameters $E_0$, $S$, $\sigma_{ho}$, $\gamma$, thus being indicated, in the follow, by the expression: $L(E, t|E_0, S, \sigma_{ho}, \gamma)$. 

2.2. Absorption and luminescence processes
Chapter 3

Experimental equipment and materials

3.1 Experimental equipment: time resolved luminescence

In this section we are going to describe the experimental equipment used for acquiring the luminescence data. As displayed by the picture in figure 3.1, it mainly consist in an assembled instrument constituted by a laser source, a sample chamber, a dispersion system and a detection one.

3.1.1 Excitation source: tunable laser

All luminescence measurements were performed under pulsed laser excitation with a tunable laser (Vibrant, Opotek [77]). It is constituted by a Q-switched Nd:YAG laser, which emits photons of \(\lambda=1064\) nm in pulses of 5 ns temporal halfwidth. This process is controlled by a flashlamp which pumps the laser media operating at a constant frequency. An electro-optical switch controls the emission of the laser by changing quickly the quality factor of the cavity and allowing the emission of the energy stored inside the crystal. For further details about the process of generation of the laser pulses with the use of cavity quality factor switching, we refer to specific bibliography [78–80]. The repetition rate of the Q-switching process can be varied from 1 to 10 Hz but in our measurements it was fixed to the higher frequency to obtain the highest signal to noise ratio for a chosen time duration of experiments.
3. Experimental equipment and materials

**Figure 3.1:** Picture of the equipment used in the experimental measurements performed for this PhD thesis. The tunable laser source (on the left), the chamber with a sample placed in back scattering geometry (centre), the spectrograph and the CCD detector (on the right) are indicated. The blue and the red arrows schematically represent the excitation beam and the collected luminescence signal, respectively.

**Figure 3.2:** Schematic representation of the tunable laser Opotek: (1) ND:YAG laser (1064 nm), (2) non-linear crystal for second harmonic generation (532 nm), (3) non-linear crystal for third harmonic generation (355 nm), (4) optical parametric oscillator, (5) polarizer, (6) UV module.
In figure 3.2 is reported the diagram of our laser source. The photons emitted by the ND:YAG laser (labeled with number 1 in figure) are guided by two mirrors towards two different non-linear crystals: the first one (2) generates the second harmonic signal (532 nm) and the second crystal (3) produces the third harmonic obtaining photons of ∼355 nm wavelength. These nonlinear conversion processes depend critically on the relative orientation of the polarization axis of the incident beam with respect to the crystals axis. The process is highly efficient only when the condition of phase matching is ensured, that is when the phase velocities of the frequency-doubled and the fundamental waves are the same. To this purpose two different knobs allow to finely vary the crystal axes thus tuning the non-linear conversion process and obtaining the maximum output power. The laser beam reaches another non-linear optical device (4), named Optical Parametric Oscillator (OPO). This passive device is the most important element of our laser source because it can convert a single input laser beam of frequency $\nu_p$ in two beams, named Signal and Idler, having lower frequencies $\nu_s$ and $\nu_i$ respectively, linked to the pump frequency $\nu_p$ by the relation:

$$\nu_p = \nu_s + \nu_i. \quad (3.1)$$

This conversion process takes place in a beta barium borate (BBO) crystal and requires phase-matching condition too; it is obtained with a fine tuning of the axis of the non-linear birefringent BBO via software controlling. Varying the crystal axis it is possible to obtain as output Idler and Signal with different frequencies satisfying relation (3.1). In figure 3.3 are shown the range of wavelengths obtained varying the BBO crystal axis; the wavelength varies from ∼400 to ∼700 nm for the Signal beam and ∼700 to ∼2000 nm for the Idler beam. These two output beams are orthogonally polarized so that one of them can be discriminated by using a simple polarizer (5) placed in front of the output slit of OPO: manually choice of the direction of the polarizer ensures the correct choice of the laser beam. The spectral bandwidth of the output beam varies slightly with the wavelength but it remains below 0.3 nm.

If for experimental purposes, it is required a laser beam with frequency in the UV range, the OPO beam must be redirected to another module (6) which halve again its wavelength.

Finally, we can use a laser source with a wavelength tunable in the range 210-355 nm (maximum energy density of 1 mJ/cm$^2$ per pulse) and in the visible range 355-800 nm (maximum energy density of 10 mJ/cm$^2$ per pulse) with 1 nm possible
3. Experimental equipment and materials

3.1.2 Detection system: the CCD camera

The laser beam passes through two collinear prisms for a fine redirection in horizontal and vertical directions, with the aim of laser energy maximization onto the sample under investigation. The luminescence signal emitted by the sample is collected in a standard back-scattering geometry (see picture in figure 3.1) by a lens and focused towards the detection system through a slit. The width of the slit can be manually controlled from 0 to 3 mm with a sensitivity of 5 µm. The luminescence light thus arrives to the detection system, where it is dispersed by a spectrograph and collected by an intensified charge coupled device (CCD) camera which measures its intensity as a function of wavelength.

The dispersion system is a Czerny-Turner spectrograph (SpectraPro 2300i, PI-Acton [81]), with 300 mm focal length, equipped with three different gratings (1200, 300 and 150 grooves/mm). The proper grating and slit’s width were chosen to satisfy requirements of light sensitivity, dispersed range and wavelength dispersion. Indeed, high density of grooves gives a low sensitivity to external light, but a small bandwidth on a narrow spectral range and viceversa. In all measurements performed in this work

Figure 3.3: Wavelength of Signal (red curve) and Idler (black curve) beams for different axis angle of BBO crystal.
3.1. Experimental equipment: time resolved luminescence

The most important element of the detection system is the air-cooled intensified Charge Coupled Device camera (PIMAX, PI-Acton [81]) constituted by an array of 1024x256 pixels and an intensifier stage which can be activated to “see” photons (gating ON) or not (gating OFF).

The photons collected from the sample chamber pass through the input window (number 1 in figure 3.4), strike the photocathode (2) which releases electrons because of photoelectric effect. When the photocathode has a negative voltage with respect to the micro channel plate (MCP) one (3), the released electrons will be attracted to the MCP input (gating ON). If the CCD is gated OFF it is applied a reverse difference of potential and the gating acts like a shutter preventing the CCD to see the input light because the generated electrons are not attracted by the MCP.

Since the voltage at the MCP output is positive with respect to that at the input, the electrons are accelerated into the MCP channels hitting their walls and generating additional electrons, thus resulting in an electrons gain. The amount of this gain is controlled by the user increasing or decreasing the voltage of the MCP output. The electrons which are going out from the channel are further accelerated by a constant high voltage (5-8 kV) and strike the phosphor coating on the fluorescent screen (4) causing it to release green photons. Because of the MCP gain, there are now many photons for each external photon that had been struck the photocathode surface. Thus the overall system acts as an image intensifier when is gated ON. The photons
3. Experimental equipment and materials

released by the coating are transferred to the surface of the CCD via fibre-optics bundle (5) producing charge at the pixels (6) they strike. Charges are accumulated in the pixel wells of the CCD until the MCP is gated ON. The accumulated charge is then shifted to the serial register where it is read out to an on-chip amplifier that converts the charge to an analog voltage. This voltage is digitally encoded and transmitted to a computer.

The timing of the gating process can be controlled by software instructions. The detection system can be triggered via the excitation source in order to acquire the emitted light only in a given temporal window well defined with respect to the laser pulses. The CCD can accumulate (when the MCP remains gated ON) in a time window defined by the width parameter $t_W$ and by its delay $t$ from the origin of the time scale. To this purpose the electric pumping signal of the laser lamp is sent by a coaxial cable to the temporal controller of the CCD camera and used as external trigger signal. Thanks to this “temporal link” it is possible to acquire experimental data before, during and after the laser pulse but, as we will see in the section 3.1.4, only a part of this signal is processed in the data analysis.

3.1.3 Low temperature equipment

As we have discussed in the theoretical chapter 2 our approach is based on the absence of non-radiative de-excitations channels from the upper electronic state. In general the non-radiative channels are due to interaction with vibrations of the system, and are so proportional to the temperature. For this reason all luminescence spectra were obtained on samples kept at cryogenic temperature. To ensure the thermal stability, high vacuum ($\sim 10^{-6}$ mbar) was obtained with a turbo-molecular pump (Mini Task, Varian [82]) in a liquid helium continuous flow cryostat (Optistat CF-V, Oxford Instruments [83]) equipped with four optical windows in Suprasil material (Heraeus Quartzglas [84]), a synthetic silica transparent to UV light above 180 nm. Thanks to a transfer tube and an external pump the liquid helium was continually pumped on a copper element inside the cryostat. Thermal equilibrium is achieved by an automatic temperature controller (Oxford-ITC503, Oxford Instruments [83]), which simultaneously controls the He flow into the tube and an electric current input on a heating resistor, placed near the copper elements as well, where the sample holder is fixed. With this apparatus the sample reaches, after waiting almost 30 minutes for thermalization, the experimental temperature which is typically of 25 K. When the working temperature is different it will be indicated. The cryostat which
contains the sample-holder is inserted in the sample chamber with a home-made positioning system, which permits fine translational and rotating movements around the vertical axis passing through the sample.

3.1.4 Methods

The typical measurements performed for this research work is a time resolved luminescence spectra, which consists in a matrix of 1024 rows and \( N+1 \) columns: the first column is formed by the wave numbers \( \lambda \), whereas the others columns are formed by the CCD counts \( L(\lambda) \) at each pixels for the \( N \) acquired time intervals.

The dispersion of wavelengths is done long the direction of the 256 rows, formed by 1024 pixels. In the spectroscopy configuration the system automatically displays on a graph the sum of the accumulated signals on all 256 pixels in a column as a function of the 1024 pixels positions.

Prior to any luminescence measurement is acquired a “dark” spectrum (with the MCP gated OFF) in the same experimental condition as a “normal” spectrum. The dark will be automatically subtracted, via software, from each normal PL acquisition to eliminate possibly spurious signals impressed on the CCD, to subtract the accumulated thermal noise or to eliminate external light background. Because of the physical connection between the CCD camera and the spectrograph, not all pixels’ area of the CCD is uniformly illuminated. These shadow effect is named vignetting and leaves almost 630 useful pixels illuminated with slight differences. We have taken into account this shadowing effect correcting each spectrum for the response of the system acquired by using a narrow laser line of constant wavelength and intensity, registered in different positions which cover the CCD (this can be easily obtained by changing the dispersed spectral range of the used monochromator).

Other source of correction we have done is the dependence of the detection system from the wavelength of incident photons dividing all spectra for the proper spectral response as indicated in the technical sheets of the spectrograph for the used grating.

Moreover, the CCD counts are directly proportional to the luminescence spectral density \( \frac{dI}{d\lambda} \), that is the intensity collected with a constant spectral bandwidth \( d\lambda \). In the next chapters, all PL spectra \( L(E) \) will be shown as a function of the energy \( E \) instead of wave number \( \lambda \). Because of the relation between these two physical quantities \( E = \frac{hc}{\lambda} \) the spectral density \( \frac{dI}{dE} \) with respect to \( E \) must be multiplied for \( \lambda^2 \) (spectral dispersion) because to a constant spectral bandwidth in \( \lambda \) corresponds a spectral bandwidth which depends from the emission energy \( E \) [85]. Thus the
luminescence signal $L(E)$ results:

$$L(E) = \frac{dI(E)}{dE} = \frac{dI(\lambda)}{d\lambda} \cdot \left| \frac{d\lambda}{dE} \right| \propto L(\lambda) \cdot \lambda^2. \quad (3.2)$$

Finally, to the so corrected spectra, a reference straight line was subtracted to eliminate possible residual background, and we rejected those spectra which contain the narrow signal of the exciting laser pulse scattered from the sample and sample-holder. This last procedure ensures us that we are observing the decay of luminescence signal after the end of the exciting pulse and that we can analyze it with a single exponential decay function\(^1\). The falling time of the laser pulse is of one-two nanoseconds and typically the firsts three-four spectra were deleted.

In general, an emitting material could re-absorb the emitted photons, affecting the spectral features of luminescence spectra. In our experiments we have used materials with an absorption coefficient, in the spectral region of emission, so low to avoid any kind of correction for this effect.

### 3.2 Materials

We have chosen ODC(II) in silica as representative defects for colour centres in an amorphous material. The complete analysis we have performed in this thesis deals with all three kinds of ODC(II) related to silicon, germanium and tin atoms.

- **Silicon ODC(II)**
  To study the first kind of ODC(II) related to intrinsic silicon atoms we have used two different Type IV (see classification in section 1.1) silica materials: the first one is Suprasil 300 and the second one is Suprasil F300, both commercial trademarks of Heraeus Quartzglas [84]. These two materials, hereafter named S300 and F300 respectively, are characterized by a nominal concentration of metallic impurities $<$1 ppm in weight and a low content of OH groups ($<$1 ppm). If excited with $\sim$5 eV photons, both materials show the typical activity of the fast luminescence $S_1 \rightarrow S_0$ of as grown Si-ODC(II) whose decays have the same value of 4.5 ns measured at the emission peaks of the PL bands

\(^1\)This is not the unique reason which permits a mono-exponential analysis of our PL decays, because it is also important the absence of several non-radiative channel which can give different de-excitation pathways, as discussed in section 1.4.
3.2. Materials

Figure 3.5: Low temperature luminescence of F300 (white circles) and S300 (black triangles) materials, excited under photons of $\sim$5 eV energy. The spectra represent the luminescence signals collected with the CCD in a time interval of 0.5 ns after the fall front of the laser pulse (see section 3.1.2).

shown in figure 3.5. The luminescence of a sample ($5 \times 5 \times 1$ mm sized) of dry synthetic S300 silica will be studied in chapter 5.

We have also performed measurements on the F300 material to compare the PL of as-grown and radiation induced Si-ODC(II). To this purpose a F300 slab was cut in different samples and each piece was irradiated with fast electrons at different doses. As expected from previous literature [6, 45], we observe the PL activity of radiation induced Si-ODC(II) as we will show in section 6.1. Finally, to go further in detail on the effect of irradiation processes we will discuss in section 6.2 other two S300 silica samples processed with $\gamma$-rays and neutron particles, respectively.

- **Germanium ODC(II)**

  For the second kind of ODC(II) related to extrinsic germanium atoms we have used a dry silica of Type I, the Infrasil 301, which is also a commercial trademark of Heraeus Quartzglas [84]. This material, hereafter named I301, has a typical concentration of impurities of $\sim$20 ppm in weight [84]. In particular, as-grown I301 contains a $\sim$1 ppm concentration of Ge impurities, due to contamination of the quartz from which the material was produced. Previous
3. Experimental equipment and materials

studies demonstrated that in this material a consistent portion of the Ge impurities are arranged as Ge-ODC(II) defects [5]. Moreover, the close resemblance between the optical properties of I301 and sol-gel silica samples doped with Ge atoms (as we will see in figure 4.11), ensures us that in I301 sample the contribution to PL of possible intrinsic Si-ODC(II) defects is negligible [5, 18].

- Tin ODC(II)
  The third silica sample, hereafter named Sn-doped silica, was prepared by the sol-gel method (see section 3.2), doped with 2000 ppm of Sn atoms and rod shaped with a diameter of 4 mm and thickness of 1.4 mm. Solgel synthesis from hydrolysis of tetraethoxysilane and dibutyl-tin-diacetate was employed to obtain silica containing tin in substitutional position with respect to silicon atoms, avoiding Sn segregation [86]. The final material was obtained heating the xerogels in O$_2$ with a thermal ramp (4 °C/h) up to 1050 °C. Inductively-coupled-plasma spectroscopy analysis of the Sn concentration after the thermal treatment revealed no change of tin content above the uncertainty (about 10%) of the nominal value [86]. Previous studies shown that the tin impurities form Sn-ODC(II) defects with a global optical activity (OA and PL) consistent with literature data [23, 31, 86].

- Crystal luminescence activities
  We have chosen lithium fluoride as main representative of a crystalline material, hereafter indicated with LiF. Specifically, LiF is a material employed in the production of high-quality optical elements to be used in the infrared, visible, and particularly in the ultraviolet spectral regions. In particular, to probe the features of colour centres of “crystalline” defects we have studied F-type-centres in LiF. F-centres are formed by electrons trapped in anion vacancies and are the subject of active investigation in the areas of colour centre lasers, radiation dosimetry and integrated optics (see Ref. [87] and references therein). A specimen (5 × 5 × 1.25 mm sized) of LiF was irradiated at room temperature with electrons of 3 MeV energy, for a total dose of 15 kGy. The purpose of irradiation was to induce in the sample the formation of luminescent F-type centres. As we will see in section 4.2, the investigated optical activity of F-centres in our LiF sample is a “fast” luminescence (ns), due to an allowed electronic transition, with emission features (spectral peak, spectral width and lifetime) useful for a comparison with the “fast” luminescence of Ge-ODC(II)
in silica.

Finally, to give more generality and to further confirm our results on point defects in crystalline materials, we have also carried out the same experiments on a “slow” (µs) luminescence related to a forbidden electronic transition. To this aim we have performed measurements on the PL signal observed in an as-grown commercial sapphire sample (α-Al₂O₃) provided by A.D. Mackay Inc. (Broadway, New York [88]) and rod flame polished, as we are going to describe in section 4.3.
Chapter 4

Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

In general, the theoretical background exposed in chapter 2 is used indifferently to study point defects in a crystal as well in an amorphous matrix. Previous results have shown that heterogeneity in silica conditions strongly the optical activity of colour centres (see section 1.4) and thus in this chapter our aim is modeling theoretically the effect of inhomogeneity and thus trying to check the validity of our hypothesis with proper experimental measurements.

4.1 Modeling the heterogeneity in silica

The equations exposed in chapter 2 describe the absorption and luminescence activities of a single point defect, or as well as of an ensemble of identical ones in a crystal. Indeed in this kind of materials, it is assumed that each defects is representative of all similar others, and its optical activity is a homogeneous feature. For defects in an amorphous matrix, we can argue the hypothesis of a population of identical defects to fail. Indeed, each point defect interacts with different environments and it is possible that this conformational heterogeneity causes a site-to-site statistical distribution of one or more homogeneous properties of single defects. For ease of the reader, we report here the expression (2.21) of the luminescence of a statistical ensemble of point defects in a crystal, together with the related expression (2.16) for
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

The lifetime $\tau$:

$$L(E, t|E_0, S, \sigma_{ho}, \gamma) \propto \gamma \sum_k |M_{0k}|^2 E^3 e^{-t/\tau} \cdot \delta(E - (E_0 - k\hbar\omega_p))$$  \hspace{1cm} (4.1)

$$1/\tau = \gamma \sum_k |M_{0k}|^2 (E_0 - k\hbar\omega_p)^3.$$  \hspace{1cm} (4.2)

Here we again stress that the PL signal expressed in Eq. (4.1), at an energy $E$ and a time $t$, depends from four homogeneous parameters (indicated after the vertical symbol $|$): the ZPL position $E_0$, the half Stokes shift $S$, the homogeneous half-width $\sigma_{ho}$ and the parameter $\gamma$ proportional to the oscillator strength $f$.

The simplest model we can put forward to take into account the disorder effects in a glassy matrix is to introduce a gaussian distribution of the parameter $E_0$, peaked at $\hat{E}_0$ and with an inhomogeneous half-width $\sigma_{in}$; in this scheme, the other homogeneous parameters $\gamma$, $S$, and $\sigma_{ho}$ are still considered as undistributed. Within these hypotheses, the global PL signal $L^*(E, t)$ emitted by an ensemble of non-identical point defects can be now expressed as the convolution of the homogeneous shape $L(E, t)$ with the inhomogeneous distribution of $E_0$:

$$L^*(E, t|\hat{E}_0, \sigma_{in}, S, \sigma_{ho}, \gamma) \propto \int L(E, t|E_0, S, \sigma_{ho}, \gamma) \cdot e^{-\frac{(E_0 - \hat{E}_0)^2}{2\sigma_{in}^2}} dE_0.$$  \hspace{1cm} (4.3)

Eqs. (4.1) and (4.3) lead us to predict a difference between the PL signals of defects in crystalline and amorphous solids. Indeed, when the inhomogeneous broadening $\sigma_{in}$ is almost zero, as expected for point defects in a crystalline matrix, Eqs. (4.1) and (4.2) have to be used, and the radiative lifetime $\tau$ should be independent from the spectral position at which it is measured within the emission band. In fact, $\tau$ is a function of the homogeneous parameters $E_0$, $\gamma$, $S$, and $\sigma_{ho}$, which are expected to be the same for all defects in the crystalline solid.

In contrast, in an amorphous solid a PL band due to an ensemble of point defects can be thought as arising from the overlap of several bands with different $E_0$ as described by our hypothesis and so by Eq. (4.3), and thus featuring different lifetimes because of their dependence on $E_0$. Hence, when $\sigma_{in}$ is comparable with $\sigma_{ho}$ it should be possible to experimentally observe a dispersion in $\tau$ by measuring the decay of the PL signal at different emission energies.
Moreover, from the spectral viewpoint, the shape of a band arising from the overlap of sub-bands with different lifetimes should vary in time, so that the position of its first moment $M_1(t)$, calculated by the usual expression:

$$M_1(t) = \frac{\int E L^* (E, t) dE}{\int L^* (E, t) dE}$$  \hspace{1cm} (4.4)

should depend on time. Therefore, in our hypothesis, both the dispersion of $\tau$ within the emission band and the time dependence of the first moment can be used in principle as experimental probes of inhomogeneous effects.

It is worth noting that according to simplified Eq. (2.20), $\tau$ strongly depends on the first moment of the emission band, $E_{em} = E_0 - S$, and more weakly on the parameter $\gamma$. This leads to $E_0$ as the parameter of choice to be distributed in our model. Moreover, a gaussian distribution of $E_0$ was experimentally demonstrated for the NBOHC (Non-Bridging Oxygen Hole Centre) point defect in silica, for which the zero-phonon line can be directly observed by site-selective spectroscopy (see section 1.3) at low temperatures [54, 89, 90]. On the other side, we acknowledge that the predictions expressed by Eq. (4.3) can be obtained by introducing a distribution of the half Stokes shift $S$ keeping $E_0$ undistributed. Data reported later on in this thesis do not allow to discriminate between these two possibilities.

Finally, to get further insight into the meaning of Eq. (4.3) it is useful to consider the case in which the inhomogeneous half-width is much larger than the homogeneous one. In this case, the inhomogeneous lineshape is a slowly varying function with respect to the homogeneous term $L(E, t)$ so that, to the purposes of integration, the latter can be approximated as $\delta (E - (E_0 - S)) \cdot e^{-t/\tau}$, with $\tau$ given by Eq. (2.20).

By substituting in Eq. (4.3) we get that:

$$L^* (E, t) \propto e^{-\gamma E^3 t} \cdot e^{-\frac{(E_0 - E)^2}{2\sigma_{in}^2}}.$$  \hspace{1cm} (4.5)

This expression predicts an exponential decay whose $\tau = \gamma^{-1} E^{-3}$ depends cubically from the experimental observation energy $E$ within the inhomogeneous band.

In the intermediate situation of non-negligible homogeneous half-width, Eq. (4.3) deviates in principle from a single exponential decay, as it contains contributions with different values of $\tau$. However, we verified that the typical values of the parameters which will be used in the following to fit experimental data ($E_0$, $\sigma_{in}$, $S$, $\sigma_{ho}$, $\gamma$), correspond to predicted decay curves that always remain very close to a single exponential for all practical purposes. From a theoretical point of view, we can define in
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

general \( \tau(E) \) as the time in which \( L^*(E,t) \) (at a fixed \( E \)) decreases by a \( 1/e \) factor from \( L^*(E,0) \). With this definition, we can summarize the above considerations as follows: the \( \tau(E) \) curve (with \( E \) varying within the observed emission band) is expected to vary progressively from a constant value (for a completely homogeneous system) to an inverse cubic dependence (for a completely inhomogeneous system) with increasing inhomogeneous/homogenous ratio.

To check the validity of our model we have performed experimental measurements (described in the following sections) on luminescence of crystalline and amorphous defects. Firstly, we show data acquired on “fast” (allowed transitions) luminescence in point defects in silica and in a crystal. After that, we are going to confirm our model also analyzing data of “slow” (forbidden transitions) luminescence in other two representative samples of the two material categories.

4.2 Fluorescence in silica and in crystalline lithium fluoride

In this section our aim is to check experimentally the validity of our theoretical model presented in section 4.1. We chose F-type-centres in crystalline lithium fluoride (LiF) and ODC(II) related to germanium atoms (see previous section 1.1), in amorphous natural silica as model point defects on which testing our approach. Indeed, both centres feature broad near-gaussian luminescence bands in the ultraviolet (UV) range with close decay lifetime values (~8 ns), and they have both been widely studied in literature because of their important technological applications. As already discussed in the introduction we want remark that the choice of ODC(II) as model point defects in amorphous materials appears more appreciable if is considered the absence of this kind of centres in the crystalline counterpart material (quartz).

4.2.1 Experimental results

All luminescence signals in the I301 sample were acquired with a 300 grooves/mm grating with a spectral bandwidth of 2 nm, while the signals in LiF sample were measured with a a 150 grooves/mm grating with a 2.5 nm spectral bandwidth.

In figure 4.1 is shown the absorption spectrum of I301 silica sample in the UV spectral region. The observed band is due to Ge-ODC(II) centres and in particular
4.2. Fluorescence in silica and in crystalline lithium fluoride

**Figure 4.1:** Absorption spectrum in the UV region for the I301 silica sample. The arrow indicates the excitation energy used in the luminescence measurement (5.17 eV).

to the transition between the first two singlet electronic states $S_0 \rightarrow S_1$ (see scheme of electronic levels in figure 1.1).

In figure 4.2 we show a typical low temperature time-resolved measurement of the PL activity of Ge-ODC(II) in the I301 sample, performed under laser excitation at 240 nm (5.17 eV) on the peak of the related absorption band as shown by the arrow in figure 4.1. The laser energy density per pulse was fixed to $0.30 \pm 0.02$ mJ/cm$^2$, a value which ensures us that there was not bleaching of pre-existent point defects (or creation of new ones) during the experiment [91]. The PL decay was followed by performing acquisitions with the same integration time $t_W = 1$ ns at different delays $t$, going from 0 to 60 ns from the laser pulse.
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

**Figure 4.2:** Low temperature decay of the luminescence band of Ge-ODC(II) in the I301 silica sample, excited at 240 nm (5.17 eV).

**Figure 4.3:** Normalized data of figure 4.2 in a contour plot. The continuous line corresponds to the position of the first moment of the PL band as a function of time. The position of the first moment at $t=0$ is reported (dashed line) as a reference.
4.2. Fluorescence in silica and in crystalline lithium fluoride

Figure 4.4: Normalized spectra at three time delay from the laser pulse: $t=0$ (black squares), $t=15$ ns (red triangles) and $t=30$ ns (blue circles). The dashed lines with the same colour correspondence indicate the positions of the first moment of the relative PL bands.

Figure 4.3 shows the normalized spectra of figure 4.2 in a contour plot where hotter colours indicate higher values of luminescence signals. With the dashed line we indicate the position of the first moment $M_1(0)$ at the end of the laser pulse ($t=0$) whereas the continuous line indicates the first moment $M_1(t)$ as a function of time delay. The two lines are not superimposed indicating a red shift of $M_1(t)$ with respect to the initial value, which can be thought as a temporal evolution of the PL lineshape. Figure 4.4 shows three representative normalized spectra at different delay time from the laser pulse: $t=0$ (black squares), $t=15$ ns (red triangles) and $t=30$ ns (blue circles). The dashed lines with the same colour correspondence indicate the positions of the first moment of the relative PL bands, showing again the shift of the first moment as a function of the time.

In figure 4.5 we report the signal acquired for $t=0$, corresponding to the highest spectrum of figure 4.2. The PL band of Ge-ODC(II), as acquired immediately after the end of the laser pulse, is peaked at $\sim 4.4$ eV and has a $\sim 0.45$ eV FWHM consistent with literature data [18].

Completely analogous time-resolved measurements were carried out on the PL activity of F-type centres in the LiF sample. This specimen was excited at 450 nm (2.76 eV), as indicated with an arrow in the absorption spectrum of LiF sample shown in figure 4.6, and its luminescence was collected by varying $t$ from 0 to 100 ns.
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

![Figure 4.5: Low temperature luminescence of Ge-ODC(II) in the I301 sample. PL band is obtained by exciting at the maximum of the absorption band and acquired for \( t=0 \) and with \( t_W=1 \) ns. The continuous line is the result of the fitting procedure by our theoretical model. The Poissonian homogeneous shape is also shown (see discussion).](image)

We report in figure 4.7 the luminescence signal detected in LiF at \( t=0 \). It is apparent that the PL signal of LiF comprises two contributions peaked at \( \sim 2.3 \) eV and \( \sim 1.8 \) eV. These signals are known to be associated with two different defects, the \( F_3^+ \) and \( F_2 \) centres respectively, both consisting in aggregates of F-type centres \([87, 92]\). In particular, the main \( \sim 2.3 \) eV band with a \( \sim 0.27 \) eV FWHM is due to \( F_3^+ \), consisting in two electrons localized on three adjacent anion vacancies \([87]\).

For each activity (Ge-ODC(II) and \( F_3^+ \)), one can extract the time dependence of the first moment of the luminescence bands from the time-resolved measurements\(^1\) (e.g. those in figure 4.2 in the case of Ge-ODC(II)). Data so-obtained are reported in figure 4.8. The origin of the time scale corresponds to \( t=0 \).

We observe that the PL activity in silica shows an approximately linear decrease in the first moment as a function of time, while this decrease is not observed in LiF, where the first moment of the \( F_3^+ \) centres band has a constant value within experimental sensitivity. As already discussed in the theoretical section 4.1, the progressive

\(^1\)As regard of the PL activity of the LiF sample, we have fitted the total lineshape with different gaussian curves to include the two luminescenc contributions. Then, in order to analyze the \( F_3^+ \) centres only we have calculated the first moment of those gaussian related only to the high energy PL band.
4.2. Fluorescence in silica and in crystalline lithium fluoride

Figure 4.6: Absorption spectrum in the UV region for the LiF crystalline sample. The arrow indicates the excitation energy used in the luminescence measurement (2.76 eV).

Figure 4.7: Low temperature luminescence of F-centres in the LiF sample. PL bands are obtained by exciting at the maximum of the absorption band and acquired for \( t = 0 \) and with \( t_W = 1 \) ns. The continuous line is the result of the fitting procedure by our theoretical model. The Poissonian homogeneous shape is also shown (see discussion).
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

**Figure 4.8:** First moment of the emission band of Ge-ODC(II) (white circles) and of $F_3^+$ (white squares). The continuous lines are the results of the fitting procedure by our theoretical model (see discussion).

Shift of the PL peak position observed for ODC(II) defects can be alternatively understood as a dependence of the luminescence lifetime from the spectral position within the emission band. Hence, in figure 4.9 we report the values $\tau(E)$ of the PL lifetime as a function of the emission energy. The lifetimes were estimated for both PL activities by least-square fitting data from time-resolved spectra at different emission energies with an exponential function $I(t) = I(0)e^{-t/\tau}$. To show the accuracy of this procedure we report in figure 4.10 the experimental decays (coloured circles) as measured at different emission energies inside the PL band of Ge-ODC(II) centres, together with the fitting exponential curves (coloured lines).

At the chosen temperature, the decays are purely exponential for both activities [22, 93]. Figures 4.9 and 4.10 show that the lifetime of Ge-ODC(II) centres in silica strongly varies within the emission band: $\tau$ goes from $\sim 7$ ns to $\sim 11$ ns. On the contrary, the lifetime of $F_3^+$ centres is almost constant in the observed range of emission energies. The above results were obtained exciting at the absorption peak for both PL activities. We performed the same measurements for different excitation energies within the absorption band, and a weak dependence of lifetime from this

---

$^2$In regard to LiF, the fits were carried out in the range $\sim 2.10$ to $2.60$ eV so as to avoid the region of the $F_3^+$ emission band possibly affected by the overlap with the signal due to $F_2$. 

52
4.2. Fluorescence in silica and in crystalline lithium fluoride

Figure 4.9: Decay lifetime as estimated by fitting with an exponential function data at different emission energies within the emission band of the Ge-ODC(II) centres in the I301 sample (white circles) and of the $F_{3}^{+}$ in the LiF sample (white squares). The continuous lines are the results of the fitting procedure by our theoretical model (see discussion).

Figure 4.10: Experimental decays (coloured circles) of Ge-ODC(II) centres as measured in the I301 sample for different emission energies and corresponding fitting curves with mono-exponentials functions (coloured lines).
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

Figure 4.11: Emission bands of Ge-ODC(II) in the I301 silica sample (white circles) and in a Ge-doped sol-gel silica sample (black triangles). In the inset is reported the lifetime dispersion for both samples.

parameter was evidenced, consistently with previous results [22]. We are going to discuss this dependence in the chapter 7.

Finally, to avoid any ambiguity on the interpretation of the present results due to potential coexistence of the overlapping PL activity of Si-ODC(II) in natural fused silica we have compared the PL activity of the I301 silica sample with the same one excited in a sol-gel silica sample doped with 1000 ppm of Ge atoms, prepared as described in Ref. [5]. This kind of preparation guarantees that the Ge-ODC(II) optical activity is predominant, in particular, respect to that of the intrinsic Si-ODC(II) which is virtually absent. In figure 4.11 we thus report the emission lineshape related to I301 sample (white circles) and to Ge-ODC(II) activity obtained on the sol-gel sample (black triangles) and in the inset the dispersion of lifetimes for both samples; the comparison permits to state that both materials are representative of Ge-ODC(II) centres.

4.2.2 Discussion

The results in figures 4.8 and 4.9 qualitatively confirm the predictions of our theoretical analysis, i.e. that the dependence of the lifetime on the emission energy or, equivalently, the progressive red-shift of the emission peak with time, are charac-
4.2. Fluorescence in silica and in crystalline lithium fluoride

teristic features of luminescent defects embedded in a glassy matrix, as opposed to “crystalline” defects, here monitored by the luminescence of $F_3^+$ centres. We again stress that the non-radiative decay channels are almost completely quenched for both PL signals at the temperature at which the experiments were performed [22, 87]. As a consequence, it is a very good approximation to consider the luminescence decay to be purely radiative. The main point of the following discussion is to fit all experimental data by our model and extract the values of the homogeneous and inhomogeneous widths of the PL emission bands and other interesting physical parameters.

For both investigated PL activities we have performed numerical integration of Eq. (4.3) to obtain a set of three theoretical curves which simultaneously fit i) the shape of the PL band at $t=0$, ii) the time dependence of the first moment (calculated by Eq. (4.4)) and iii) the dependence of $\tau$ on emission energy\(^3\). To increase the reliability of the fit procedure, the half Stokes shift $S$ was fixed to the value obtained experimentally by measuring the difference between the spectral positions of the absorption and emission peaks: $S=0.38$ eV and $S=0.24$ eV in silica and LiF, respectively. In this way, the fitting procedure was performed by varying only four free parameters, $\hat{E}_0$, $\sigma_{in}$, $\sigma_{ho}$ and $\gamma$. From the experimental point of view, the vibrational sub-structure of homogeneous luminescence bands cannot usually be resolved due to the bandwidth of the measuring system and to further broadening effects due for instance to the coupling with several low energy modes. To take into account this effect, the homogeneous lineshape, Eq. (4.1), was convoluted with a gaussian distribution of a narrow half-width $\hbar\omega_p$ before being inserted into Eq. (4.3).

The continuous lines in figures 4.5, 4.7, 4.8 and 4.9 represent the results of our fitting procedure. It is worth underlining the goodness of the fit, obtained by using only four parameters, and considering especially that data in figures 4.8 and 4.9 take into account simultaneously all data acquired in a time-resolved PL measurement (typically $\sim 600$ spectral positions for each of the $\sim 100$ temporal acquisitions of figure 4.2). Table 4.1 summarizes the best parameters obtained via our fitting procedure for the two investigated PL activities. From data in table 4.1 we can also calculate the Huang-Rhys factor $H = S^2/\sigma_{ho}^2$, the vibrational frequency $\hbar\omega_p = \sigma_{ho}^2/S$, the

\(^3\)The lifetimes predicted by the model were estimated by least-square fitting the decay curves (not reported) predicted by Eq. (4.3) at different emission energies with a single exponential. It is worth noting that the simulated data (as real data) feature no appreciable non-exponential behaviour in the timescale of experimental data, at least when the parameters of the model are close to the best-fit ones.
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

Table 4.1: Upper section: best fitting parameters obtained by our theoretical model for the investigated PL activities. Lower section: Values of $\lambda$, $\sigma_{\text{tot}}$, $h\omega_p$, $H$, and $f$, as calculated from best fitting parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_0$ [eV]</th>
<th>$\sigma_{\text{in}}$ [meV]</th>
<th>$\sigma_{\text{ho}}$ [meV]</th>
<th>$S$ [eV]</th>
<th>$\gamma$ [$10^6 \text{eV}^{-3} \cdot \text{s}^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I301</td>
<td>4.70±0.05</td>
<td>177±10</td>
<td>93±12</td>
<td>0.38±0.02</td>
<td>1.41±0.09</td>
</tr>
<tr>
<td>LiF</td>
<td>2.50±0.02</td>
<td>20±10</td>
<td>109±6</td>
<td>0.24±0.02</td>
<td>10.0±0.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ (%)</th>
<th>$\sigma_{\text{tot}}$ [meV]</th>
<th>$h\omega_p$ [meV]</th>
<th>$H$ [eV]</th>
<th>$f$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I301</td>
<td>78±5</td>
<td>200±10</td>
<td>23±6</td>
<td>17±5</td>
<td>0.07±0.02</td>
</tr>
<tr>
<td>LiF</td>
<td>3±2</td>
<td>111±6</td>
<td>51±7</td>
<td>5±1</td>
<td>0.32±0.04</td>
</tr>
</tbody>
</table>

The total half-width (from $\sigma_{\text{tot}}^2 = \sigma_{\text{in}}^2 + \sigma_{\text{ho}}^2$), and finally we introduce the parameter $\lambda = \sigma_{\text{in}}^2/\sigma_{\text{tot}}^2$ which estimates the degree of inhomogeneity: in fact it is comprised between 0 ($\sigma_{\text{in}}=0$, that is no heterogeneity) and 1 ($\sigma_{\text{in}} = \sigma_{\text{tot}}$, that is a completely inhomogeneous band). All these quantities are reported in table 4.1 as well. The mean vibrational frequencies $h\omega_p$ for the I301 and LiF samples result to be 23±6 and 51±7 meV, respectively. These values confirm a posteriori the goodness of the approximation of no population of the excited vibrational levels (0 K degrees approximation), as discussed in the theoretical analysis of chapter 2. Indeed, the experimental temperature (25 K) corresponds to a Boltzmann energy of $\simeq 2 \text{ meV}$ unable to populate the first excited vibrational level far almost $\simeq 23 \text{ meV}$ from the ground level.

As expected, $\lambda$ is very small for the LiF defects in comparison with the amorphous ones: $\sim 3\%$ against $\sim 78\%$. These values correspond to $\sigma_{\text{in}}$ being about 0.2 times and 2 times $\sigma_{\text{ho}}$ in LiF and SiO$_2$ respectively. To show that our result on the inhomogeneous width is related to a general feature of amorphous silica, we want here mention another work based on the stability of point defects in silica undergoes to thermal treatments in controlled atmospheres [94]. In particular was found that ODCs(II) show a characteristic reactivity with water which can be explained only

\footnote{Alternatively, one can estimate $\sigma_{\text{tot}}$ directly from experimental data, so obtaining a consistent value.}
supposing a distribution of activation energy for the reactions. This distribution can be considered as a mirror of the inhomogeneous distribution of geometrical features in the local environments of ODC(II) as we supposed for their optical activities of luminescence [94]. We note also that the inhomogeneous broadening in the crystalline sample is not exactly zero; beside the approximations in our model, we note that a real crystal is always distorted by some dislocations, strains or other imperfections distributed at random into the matrix.

The obtained value of \( \lambda \) for Ge-ODC(II) shows that for a defect embedded in a glassy matrix the inhomogeneous width can be prominent with respect to the homogeneous one. This conclusion may be at variance with previous suggestions that \( \sigma_{ho} \) and \( \sigma_{in} \) are typically comparable [18].

In figures 4.5 and 4.7 we also show the discrete Poissonian homogeneous lineshape of half-width \( \sigma_{ho} \) and ZPL position \( \hat{E}_0 \), as obtained by our fit procedure for both investigated activities. As already pointed out, the crystalline PL band is completely described by the homogeneous shape,\(^5\) whereas the silica PL band is not reproduced without taking into account inhomogeneous effects. It is also worth noting that the

\(^5\)As explained above, the homogeneous shape is obtained by a convolution of the discrete Poissonian with a narrow gaussian curve of half-width \( h\omega_p \) to take into account further homogeneous broadening effects and the experimental bandwidth.
value $\hbar \omega_p = 23 \pm 6$ meV obtained via our fitting procedure is very close to the value of 26$\pm$2 meV found for the same defect by the analysis of the temperature dependence of the experimental absorption linewidth [68]. Moreover, $\hbar \omega_p$ is in good agreement with experimental and computational works on silica glasses which predict the presence of vibrational modes of low frequency [23, 95, 96].

It is also important mentioning other research works on silica, focused on the role played by disorder in modifying the main features of the VUV absorption edge, that is the electronic absorption transitions related to states in the valence and conduction bands [97, 98]. Indeed, in these works the frequency of the mean vibrational mode responsible of the observed thermal dependence of the edge in silica was estimated. For dry silica (the same kind as I301 material) the value 79$\pm$8 meV was determined [97], whereas for wet silica (type III) the value 32$\pm$5 meV [98] was obtained. In this second case the presence of silanol groups (OH molecules bonded to an Si atom) affects the vibrational properties of the amorphous network, in particular favoring softer vibrational modes [98]. In general, considering the different approaches and techniques, both results can be successfully compared with the value found here for the mean vibrational frequency, 23$\pm$6 meV. We remark also that the absorption edge is a properties of the amorphous system as a whole and thus the agreement with our result is particular valuable. All these results further confirm the correctness of our analysis.

To show the accuracy of our fitting procedure in determining $\lambda$, in figure 4.12 we compare the experimental lifetimes of Ge-ODC(II) in the I301 sample with the predictions of our model obtained for different $\lambda$ values. The theoretical $\tau(E)$ curves are obtained by keeping $\sigma_{tot}$ fixed to the value which best fits the overall experimental shape of the PL band. This analysis clearly evidences a continuous transition from constant lifetimes for $\lambda=0$ (that is a completely homogeneous PL band), to an inverse cubic dependence of $\tau$ from emission energy (dashed line) for $\lambda=1$ (that is a completely inhomogeneous PL band).

Finally, the oscillator strength $f$ reported in table 4.1 is calculated substituting the value of $|D|^2$, calculated from the fitting parameter $\gamma$, in the expression 2.11, where we have also used for $E_{Abs}$ the value $\tilde{E}_0 + S$. In regard to the effective field correction (see page 26), the term $\frac{1}{n} \left( \frac{E_{eff}}{E_{ext}} \right)^2$ calculated within the Onsager model [2, 12], results to be close to unity both in SiO$_2$ (n$\sim$1.5) and in LiF (n$\sim$1.4) in the investigated spectral range. The oscillator strength found here for Ge-ODC(II) in silica is consistent with the range of values reported in literature [18]: 0.03-0.07. For $F_{3+}^3$ centres in LiF our
4.3. Phosphorescence in silica and in crystalline sapphire

The main assumption of our model that all amorphous effects can be completely accounted for by a simply gaussian distribution of a single homogenous parameter (i.e. zero phonon line) is strongly corroborated by the excellent agreement between theoretical curves and data. On the other side, a distribution of the emission peak $E_0 - S$ is strongly suggested \textit{a priori} by the almost Einstein-like proportionality of $1/\tau$ on $E^3$ shown by experimental data in figure 4.12.

Moreover, as ulterior example of a direct connection between geometrical distribution in silica matrix and spectral features, in figure 4.13 (adapted from [100]) we report the energy values of ground ($S_0$) and electronic excited levels ($T_0$, $S_1$, $T_2$) estimated by ab-initio theoretical calculations [2], calculated for a simplified model of the Ge-ODC(II), that is a two-fold coordinated Ge atom linked to two O atoms terminated with hydrogen ones [100]. It is possible to observe that to each O-Ge-O angle corresponds a different energy value of electronic levels. In a amorphous matrix, where is reasonable a statistical distribution of the angle, this dependence could map itself in a spectral distribution of the energy of electronic levels. This could be the microscopical justification of the dispersion of the ZPL here supposed and in principle could be suggest a way to determine the statistical distribution of the angle O-Ge-O.

It is important noting that in our theoretical scheme $\gamma$ and thus $|D|^2$ are assumed as undistributed parameters. This means that the oscillator strength given by Eq. (2.11) can be distributed only as a consequence of the variations of $E_{Abs}$ associated with different homogeneous absorption sub-bands.

Finally, at this point is important to discuss the possibility of a spectral hole burning experiments (SHB) on this kind of defects. As observed in section 1.3 the SHB absorption spectrum reveals a hole $2\sigma_{ho}$ wide. Our results give $2\sigma_{ho}=186\pm24$ meV for the hole width which should be compared with the total width $\sigma_{tot}=200\pm10$ meV. We can conclude that observing so wide a hole in the OA band is very difficult, indeed it should appear as a global decrease in the total absorption signal. From a general point of view we can thus conclude that our experimental and analysis approach can be successfully used to analyze inhomogeneous systems described by any values of the $\lambda$ parameter, whereas at variance spectral hole burning technique can be applied only to those systems characterized by values of $\lambda$ parameter close to one.
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

Figure 4.13: Energy dependence of the O-Ge-O angle value of ground and excited electronic levels for the molecule sketched in the lower part of the figure. The arrows indicate the absorption and luminescence process (adapted from [100]).

4.3 Phosphorescence in silica and in crystalline sapphire

In the previous section we have introduced a new experimental investigation approach, based on time-resolved luminescence measurements, which was able to yield an experimental estimation of the homogeneous and inhomogeneous linewidth of the fast (ns lifetime) ODC(II) luminescence band due to decay from the first excited singlet electronic state ($S_1$). In this section we generalize our analysis applying this approach to the same model defect, i.e. the ODC(II) in silica, studying also the “slow” band assigned to the de-excitation from the first triplet $T_1$ state. This phosphorescence band is here excited directly populating the $T_1$ state to avoid possible inhomogeneous effects arising from the ISC process when excited from the $S_1$ state, as suggested by previous evidences [22, 68]. Our aim is to find out whether our approach is applicable also to a “slow” ($\mu$s lifetime) triplet emission band and if the extent of inhomogeneous effects affecting triplet and singlet emission processes are comparable or not.

Finally, in order to compare the results with those obtained in a system where
4.3. Phosphorescence in silica and in crystalline sapphire

Figure 4.14: Time evolution of the lineshape of triplet Ge-ODC(II) PL signals excited at 3.75 eV. Different spectra detected at different time delays from the laser pulse are shown. The dashed line follows the position of PL peaks as a guide to the eyes.

Inhomogeneous effects should be absent, we report the same study performed on a “slow” PL in an as-grown commercial sapphire sample ($\alpha$-Al$_2$O$_3$) provided by A.D. Mackay Inc. and rod flame polished [88]. Moreover, although the luminescence activity of defects in irradiated or doped sapphire was extensively studied in the past, several aspects about the decay kinetics, defects inter-conversion processes, band attributions and structural models of the emitting defects are not clear yet [101–103].

4.3.1 Experimental results

We show in figure 4.14 the time-resolved spectra of the triplet ($T_1 \rightarrow S_0$) (see the general level scheme in figure 1.1) PL activity of Ge-ODC(II) in the I301 silica sample. The measurements were performed under laser excitation at 330 nm (3.75 eV), corresponding to the $S_0 \rightarrow T_1$ absorption peak, with an energy density per pulse of 1.00±0.02 mJ/cm$^2$. The PL signal was collected by using the 300 grooves/mm grating (blaze at 500 nm) with a 4 nm spectral bandwidth. The PL decay was followed by performing different acquisitions with the same integration time $t_W=15$ µs at different delays $t$, going from 0 to 300 µs from the laser pulse. The dashed line drawn in figure 4.14 follows the emission peaks at different time delay $t$ and it appears not
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

**Figure 4.15:** Panel-a: Luminescence emission lineshape of triplet Ge-ODC(II) activity as measured upon excitation at 3.75 eV, immediately after the end of laser pulse ($t=0$). Panel-b: decay kinetics observed at the peak emission energy (3.1 eV). Panel-c: Decay lifetimes as a function of the emission energy. Panel-d: First moment of the emission band as a function of time delay. The continuous lines represent the results of the fitting procedure by our theoretical model (see discussion).

vertical, indicating an experimental detectable red shift of luminescence band during the decay.

In figures 4.15-(a) and 4.16-(a) we report the signals acquired at $t=0$ for the two PL activities of the Ge-ODC(II), corresponding to the most intense spectra of figures 4.14 and 4.2, respectively. The triplet PL band of Ge-ODC(II), as acquired immediately after the end of the laser pulse, is peaked at $\sim$3.1 eV and features a 0.44 eV width (Full Width at Half Maximum, FWHM).

Analogous time-resolved measurements were carried out on the PL activity in the sapphire sample by using a 230 nm (5.40 eV) excitation wavelength, and a 150 grooves/mm grating (blaze at 300 nm) with a 8 nm bandwidth. The decay was followed varying $t$ from 0 to 400 µs and with $t_W=4$ µs. We report in figure 4.17-(a) the spectrum acquired for $t=0$: the PL band observed in sapphire, as acquired immediately after the end of the laser pulse, is peaked at $\sim$2.9 eV and features a 0.60 eV FWHM.

The spectroscopic parameters of the signal in figure 4.17-(a) are consistent with a

---

6For better comparison between singlet and triplet luminescence of Ge-ODC(II) we rearrange in this new figure 4.16 the experimental results found in section 4.2 for the singlet luminescence.
4.3. Phosphorescence in silica and in crystalline sapphire

Figure 4.16: Panel-a: Luminescence emission lineshape of singlet Ge-ODC(II) activity as measured upon excitation at 5.17 eV, immediately after the end of laser pulse ($t=0$). Panel-b: decay kinetics observed at the peak emission energy (4.4 eV). Panel-c: Decay lifetimes as a function of the emission energy. Panel-d: First moment of the emission band as a function of time delay. The continuous lines represent the results of the fitting procedure by our theoretical model (see discussion).

Figure 4.17: Panel-a: Emission lineshape of sapphire PL activity as measured upon excitation at 5.40 eV, immediately after the end of laser pulse ($t=0$). Panel-b: decay kinetics observed at the peak emission energy (2.9 eV). Panel-c: Decay lifetimes as a function of the emission energy. Panel-d: First moment of the emission band as a function of time delay.
luminescence signal previously observed in literature, and associated either to the so-called P-centre (an anion-cation vacancy pair featuring a charge transfer transition) as proposed by a few works [104, 105], or to an extrinsic defect as proposed in Ref. [106]. However, it is worth noting that the detailed structural model of the centre responsible for the observed luminescence is not relevant here. Indeed, to the purposes of the present work we are going to discuss this signal only as a model of a slow luminescence of a defect in a crystalline oxide and, as we will see, it presents a \( \sim \mu s \) lifetime.

From all time-resolved measurements one can extract the lifetime dispersion curves, namely the dependence of the decay lifetimes from emission energy. To this purpose, the lifetimes were obtained by a fitting procedure of PL data at a given emission energy, carried out with a single exponential function for both activities of Ge-ODC(II), and with a double exponential function for sapphire PL activity, which may suggest the coexistence of two slightly different varieties of the optically active centre. Representative decays (and relative fitting curves) measured at the band peak energies, 3.1 eV, 4.4 eV and 2.9 eV for triplet Ge-ODC(II), singlet Ge-ODC(II) and sapphire PL signals, are reported in figures 4.15-(b), 4.16-(b), and 4.17-(b) respectively.

The lifetime of the triplet Ge-ODC(II) (figure 4.15-(c)) varies from \( \sim 130 \) to \( \sim 100 \) \( \mu s \) for emission energies increasing from 2.8 to 3.5 eV, while, as we already seen, that of the singlet Ge-ODC(II) (figure 4.16-(c)) varies from \( \sim 11 \) to \( \sim 7 \) ns in the 3.8-4.8 eV range. Finally, in the sapphire sample lifetime dispersion is not observed: indeed, the two lifetimes characterizing the luminescence decay are independent from emission energy: they remain fixed to \( \tau_A = 34 \) \( \mu s \) and \( \tau_B = 64 \) \( \mu s \) all over the range of the PL band.\(^7\)

As we known from previous discussions done in section 4.2, the observed energy dependence of the luminescence lifetime is expected to cause a progressive red shift of the first moment of the band, due to different temporal evolutions of different parts of the PL band. From measured spectra we have thus calculated the time dependence of the first moment of the luminescence bands: the results are reported in figures 4.15-(d), 4.16-(d) and 4.17-(d) for triplet Ge-ODC(II), singlet Ge-ODC(II) and sapphire activities respectively. The horizontal axes represent the time delay from the laser

\(^7\)It is worth noting that the double exponential behaviour of P-centre luminescence in sapphire is unknown at the best of our knowledge. In Ref. [104] the authors found a lifetime of \( \sim 50 \) \( \mu s \) which is consistent with the mean of the two lifetimes found here. It is beyond the aim of this work to investigate about the reason behind these decay features.
pulse in units of the lifetime $\tau_0$: for both Ge-ODC(II) activities $\tau_0$ is defined as the lifetime of PL signal at the central emission energies, 114 $\mu$s and 8.7 ns for triplet and singlet decays, respectively. For sapphire activity $\tau_0$ is chosen to be the mean value of the two experimental lifetimes $\tau_A$ and $\tau_B$. The choice of dividing the time scale for the parameter $\tau_0$ allow us the direct comparison between luminescence decays in different orders of time magnitude (nanosecond and microsecond). We observe that even the slow PL activity in silica, as the fast one, features an approximately linear red shift of the band as a function of time, whereas the first moment of the PL activity in sapphire has a constant value indicating the absence of luminescence spectral dispersion and consistent with the results found for the lifetime.

### 4.3.2 Discussion

The comparison between results on the oxygen deficient centres in SiO$_2$ and the defects in sapphire confirms what we had previously found on “fast” luminescence, and thus that the distribution of lifetimes measured for different emission energies and the correspondent red-shift of first moment of the band as a function of delay time, are peculiar features of defects embedded in amorphous solids as opposed to defects in crystals, where such effects are not observed. Present results yield a strong generalization of previous findings presented in section 4.2: indeed, data reported in section 4.3.1 demonstrate that the PL dispersion effect occurs also for the slow ($\mu$s) triplet luminescence of the Ge-ODC(II), so being independent from the temporal range of the decay kinetics as well as from the nature of the transition.

Moreover, in previous works on the PL of ODC(II) [22, 24, 37] the observed experimental results were associated with the inhomogeneous dispersion of the rates of ISC between $S_1$ and $T_1$. Our measurements, by using direct excitation towards the triplet state, overcome the ISC process excluding each possible interference of its related heterogeneity and giving direct information about the inhomogeneity of the $T_1$ electronic level.

Also, dispersion effects are absent in sapphire defects, similarly to what previously observed in LiF in section 4.2.1, and notwithstanding the double-exponential decay kinetics.

On the whole, our results suggest luminescence spectral dispersion to be a general optical property which allows to clearly discriminate the behaviour of defects embedded in amorphous solids from crystalline ones. At least, this appears to be true for oxides. Also, it is worth stressing that the lifetime of a PL band of defects
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

in a solid is widely regarded as a strong fingerprint of the defect, which can be used to unambiguously recognize it by time-resolved PL measurements. It is worth noting that, without taking care of lifetime dispersion effects evidenced here, lifetime differences as large as $\sim 30\%$ in amorphous systems can wrongly be regarded as signatures of different defects.

These experimental results can be discussed in the framework of the theoretical model presented in section 4.1 based on the hypothesis of gaussian distribution (centre $E_0$ and half-width $\sigma_{in}$) of the zero phonon energy $E_0$. This hypothesis accounts for the effect of the different environments which can accommodate different members of an ensemble of point defects in an amorphous matrix. As we did in section 4.2.2 the half Stokes shift $S$ of the triplet luminescence of Ge-ODC(II) is fixed to the experimental half difference between excitation energy and luminescence peak energy values: 0.30 eV. The continuous lines in figures 4.15 and 4.16 represent the results of our fitting procedure, while the histograms show the discrete Poissonian homogeneous lineshapes of half width $\sigma_{ho}$ as obtained by our fit procedure. Since the PL dispersion effect found here for Ge-ODC(II) is not evidenced in sapphire luminescence, we again argue that in a crystal, beside a few imperfections due to dislocations or strains, the inhomogeneous effects (and thus the related width) are virtually absent. As a consequence the red shift of the first moment of PL band and the dispersion of lifetimes are not possible, consistently with experimental results (see figure 4.17).

Upper part of table 4.2 resumes the best parameters obtained by our fitting procedure for the two luminescence transitions of Ge-ODC(II). In the lower part of table 4.2 we also report the parameter $\lambda = \sigma_{in}^2 / \sigma_{tot}^2$ which estimates the degree of inhomogeneity. On one hand, the results on the parameter $\lambda$ evidence that inhomogeneous effects strongly affect both the electronic transitions of the ODC(II) defects in silica. On the other side, the value of $\lambda$ for triplet emission of Ge-ODC(II) (56%) is smaller than that found for singlet emission (78%). Hence, the width of the inhomogeneous distribution turns out to be greater for the $S_1 \rightarrow S_0$ transition than for the $T_1 \rightarrow S_0$ one. This finding can be qualitatively visualized by comparing figure 4.15-(c) with figure 4.16-(c): in fact, the relative lifetime increase observed by moving leftwards by a FWHM on the horizontal axis is lower ($\sim 20\%$) for the triplet PL than ($\sim 35\%$) for the singlet PL band.

To confirm this result found on Ge-ODC(II), we have performed same kind of measurements on singlet and triplet luminescence activities on a sol-gel silica sample
4.3. Phosphorescence in silica and in crystalline sapphire

Table 4.2: Upper section: best fitting parameters obtained by our theoretical model for the investigated germanium related PL activities. Lower section: Values of $\lambda$, $\sigma_{\text{tot}}$, $\hbar\omega_p$, $H$, and $f$, as calculated from best fitting parameters

<table>
<thead>
<tr>
<th>Ge-ODC(II)</th>
<th>$E_0$ (±0.05) [eV]</th>
<th>$\sigma_{\text{in}}$ [meV]</th>
<th>$\sigma_{\text{ho}}$ [meV]</th>
<th>$S$ (±0.02) [eV]</th>
<th>$\gamma$ [eV$^{-3}$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triplet PL</td>
<td>3.38</td>
<td>140±8</td>
<td>125±16</td>
<td>0.30</td>
<td>(2.92±0.18) $10^2$</td>
</tr>
<tr>
<td>Singlet PL</td>
<td>4.70</td>
<td>177±10</td>
<td>93±12</td>
<td>0.38</td>
<td>(1.41±0.09) $10^6$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ge-ODC(II)</th>
<th>$\lambda$ (%)</th>
<th>$\sigma_{\text{tot}}$ [meV]</th>
<th>$\hbar\omega_p$ [meV]</th>
<th>$H$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triplet PL</td>
<td>56±4</td>
<td>188±9</td>
<td>52±14</td>
<td>6±2</td>
<td>(3.3±0.5) $10^{-5}$</td>
</tr>
<tr>
<td>Singlet PL</td>
<td>78±5</td>
<td>200±10</td>
<td>23±6</td>
<td>17±5</td>
<td>0.07±0.02</td>
</tr>
</tbody>
</table>

heavily doped with tin atoms. The purpose of doping is to obtain the iso-structural Sn-ODC(II) defects with related PL activity. In table 4.3 are reported the results of our fitting procedure on the experimental data (not shown) on the Sn-doped sample. We observe that, also for fast and slow luminescence of Sn-ODC(II), the inhomogeneous parameter $\lambda$ is considerable less for the triplet activity (40%) with respect to the singlet one (90%), confirming the results found for Ge-ODC(II). As regard, can be interesting to perform analogous measurements on the slow phosphorescence band of Si-ODC(II) to extend with more generality this result.

These results on germanium and tin atoms leads to an important consideration about the meaning of inhomogeneity: the inhomogeneous width has to be considered as a property of a specific electronic transition occurring at the defect site, rather than a property of the defect. As a matter of fact, the physical property of the defect which lies at the root of inhomogeneity effects is the site-to-site distribution of the structural parameters, such as bond angles and lengths. In this sense, the statistical distribution of $E_0$ should be regarded as a convenient, and synthetic, representation of inhomogeneity effects; the form and width of such a distribution are determined in principle by the detailed dependence of the zero phonon line $E_0$ from

---

8The description of this sample can be found in section 3.2 and the main results on the singlet PL activity of Sn-doped sample can be found in chapter 5 where are compared all singlet PL activities of silicon, germanium and tin ODC(II).
4. Luminescence activities of point defects in crystals and glasses: quantification of heterogeneity

**Table 4.3:** Upper section: best fitting parameters obtained by our theoretical model for the investigated tin related PL activities. Lower section: values of $\lambda$, $\sigma_{tot}$, $\hbar\omega_p$, $H$, and $f$, as calculated from best fitting parameters.

<table>
<thead>
<tr>
<th>Sn-ODC(II)</th>
<th>$E_0$  $\pm 0.05$ [eV]</th>
<th>$\sigma_{in}$ [meV]</th>
<th>$\sigma_{ho}$ [meV]</th>
<th>$S$  $\pm 0.02$ [eV]</th>
<th>$\gamma$ [eV$^{-3}$ · s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triplet PL</td>
<td>3.35</td>
<td>140$\pm$8</td>
<td>170$\pm$21</td>
<td>0.30</td>
<td>(4.2 ± 0.3)$10^3$</td>
</tr>
<tr>
<td>Singlet PL</td>
<td>4.52</td>
<td>195$\pm$10</td>
<td>65$\pm$10</td>
<td>0.41</td>
<td>(2.00±0.12)$10^6$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sn-ODC(II)</th>
<th>$\lambda$ (%)</th>
<th>$\sigma_{tot}$ [meV]</th>
<th>$\hbar\omega_p$ [meV]</th>
<th>$H$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triplet PL</td>
<td>40$\pm$4</td>
<td>220$\pm$11</td>
<td>98$\pm$20</td>
<td>3$\pm$1</td>
<td>(4.7±0.6) $10^{-4}$</td>
</tr>
<tr>
<td>Singlet PL</td>
<td>90$\pm$5</td>
<td>206$\pm$10</td>
<td>10$\pm$4</td>
<td>40$\pm$10</td>
<td>0.10±0.02</td>
</tr>
</tbody>
</table>

the microscopical structural parameters. Only quantum mechanical calculations can investigate the form of this mapping function, and may allow to understand why it ultimately results in a larger degree of inhomogeneity affecting the $S_1 \rightarrow S_0$ transition as compared to the $T_1 \rightarrow S_0$ transition of Ge-ODC(II) (or Sn-ODC(II)). Also, more experimental investigations are needed to find out whether this difference between triplet and singlet emissions is a general property of defects in amorphous systems or a peculiar feature of oxygen deficient centres in silica.

Finally, the value of the oscillator strength found here for the triplet band of Ge-ODC(II), is in agreement with the value $1.2 \cdot 10^{-5}$ reported in a review paper about oxygen deficiency centres in silica [18].

From data in the upper part of tables 4.2 and 4.3 we can also calculate the Huang-Rhys factor $H = S^2 / \sigma_{ho}^2$, the vibrational frequency $\hbar\omega_p = \sigma_{ho}^2 / S$, the total width (from $\sigma_{tot}^2 = \sigma_{in}^2 + \sigma_{ho}^2$). All these quantities are summarized in the lower part of tables 4.2 and 4.3.

### 4.4 Conclusions

In this chapter we have investigated the inhomogeneous properties of point defects in a glassy matrix, namely the effect of heterogeneity on optical activity. We have proposed a theoretical model, based on an extension of the standard theory of the
optical properties of point defects, incorporating a statistical distribution of the zero phonon line to account for the effects of the non-equivalent environments probed by each point defects in an amorphous matrix as opposed to a crystalline one. This model enlightens a direct connection between the dispersion of the radiative decay lifetime within a luminescence band as a function of emission energy and the inhomogeneous properties of defects in a glassy environment.

To confirm our prediction we have experimentally studied by time-resolved luminescence the extrinsic (Ge-related) oxygen deficient centres in amorphous silicon dioxide. Both the singlet and the triplet PL of the defect feature a dispersion of decay lifetimes within the emission band and a temporal red shift of their first moment (luminescence spectral dispersion). Comparison with luminescence of aggregates of F-centres in a crystalline sample of LiF defect and luminescence signal in a crystalline sample of sapphire confirms that these effects are peculiar of centres embedded in disordered solids. Our model is able to fit all experimental data and to provide an estimate of the ratio $\lambda = \sigma_{\text{in}}^2/\sigma_{\text{tot}}^2$ between the inhomogeneous and the total width. Moreover it allows us to determine the homogeneous parameters of ODCs: homogeneous width, oscillator strength, Huang-Rhys factor and the frequency of the vibrational local mode.

Finally, we find that the degree of inhomogeneity experienced by the triplet luminescence bands of germanium and tin ODC(II) is appreciably less than by the singlet ones indicating that the dispersion of homogeneous features in silica is probed by the electronic transition and is not a general characteristic of the type of defect.

Results found in this chapter have been published on and have been accepted for the publication on two scientific journals specialized in condensed matter and material physics; see list of publications at number 2 and 3, respectively in the Scientific Activity section.
Chapter 5

Inhomogeneous width of isoelectronic Si/Ge/Sn-ODC(II)

In chapter 4 we have successfully modeled the effect of the heterogeneity in silica by using the simple hypothesis of gaussian distribution of one homogeneous parameter, that is the zero phonon line $E_0$. Our theoretical viewpoint has been corroborated by experimental data acquired on both fast and slow luminescence decays in silica and in crystalline materials. In this chapter our aim is to go deeper in detail on a main topics of ODC(II) in silica: the luminescence of the isoelectronic series of ODC(II) related to silicon, germanium and tin atoms.

As we discussed in chapter 1 the ODC(II) can be observed in two extrinsic variants which, together with the intrinsic counterpart of this kind of point defect, form the so called isoelectronic series: same kind as imperfections based on three different atoms (silicon, germanium and tin) belonging to the same group as the periodic table and thus characterized by similar optical features. Previous optical measurements on the related luminescence bands have already suggested that ODC(II) are significantly affected by inhomogeneous effects [23, 67–69]. However, before of the partial result on Ge-ODC(II) presented in previous chapter, no quantitative estimation of their degree of inhomogeneity exists.

To fill this lack, in this chapter our aim is, by using our model, to study how the heterogeneity reflects itself in the PL properties of Si, Ge and Sn-ODC(II). We are going to show that low temperature time-resolved PL measurements reported here clearly confirm the presence of inhomogeneous effects and, furthermore, they provide for the first time the possibility of estimating the inhomogeneous and homogeneous
5. Inhomogeneous width of isoelectronic Si/Ge/Sn-ODC(II)

Figure 5.1: Lineshapes of Sn-ODC(II) PL activity at 10 K as excited by \( \sim 5 \) eV laser pulse. Different curves measured at different time delays from the laser are shown. The dashed line follows the PL peak position for eyes-guiding purpose.

widths of ODC(II) emission bands, and analyze how they depend on the nature of the central atom. We report measurements performed on three samples: i) a synthetic S300 sample; ii) the same fused silica sample named I301 investigated in chapter 4; iii) and a Sn-doped sample (see descriptions in section 3.2). These three samples were chosen because they contain, respectively, Si-ODC(II), Ge-ODC(II) and Sn-ODC(II) defects in the as-grown state. The laser energy density per pulse was fixed to 0.30\( \pm \)0.02 mJ/cm\(^2\).

5.1 Experimental results

In figure 5.1 we show a typical time-resolved measurement of the PL activity of Sn-ODC(II) in the Sn-doped silica sample. The measurement was performed at 10 K\(^1\) under laser excitation at 248 nm (5.00 eV) on the peak of the related \( S_0 \rightarrow S_1 \) Sn-ODC(II) absorption band. The PL signal was monitored, with the same integration time \( t_W = 0.5 \) ns, at different delays \( t \), going from 0 to 60 ns from the laser pulse. The

\(^1\)For this sample we have not used the usually 25 K because for Sn-ODC(II) the ISC process is active at lower temperature than Si and Ge-ODC(II).
dashed line reported in figure 5.1 follows the peak positions of PL band as a function of the delay time from the laser pulse: there is a clear evidence of a progressive change of the observed PL lineshape, whose peak moves from 4.2 eV at \( t=0 \) to 4.1 eV at \( t=28 \) ns.

In figure 5.2-(c) we report the signal acquired at \( t=0 \), corresponding to the most intense spectrum in figure 5.1. The PL band of Sn-ODC(II), as acquired immediately after the end of the laser pulse, is peaked at \( \sim4.2 \) eV and features a 0.48 eV FWHM.

Analogous time-resolved measurements were carried out on the PL activity of Si-ODC(II) defects in the S300 sample by using a 248 nm (5.00 eV) excitation wavelength on the peak of the related \( S_0 \rightarrow S_1 \) absorption band. The decay was followed varying \( t \) from 0 to 20 ns and with \( t_W=0.5 \) ns. We report in figure 5.2-(a) the spectrum acquired at \( t=0 \): the PL band of Si-ODC(II), as acquired immediately after the end of the laser pulse, is peaked at \( \sim4.45 \) eV and features a 0.35 eV FWHM.

Finally, to complete the PL data on the isoelectronic series and to give an unify view, we report in figure 5.2-(b) the same experimental data acquired on the I301 sample already shown in chapter 4.

For each of the three activities (Si-ODC(II), Ge-ODC(II), Sn-ODC(II)), we calculated the PL decay lifetime \( \tau(E) \) at different emission energies \( E \). At the chosen temperatures, the decay kinetics of all the three activities result to be single-exponential due to quenching of the non-radiative decay channels \([18, 19, 22, 23]\). As a consequence, the radiative lifetimes were obtained by fitting data at several values of emission energies \( E \) with a single exponential function (5.1):

\[
I(E, t) = I(E, 0)e^{-t/\tau(E)}.
\]

In figure 5.3 we report so-calculated lifetimes dispersion curves \( \tau(E) \) for all PL activities, we observe that they feature a dispersion of the radiative lifetime as a function of the emission energy: the lifetime goes from \( \sim4 \) to \( \sim5 \) ns for the Si-ODC(II), from \( \sim7 \) to \( \sim11 \) ns for the Ge-ODC(II) and from \( \sim5 \) to \( \sim9 \) ns for the Sn-ODC(II). Also, we calculated by numerical integration from time-resolved spectra the time dependence of the first moment \( M_1(t) \) of the luminescence bands as described by Eq. 4.4. The temporal behaviour of first moments for the three PL activities are reported in figure 5.4, where the horizontal axis represents the time delay \( t \) from the laser pulse in units of the central lifetime \( \tau_0 \) observed at the peak emission energy (indicated in figure 5.3). We observe that all PL activities in silica feature an approximately linear decrease in the first moment \( M_1(t) \) in time, with a negative slope increasing with the atomic weight of ODC(II) defects. As already discussed in chapter 4, the
5. Inhomogeneous width of isoelectronic Si/Ge/Sn-ODC(II)

Figure 5.2: Low temperature luminescence lineshape of Si-ODC(II) (panel-a), Ge-ODC(II) (panel-b) and Sn-ODC(II) (panel-c) at $t=0$. The continuous line is the result of the fitting procedure by the theoretical model exposed in chapter 4; the dashed line is the homogeneous Poissonian line shape (see discussion).
5.1. Experimental results

**Figure 5.3:** For Si-ODC(II) (squares), Ge-ODC(II) (circles) and Sn-ODC(II) (triangles) decay lifetime as measured at different emission energies within the emission band. The continuous line is the result of the fitting procedure by our theoretical model (see discussion).

**Figure 5.4:** For Si-ODC(II) (squares), Ge-ODC(II) (circles) and Sn-ODC(II) (triangles) first moment of the emission band. The continuous line represents the result of the fitting procedure by our theoretical model (see discussion).
two results are directly connected: indeed, the dependence of the lifetime from the
spectral position within the emission band corresponds to (and can be alternatively
understood as) a progressive shift of first moment of PL bands; moreover the dif-
ferent dependencies of $\tau$ from emission energy of figure 5.3 correspond, as expected,
to different slopes in figure 5.4. Summing up, these experimental findings are the
ultimate reasons that bring about the observed dispersion of the emission lineshape
as observed representatively in figure 5.1 for the Sn-doped sample.

5.2 Discussion

We can use the theoretical model proposed in chapter 4 that allows to under-
stand the behaviour of ODC(II) in figures 5.3 and 5.4 namely the distribution of
lifetimes measured at different emission energies and the correspondent red-shift of
the first moment of the singlet PL band as a function of delay time. As discussed
in the previous chapter we suppose that the ODC(II) PL band arises from the in-
homogeneous overlap of bands peaked at different energies, statistically distributed
within the defect population. Also, experimental data suggest that the degree of
inhomogeneity increases while moving along the Si/Ge/Sn series. In fact, both the
slope of $\tau(E)$ (figure 5.3) and that of $M_1(t)$ (figure 5.4) grow with increasing atomic
weight of the central atom, thus suggesting the occurrence of progressively stronger
inhomogeneous effects.

This argument can be made quantitative by fitting experimental data, for each of
the investigated PL activities, with our model [Eq. (4.3)] in order to estimate $\sigma_{in}$ and
$\sigma_{ho}$. Specifically, we have determined by least-square optimization the best values of
the parameters ($\tilde{E}_0$, $\sigma_{in}$, $\sigma_{ho}$ and $\gamma$) that produce a set of three theoretical curves
simultaneously fitting the PL shape at $t=0$ (figure 5.2), the dispersion of the decay
lifetimes (figure 5.3) and the kinetics of the first moment (figure 5.4). The continuous
lines in figures 5.2, 5.3 and 5.4 represent the results of our fitting procedure. It is
worth noting the goodness of the fit obtained by using only four free parameters
considering the contemporaneously minimization on spectral and temporal data.
Only for the lineshape at $t=0$ of Sn-ODC(II) the fitting curve does not reproduce
well the experimental data: this could be due to the presence of another spurious
PL signal at lower energy which apparently enlarges the band, or to the partial
failure for this defect of the approximations inherent in our model, e.g. more than
one homogeneous parameter to be distributed or different statistical distribution for
5.2. Discussion

Table 5.1: Upper section: best fitting parameters obtained by our theoretical model for the investigated PL activities. Lower section: values of $\lambda$, $\sigma_{\text{tot}}$ (calculated by $\sigma^{2}_{\text{tot}} = \sigma^{2}_{\text{in}} + \sigma^{2}_{\text{ho}}$), $\hbar \omega_p$, $H$ and $f$ as calculated from best fitting parameters.

<table>
<thead>
<tr>
<th>ODC(II)</th>
<th>$E_0$ (±0.05) [eV]</th>
<th>$\sigma_{\text{in}}$ [meV]</th>
<th>$\sigma_{\text{ho}}$ [meV]</th>
<th>$S$ (±0.02) [eV]</th>
<th>$\gamma$ [10^{-6} eV^{-3} s^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>4.69</td>
<td>110±10</td>
<td>80±10</td>
<td>0.27</td>
<td>2.60±0.16</td>
</tr>
<tr>
<td>Ge</td>
<td>4.70</td>
<td>177±10</td>
<td>93±12</td>
<td>0.38</td>
<td>1.41±0.09</td>
</tr>
<tr>
<td>Sn</td>
<td>4.52</td>
<td>195±10</td>
<td>65±10</td>
<td>0.41</td>
<td>2.00±0.12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ODC(II)</th>
<th>$\lambda$ (%)</th>
<th>$\sigma_{\text{tot}}$ [meV]</th>
<th>$\hbar \omega_p$ [meV]</th>
<th>$H$</th>
<th>$f$ (±0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>65±4</td>
<td>136±10</td>
<td>24±4</td>
<td>11±4</td>
<td>0.13</td>
</tr>
<tr>
<td>Ge</td>
<td>78±5</td>
<td>200±10</td>
<td>23±6</td>
<td>17±5</td>
<td>0.07</td>
</tr>
<tr>
<td>Sn</td>
<td>90±5</td>
<td>206±10</td>
<td>10±4</td>
<td>40±10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

the $E_0$ homogeneous parameter. However, the behaviour of first moment and lifetime dispersion are still well reproduced by the theoretical model; hence, we consider the numerical results to be reliable also in this case. In figure 5.2 we also show, with dashed line, the Poissonian homogeneous lineshape of width $\sigma_{\text{ho}}$ as obtained by our fit procedure for all investigated activities.

The upper part of table 5.1 resumes the best parameters obtained for all investigated PL activities. We calculate the parameter $\lambda = \sigma^{2}_{\text{in}}/\sigma^{2}_{\text{tot}}$ which estimates the degree of inhomogeneity. The high values (>65%) of $\lambda$ show that inhomogeneous effects strongly condition the optical properties of all the ODC(II) defects in silica, $\sigma_{\text{in}}$ being the main contribution to the total width for all centres. In a sense, this could be expected a priori for a point defect found exclusively in the amorphous phase of SiO$_2$. On the other hand, it is worth noting that the degree of inhomogeneity is remarkably high, particularly for Sn-ODC(II). For this latter defect, the order of magnitude of the site-to-site fluctuations of the emission peak position results to be as large as $\sigma_{\text{in}}$~0.2 eV.

The degree of inhomogeneity, although, systematically varies along the isoelectronic series: the value of $\lambda$ of extrinsic Sn-ODC(II) defects (Sn-doped sample) is higher than that of Ge-ODC(II) extrinsic centres (I301 sample), which is in turn
5. Inhomogeneous width of isoelectronic Si/Ge/Sn-ODC(II)

higher than Si-ODC(II) intrinsic defects (S300 sample). These variations of $\lambda$ are mainly due to the growth of $\sigma_{in}$ with atomic weight, since variations of $\sigma_{ho}$ are weaker. This trend can be tentatively interpreted as follows: Ge and Sn impurities are isoelectronic to Si atoms and thus able to be accommodated in substitutional positions in the silica matrix. Nonetheless, the distortion they cause to the matrix presumably extends over a larger surrounding volume than a single SiO$_2$ tetrahedra due to their being bigger and heavier than their intrinsic counterpart. A bigger volume affected by the presence of the defect is expected to result in a higher sensitivity to site-to-site structural fluctuations, which possibly causes stronger fluctuations of $E_0$. These considerations based on experimental results are at variance with previous ones based on computational findings in Ref. [107] where it was argue that heavier Ge and Sn atoms are much less sensitive to the details of local geometry. The results reported here complete the characterization of the isoelectronic series of oxygen deficient centres in silica, by yielding information about their inhomogeneous properties, which adds to existing knowledge founded on traditional spectroscopic investigation.

Other two parameters of interest can be calculated from $\sigma_{ho}$: the vibrational frequency $\hbar\omega_p = \sigma_{ho}^2/S$ and the Huang-Rhys factor $H = S^2/\sigma_{ho}^2$. In these expressions, the parameter $S$ represents the half Stokes shift, estimated experimentally by measuring the half-difference between the spectral positions of the excitation energy and emission peaks. $S$ results to be: 0.27, 0.38 and 0.41 eV, in Si, Ge and Sn-ODC(II) respectively. Based on these values of $S$, we calculate $\hbar\omega_p$ and $H$, which are reported in the lower part of table 5.1. The vibrational frequencies found here for ODC(II) defects show that all of them are preferentially coupled with very low frequency vibrational modes, accordingly with previous experimental and computational results [23, 95, 96]. Albeit the relatively high uncertainty on $\hbar\omega_p$ as determined by the fitting procedure, data show a decreasing trend while going from the lightest to the heavier ODC(II). Qualitatively, this is to be expected if one roughly assumes that the variations in the force constant of the vibration are negligible from Si to Sn: indeed, the frequency of a mode highly localized on the central atom should in this case be inversely proportional to the square of its mass. It is possible to object that the lower $\hbar\omega_p$ frequency obtained for Sn-ODC(II) could be affected by the worse fitting result obtained on its PL lineshape; on the other side, it is worth stressing that the above discussed results on heterogeneity are poorly affected by this fact, as they mainly depend on the well fitted slope of the first moment and lifetime dispersion curves. Finally, the values of the oscillator strength found here for the Si-ODC(II) is
in excellent agreement with the value 0.15 reported in a review paper about oxygen
deficiency centres in silica [18].

5.3 Conclusions

We have studied by time-resolved luminescence the defects belonging to the iso-
electronic series of oxygen deficient centres in amorphous silicon dioxide. The dis-
persion of the emission lineshape is used as a probe to quantitatively evaluate the
influence of inhomogeneous effects on the optical properties of the defects. We pro-
vided for Si-ODC(II), Ge-ODC(II), Sn-ODC(II) an estimate of the inhomogeneous
and homogeneous widths, on the grounds of a theoretical model that satisfactorily re-
produces all experimental data based on two main simple assumptions: homogeneous
optical properties governed by coupling with a single “mean” vibrational mode, and a
Gaussian distribution of the ZPL energy accounting for structural heterogeneity. The
degree of inhomogeneity of the defects turns out to grow regularly with the atomic
weight of the central atom, while the variations of the homogeneous properties are
weaker. Along with the homogeneous width, we estimate also the other homogeneous
parameters of oxygen deficient centres: oscillator strength, Huang-Rhys factor and
mean vibrational frequency of the electron-phonon interaction.

The results found in this section have been published on a scientific journal spe-
cialized in physical chemistry: see number 4 in the list of publications in the Scientific
Activity section.
Chapter 6

Irradiation effects on inhomogeneous width of ODC(II)

In this chapter our aim is to go deeper in detail on another important topic of ODC(II) in silica, that is point defects created from an unperturbed matrix with various kind of irradiations. In the first section 6.1, by using our model, we are going to study the inhomogeneous and homogeneous features of electron irradiated silica, whereas in the second section we will deal with neutrons and γ-rays induced point defects. In general, in both sections attention is paid to the comparison between inhomogeneous properties of as-grown and induced Si-ODC(II).

6.1 Si-ODC(II) induced by β-rays

In this section we use again the same experimental and analysis approach as chapters 4 to study the luminescence activity of as-grown and β-ray (fast electrons) induced Si-ODC(II). Our aim is to find out if and how defects equilibrated in the matrix during the synthesis process differ from irradiation-induced ones as concerns the inhomogeneous properties. Also, we want to use Si-ODC(II) as a probe to explore the influence of progressive high doses of β-irradiation on the disorder of the embedding silica matrix. To this purpose, we want to provide an estimation of the inhomogeneous width of Si-ODC(II) as a function of electron irradiation dose.

As anticipated in section 3.2 here we report measurements performed on the Suprasil F300 dry synthetic silica (cylindrically shaped with 5 mm diameter). This material was chosen because it presents a low concentration (5×10^{14} \text{ cm}^{-3}) of Si-
6. Irradiation effects on inhomogeneous width of ODC(II)

**Table 6.1:** First and second column: nickname and corresponding accumulated β dose of investigated samples. Third column: peak position of the photoluminescence emission band. Fourth column: decay lifetime measured at the peak emission energy.

<table>
<thead>
<tr>
<th>Sample Nickname</th>
<th>Dose [kGy]</th>
<th>$E_{peak}$ (±0.02) [eV]</th>
<th>$\tau_0$ (±0.2) [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F300 As-grown</td>
<td>4.47</td>
<td>4.41</td>
<td>4.3</td>
</tr>
<tr>
<td>EC1</td>
<td>1.2 $10^3$</td>
<td>4.41</td>
<td>4.1</td>
</tr>
<tr>
<td>EC2</td>
<td>1.2 $10^4$</td>
<td>4.40</td>
<td>3.8</td>
</tr>
<tr>
<td>EC3</td>
<td>1.2 $10^5$</td>
<td>4.38</td>
<td>4.2</td>
</tr>
<tr>
<td>EC4</td>
<td>1.2 $10^6$</td>
<td>4.38</td>
<td>4.9</td>
</tr>
<tr>
<td>EC5</td>
<td>5.0 $10^6$</td>
<td>4.37</td>
<td>4.4</td>
</tr>
</tbody>
</table>

ODC(II), detectable by luminescence measurements, already in the as-grown form. To obtain well measurable PL signals we cut from the as-grown material a slab of 2 mm thickness, hereafter named F300. Other thinner (0.2 mm) five pieces of Suprasil F300 were cut and were β-irradiated in a Van de Graaff accelerator (2.5 MeV electrons energy) with five different doses, ranging from $1.2\cdot10^3$ to $5\cdot10^6$ kGy, as indicated in table 6.1 together with the nicknames hereafter used for these samples. These five samples also show the luminescence activity related to induced Si-ODC(II), the intensity of which progressively grows with irradiation dose due to the contribution of radiation induced centres\(^1\) adding to those present already in the as-grown material. Photoluminescence measurements were done under excitation by a pulsed laser tuned at 248 nm (5.00 eV) and energy density per pulse of 0.30±0.02 mJ/cm\(^2\), corresponding to the $S_0\rightarrow S_1$ absorption peak of Si-ODC(II). The luminescence emitted by the samples was dispersed by a spectograph equipped with a 300 grooves/mm grating (blaze at 500 nm) with a spectral bandwidth of 3 nm. The PL decay was followed by performing different acquisitions with the same integration time $t_W=0.5$ ns but at different delays $t$, going from 0 to 30 ns from the laser pulse. All measurements reported here were performed on samples kept at cryogenic temperature to ensure the absence of non-radiative de-excitation pathways from excited electronic state, that is to prevent the activation of ISC process.

\(^1\)For further details on creation mechanisms of point defects in silica under irradiation see [6].
6.1. Si-ODC(II) induced by β-rays

Figure 6.1: Time evolution of the lineshape of Si-ODC(II) luminescence signals excited at ∼5 eV in the as-grown F300 sample. The continuous line follows the position of PL peaks whereas the dashed line indicates the peak position of the most intense spectrum at $t=0$ as a guide to the eyes.

6.1.1 Experimental results

In figure 6.1 we show the time-resolved measurement on the PL activity of Si-ODC(II) in the F300 as-grown silica sample. The continuous line follows the peak position of the PL band, showing a progressive red shift as a function of delay time from the laser pulse ($t=0$) if compared with the peak position of the first spectrum reported as well as a reference along all the time scale with a dashed line. Analogous measurements were performed on all irradiated samples, the ECn series, where n indicates an integer ranging from 1 to 5 related to samples submitted to the increasing dose of electrons as explained in table 6.1. In figure 6.2 we report the estimated concentration of Si-ODC(II) defects in all samples. We remark that the main absorption band (centered at ∼5 eV) of Si-ODC(II) related to the $S_0 \rightarrow S_1$ transition does not undergo remarkable spectroscopic changes because of the irradiation process, but becomes buried by the presence, in this spectral range, of absorption bands related to other induced point defects. For this reason, the concentrations of Si-ODC(II) in-
6. Irradiation effects on inhomogeneous width of ODC(II)

![Figure 6.2: Concentration of Si-ODC(II) in all investigated ECn samples estimated by luminescence signals. The dashed line is related to the concentration of the luminescence of the as-grown F300 sample.](image)

dicated in figure 6.2 have been determined by comparison of the PL intensity of ECn samples with the intensity of the luminescence signal in the as-grown F300 sample. Indeed, for this last sample it is possible to obtain the concentration of Si-ODC(II) by using the eq. 2.12 (see section 2.2), by measuring the absorption coefficient at \( \sim 5 \text{ eV} \) and using the value \( f=0.13 \pm 0.02 \) for the oscillator strength found for Si-ODC(II) point defects\(^2\) in section 5.2.

We observe that the concentration of \( \beta \)-induced defects in the EC1 sample is comparable to that of as-grown defects in the F300 sample. Thus, to ensure that our considerations about \( \beta \)-induced defects are not affected by the presence in the irradiated samples of a significant contribution of Si-ODC(II) already present before irradiation, we prefer to neglect this first irradiated sample EC1 and to consider only the rest of samples where the induced Si-ODC(II) concentration is almost one order of magnitude greater than that of as-grown defects. In figure 6.3 panels a)-e) we report the PL signal of Si-ODC(II) acquired at \( t=0 \) in all samples: for the F300 sample in panel (a) the points correspond to the most intense spectrum reported in figure 6.1. In figure 4.16 panels f)-j) we report the PL signal of Si-ODC(II) acquired at a delay

\(^2\)As we will see in the following, the present analysis gives the opportunity to numerically estimate the oscillator strength for all irradiated samples, and the values are always close to 0.14.
6.1. Si-ODC(II) induced by \(\beta\)-rays

t=10 ns for all samples.

The PL band of Si-ODC(II) in the F300 sample, as acquired immediately after the end of the laser pulse, is peaked at 4.45±0.02 eV and features a 0.35±0.04 eV FWHM, while the PL bands of irradiated ECn samples feature a different peak positions (red shifted to 4.35±0.02 eV) and a broader FWHM starting from the EC2 sample (0.40±0.04 eV) and increasing in the remaining EC3 (0.41±0.04 eV), EC4 and EC5 samples (both show a 0.44±0.04 eV FWHM). Regarding the spectra acquired after 10 ns from the end of the laser pulse in figure 4.16 panels f)-j), they appear red shifted with respect to the corresponding spectra at \(t=0\). In particular, the amount of the shift increases along the series of irradiated samples, as can be observed comparing the position of the emission band peaks at \(t=10\) ns (vertical solid lines) with that at \(t=0\) (vertical dashed lines).

From all time-resolved measurements (as that shown in figure 6.1) one can extract the lifetime dispersion curves, namely the dependence of the decay lifetime \(\tau\) from the emission energy. As representative example we shown in figure 6.4 the lifetime dispersion in the EC3 sample. The lifetimes were obtained by a fitting procedure with a single exponential function of time-resolved PL data at several spectral positions. Hereafter we indicate with the symbol \(\tau_0\) the lifetime of each luminescence activity measured at the peak emission energy \(E_{\text{peak}}\) (as indicated in figure 6.4 for EC3 sample). \(E_{\text{peak}}\) and \(\tau_0\) values estimated for all samples are reported in table 6.1.

The lifetime of the Si-ODC(II) luminescence in EC3 sample varies from \(\sim\)4.7 to \(\sim\)3.6 ns for emission energies increasing from \(\sim\)4.0 to \(\sim\)4.7 eV. This lifetime dispersion is found for all PL activities in all samples, independently from the fact that the defects are already present in the as-grown material (F300 sample) or induced by \(\beta\)-rays (EC2-EC5). For a better comparison between as-grown and induced defects we show only the results obtained from decay analysis of F300 and EC5 samples: in figure 6.5 we report the values of the lifetimes \(\tau\) in units of \(\tau_0\), as a function of the quantity \(E - E_{\text{peak}}\), that is the shift from the peak emission position. In this way the different experimental data are superimposed in the central point with \(\tau/\tau_0 = 1\) and \(E - E_{\text{peak}} = 0\). From figure 6.5 it is clear that induced defects (EC5) feature greater lifetime dispersion than as-grown ones (F300), as evidenced by a greater slope. The observed energy dependence of the luminescence lifetimes (figures 6.4 and 6.5) is expected to cause a progressive shift of the first moment \(M_1(t)\) of the PL band, due to different temporal evolutions of different parts of the band. From measured spectra we have thus calculated the time dependence of the first moment (see expres-
Figure 6.3: Luminescence emission lineshape of Si-ODC(II) activity as measured upon excitation at $\sim$5 eV for all investigated samples. Panels a)-e): PL signals acquired immediately after the end of laser pulse ($t=0$). Panels f)-j): PL signals acquired at a fixed time delay ($t=10$ ns). The emission peak positions at $t=0$ (vertical dashed lines) and after a delay of 10 ns (vertical solid lines) are shown. The continuous curves represent the results of the fitting procedure by our theoretical model (see discussion).
6.1. Si-ODC(II) induced by $\beta$-rays

Figure 6.4: Lifetime of luminescence of Si-ODC(II) in EC3 sample as a function of the emission energy inside the PL band. Are indicated the value of the lifetime $\tau_0$ measured at the energy of the band peak $E_{\text{peak}}$. The continuous line represents the results of the fitting procedure by our theoretical model (see discussion).

Figure 6.5: Lifetime in units of $\tau_0$ as a function of emission energy subtracted of $E_{\text{peak}}$ for luminescence activity of Si-ODC(II) in F300 (as grown defects) and EC5 samples (induced defects). The continuous lines represent the results of the fitting procedure by our theoretical model (see discussion).
6. Irradiation effects on inhomogeneous width of ODC(II)

Figure 6.6: Difference between first moment at a time delay $t$ and initial first moment at $t=0$ as a function of the time delay in units of $\tau_0$. The continuous lines represent the results of the fitting procedure by our theoretical model (see discussion).

For three representative samples (F300, EC3 and EC5) we report in figure 6.6 the values of the decrease (red shift) of the first moment (i.e. $\Delta M_1(t) = M_1(t) - M_1(0)$) as a function of the time delay $t$ in units of $\tau_0$. We observe that all PL activities, both associated with as-grown defects (F300 sample) and to induced defects (EC3 and EC5 samples) feature an approximately linear red shift of the first moment of the band as a function of time. We also note that the slope of this curve, that is the “speed” at which the band shift occurs, is greater in absolute value for induced defects than for as-grown ones. Also, figure 6.6 shows that the curve slope grows as a function of irradiation dose, this being confirmed along all the EC2-EC5 series.

6.1.2 Discussion

The results found here, that is the distribution of lifetimes measured for different emission energies, and the correspondent red-shift of first moment of the bands as a function of delay time is the luminescence spectral dispersion found for similar defects in previous pages (intrinsic and extrinsic ODC(II) in chapters 4 and 5). Current

---

$\Delta M_1(t) = M_1(t) - M_1(0)$

---

3The data on EC2 and EC4 samples are not shown in figure 6.6 for sake of drawing clarity because they almost superimposed on data of EC3 and EC5 samples, respectively.
6.1. Si-ODC(II) induced by $\beta$-rays

Experimental results on induced defects can be discussed in the framework of the theoretical model developed in chapter 4. Also here, the parameter $S$ was estimated experimentally by measuring the half-difference between the spectral positions of the excitation energies and emission peaks and in following discussion it will be fixed to values $S=0.27$ and 0.31 eV for F300 sample and ECn ones, respectively.

For each samples listed in table 6.1 (excluding the EC1 sample) we have performed numerical integration of expression (4.3), varying the related homogeneous and inhomogeneous parameters, to obtain a set of three theoretical curves which simultaneously fit the shape of PL bands, the dependence of the decay lifetime vs the emission energy and the kinetics of the first moment. The continuous lines in figures 6.3, 6.4, 6.5 and 6.6 represent the results of our fitting procedure. We obtained a good fit for almost all experimental data especially considering the contemporaneous adaptation of theoretical curves to both temporal and spectral dependence. The slight disagreement between the theoretical curves and experimental data observed in fitting the PL lineshape at $t=0$ of the two most irradiated samples (EC4 and EC5), as apparent from figure 6.3, is likely due to presence of spurious signals at lower energies or to bad approximations in our model (i.e. linear phonon coupling, single mode approximation). This point will be further discussed in the following. However, we observe that also in these two cases the estimation of the parameters $\sigma_{in}$ and $\sigma_{ho}$, that are mainly determined by fitting the lifetime dispersion curve (figure 6.5) and the shift of first moment (figure 6.6), is not expected to be affected by the lower quality of the fits of the lineshapes. In this chapter, indeed, our principal aim is to estimate these important parameters ($\sigma_{in}$ and $\sigma_{ho}$) and to find out how and if they depend from the irradiation process.

The upper part of table 6.2 resumes the best parameters obtained by our fitting procedure for all investigated samples. From data in the upper part of table 6.2 we can also calculate the Huang-Rhys factor $H = S^2/\sigma_{ho}^2$, the vibrational frequency $\hbar \omega_p = \sigma_{ho}^2/S$ of the effective phonon bath and the total width (from $\sigma_{tot}^2 = \sigma_{in}^2 + \sigma_{ho}^2$). All these quantities are summarized in the lower part of table 6.2. We also report the parameter $\lambda = \sigma_{in}^2/\sigma_{tot}^2$ which estimates the degree of inhomogeneity found in each sample.

In figure 6.7 we report the values obtained for the parameters $\sigma_{in}$ and $\sigma_{ho}$ (panel-a) and for parameter $\lambda$ (panel-b), as a function of the $\beta$-irradiation dose for ECn samples in comparison with the values estimated for the as-grown defects in F300 sample (indicated with dashed lines). We see that the overall degree of inhomogeneity of the
6. Irradiation effects on inhomogeneous width of ODC(II)

Table 6.2: Upper section: best fitting parameters obtained by our theoretical model for all investigated samples. Lower section: values of $\lambda$, $\sigma_{tot}$, $h\omega_p$, and $H$, as calculated from best fitting parameters.

<table>
<thead>
<tr>
<th>Sample Nickname</th>
<th>$E_0$ (±0.05) [eV]</th>
<th>$\sigma_{in}$ [meV]</th>
<th>$\sigma_{ho}$ [meV]</th>
<th>$S$ (±0.02) [eV]</th>
<th>$\gamma$ [10^6 eV^{-3} s^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F300</td>
<td>4.69</td>
<td>110±7</td>
<td>100±12</td>
<td>0.27</td>
<td>2.67±0.16</td>
</tr>
<tr>
<td>EC2</td>
<td>4.64</td>
<td>139±8</td>
<td>94±11</td>
<td>0.31</td>
<td>3.14±0.19</td>
</tr>
<tr>
<td>EC3</td>
<td>4.63</td>
<td>141±8</td>
<td>95±11</td>
<td>0.31</td>
<td>2.89±0.17</td>
</tr>
<tr>
<td>EC4</td>
<td>4.60</td>
<td>175±10</td>
<td>93±11</td>
<td>0.31</td>
<td>2.46±0.15</td>
</tr>
<tr>
<td>EC5</td>
<td>4.61</td>
<td>180±11</td>
<td>90±11</td>
<td>0.31</td>
<td>2.80±0.17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Nickname</th>
<th>$\lambda$ (%)</th>
<th>$\sigma_{tot}$ [meV]</th>
<th>$h\omega_p$ [meV]</th>
<th>$H$</th>
<th>$f$ (±0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F300</td>
<td>55±4</td>
<td>148±9</td>
<td>37±7</td>
<td>7±2</td>
<td>0.14</td>
</tr>
<tr>
<td>EC2</td>
<td>68±4</td>
<td>168±9</td>
<td>29±6</td>
<td>11±3</td>
<td>0.16</td>
</tr>
<tr>
<td>EC3</td>
<td>70±4</td>
<td>170±10</td>
<td>29±6</td>
<td>11±3</td>
<td>0.15</td>
</tr>
<tr>
<td>EC4</td>
<td>78±5</td>
<td>198±10</td>
<td>28±6</td>
<td>11±3</td>
<td>0.13</td>
</tr>
<tr>
<td>EC5</td>
<td>80±5</td>
<td>201±10</td>
<td>26±5</td>
<td>12±3</td>
<td>0.14</td>
</tr>
</tbody>
</table>
6.1. Si-ODC(II) induced by $\beta$-rays

Figure 6.7: Homogeneous halfwidth (grey triangles) and inhomogeneous one (white circles) in panel-a and parameter $\lambda$ in panel-b, as a function of $\beta$-irradiation dose in ECn samples. The corresponding values for F300 sample are indicated with dashed lines. The continuous lines are indicated only for eyes-guiding purpose.
ensemble of point defects monotonically increases with irradiation dose, as shown by the behavior of $\sigma_{in}$ and $\lambda$ parameters. On the other hand, the homogeneous parameter $\sigma_{ho}$ remains almost constant at $\sim 95$ meV for induced defects, independently from dose, while being slightly different from the value of $\sim 100$ meV characteristic of as-grown defects. A similar slightly decrease is found for the other homogeneous parameters ($\hbar\omega_p$, $H$) as well as for $\tilde{E}_0$ (see table 6.2).

All these results can be qualitatively understood as follows: in the as-grown F300 sample, Si-ODC(II) are created in low concentration during the synthesis process and feature well defined homogeneous properties ($\tilde{E}_0=4.69\pm0.05$ eV, $\sigma_{ho}=100\pm12$ meV, $f=0.14\pm0.02$). Such defects are formed in the high temperature melt state of the silica matrix during the first stage of synthesis and thus they are stabilized in a configuration which is subsequently frozen when going down to room temperature. Hence, the homogeneous parameters found for the as-grown defects are characteristic of a structural configuration of the center (and of its environment) which is stable at the synthesis temperature. Also, the fact that the degree of inhomogeneity observed in the F300 sample is the lowest in table 6.2, suggests that at high temperatures the defects prefer to form and stabilize in specific precursor sites, likely selected by thermodynamic equilibrium conditions. In this sense, it would be interesting to study how the results on as-grown defects depend on the preparation history of the specimen.

When the $\beta$-irradiation starts, new Si-ODC(II) are created out from the unperturbed silica matrix, so that the concentration of defects in the ECn samples increases as shown in figure 6.2. These centers arise from a totally different mechanism of creation. With so high irradiation doses, we expect Si-ODC(II) to be prevalently created by knock-on events removing oxygen atoms from a normal Si-O-Si bond, followed by a structural rearrangement that accommodates the so-generated local oxygen deficiency in the form of a twofold coordinated silicon atom. In contrast with the as-grown material, in this case the stabilization of the defect and of its environment occurs at room temperature. This allows to understand the spectroscopic differences, apparent from table 6.2, between the homogeneous parameters of these centers and those of the “high-temperature” ones observed in the as-grown material. The spectroscopic distinction between Si-ODC(II) in as-grown silica and Si-ODC(II) created by $\beta$ irradiation had been already put forward in previous works [46]. Moreover, based on other works [100, 108], we argue that these homogeneous differences can be associated with different mean O-Si-O angles between as-grown and induced
6.1. Si-ODC(II) induced by $\beta$-rays

We discuss now the increase of the degree of the inhomogeneity with dose. This finding can be explained by the following simple first model. Every site of the matrix can potentially be a precursor for $\beta$-induced generation of Si-ODC(II) activated by knock-on events. However, due to the disorder of the SiO$_2$ matrix, one can expect some Si-O-Si bonds to be “weaker” than others, and to be efficiently activated starting from the lowest irradiation doses. In contrast, other sites, where the bond is stronger, should be activated only at higher irradiation doses. As a consequence, the inhomogeneous features ($\sigma_m$ and $\lambda$) of the ensemble of $\beta$-induced Si-ODC(II) are not constant with dose: increasing dose allows the growing ensemble of Si-ODC(II) to explore a broader variety of matrix sites, leading to a higher degree of heterogeneity of the environments experienced by the defects, and thus to an increase of $\sigma_m$, provided that there is a statistical correlation between the ZPL position and the degree of “toughness” of the precursor sites. This can explain the increase of the inhomogeneity parameter $\lambda$ with dose. It is also worth noting that such non-random activation of matrix sites as a function of increasing dose (which proceeds from weakest to toughest matrix sites) may suggest in principle the distribution of the zero phonon energy to be asymmetric, contrary to the gaussian assumption embedded in our theoretical model. This could be the reason behind the lower quality of the fitting results obtained for the PL lineshape measured in the two most irradiated specimens.

While the above model relies on the assumption of newly formed defects exploring nonequivalent sites within an unperturbed matrix, one has to take into account a second explanation which considers the occurrence of structural transformations of the silica host. Indeed, it is known that so high irradiation doses induce a measurable densification of the matrix, and the defects have been proposed to play a crucial role in driving this process [6]. Following to various kind of silica irradiation ($\beta$-rays, $\gamma$-rays, neutrons or swift ions) was observed a correlate, and increasing with dose, densification of the materials, up to a final modified state where the density reaches the maximum denser state of the 3-4% respect to the pristine silica value [6]. This particular state is known as the metamict phase. The shape of the distribution of the ZPL energy $E_0$ is determined in principle by the detailed dependence of $E_0$ (mapping) from the microscopical structural parameters such as the Si-O-Si angle and the Si-O distances. We argue that a progressive distortion of the volume surrounding the defects, to which a modification of the statistical distribution of these
local structural parameters is associated [6], may alter in turn the width of the inhomogeneous distribution of the ZPL energy. Such a mechanism could contribute to the observed increase of the $\sigma_m$.

This second hypothesis can be further corroborated by comparison with other experimental results which lead to a more detailed microscopic description of irradiated silica [109]. Same samples of F300 material, pristine and electrons irradiated ones, were studied by EPR spectroscopy measuring the signal of the well known paramagnetic $E'_\gamma$ centers (see section 1.2) [109]. In general, these centers turned out to be a fundamental probe of the silica material, because of their sensibility to the local surrounding, evidenced by a direct change of the hyperfine splitting associated with the $^{29}$Si isotope which is naturally present in silica [2, 18]. In that work was proposed a microscopic model where the densification process starts in small volumes surrounding the point defects created by irradiation and where structural changes increase with increasing dose only inside these small volumes. In this scheme the EPR spectrum of the $E'_\gamma$ centers is affected by these progressive structural changes and can be shown that the entire silica volume can be described as a mixture of the two material phases: a normal one related to the unperturbed parts and a denser one related to the defected zones [109]. The coexistence of these phases holds until the whole volume is completely affected by the irradiation process and the silica reaches the metamict phase.

The above study [109] has pointed out that the local densification around the defects $\delta_m = \frac{\rho - \rho_0}{\rho_0}$ increases on increasing the irradiation dose $D$ and it can be fitted by a power law function of $D$ with 0.16 as exponent [109]. Thus, the power law $D^{0.16}$ turns out to be a signature of this densification process in the modified zones and we wonder if our system reflects a similar behaviour as a function of the dose. As we told, the inhomogeneous distribution of the parameter $E_0$ is intrinsically linked to the distributions of angles and bond lengths, and we expect that the densification in the modified zones should affect the distribution of these local structural parameters and in turn that of $E_0$. Thus, considering that the variation of densification $\delta_m$ of the defected phases is small [6, 109], we can expand the inhomogeneous width $\sigma_m$ in Taylor series respect to $\delta_m$ up to the first order:

$$\sigma_m(D) \simeq \sigma_m^0 + \left( \frac{\partial \sigma_m}{\partial \delta_m} \right)_{\delta_m=0} \delta_m$$

(6.1)

where the partial derivative can be thought as a coefficient which quantify the efficiency of $\sigma_m$ to “feel” the local density. Considering the discussed dependence of $\delta_m$
from the dose as $D^{0.16}$ we finally obtain:

$$\Delta(D) = \sigma_{\text{in}}(D) - \sigma_{\text{in}}^0 \propto D^{0.16} \quad (6.2)$$

In figure 6.8 is shown the dependence from the dose $D$ of the values $\Delta(D)$, where the values $\sigma_{\text{in}}(D)$ are the inhomogeneous half widths found for the ECn samples, and the quantity $\sigma_{\text{in}}^0$ is the inhomogeneous half width of the as-grown F300 sample. As appears clear from the figure, the variations of irradiation induced inhomogeneous width are in good agreement with the power law $D^{0.16}$, indicating that also our ODC(II) point defects are sensible of the local silica environments and are probing the global change of the silica matrix proposed above and giving a further proof to the densification-model exposed in previous discussions.

Thermal treatments could provide a way to discriminate between the two interpretation models presented above. Indeed, one could try to anneal, at a temperature not high enough to reverse the densification effect, a portion of the induced population of defects. If the densification-related model is correct, the inhomogeneous width associated with the defects surviving the annealing should not change, because it is mainly determined by local structural properties not affected by the heat treatment.
6.1.3 Conclusions

In this section we studied by time-resolved luminescence the intrinsic oxygen deficient centres Si-ODC(II) observed in as-grown synthetic amorphous silicon dioxide, and the same defects induced in the same material by $\beta$-irradiation at different doses. The singlet PL of all these defects features a dispersion of decay lifetimes within the emission band and a temporal red shift of the first moment of the band. These experimental findings can be analyzed within a theoretical frame which models the effects induced by disorder in silica. We observe clear differences between the spectroscopic features of the two types of Si-ODC(II). Also, we demonstrate that the degree of inhomogeneity experienced by the induced defects increases with growing irradiation dose and is greater than that experienced by the as-grown centers. These results point to a frame where $\beta$-induced ODC(II) are slightly different from the as-grown ones, likely due to their different formation and stabilization mechanisms. As the irradiation dose increases, the inhomogeneous broadening of the PL band can be due either to the generated defects being able to explore a broader set of geometrical configurations within the silica matrix, or to a global transformation of the host which reflects in a change of the distribution of geometrical parameters and, in turn, to a different distribution of zero phonon energy.

Results found in this section have been accepted for the publication on a specialized international journal on condensed matter and material physics (see number 5 in the list of publications in the Scientific Activity section).

6.2 Si-ODC(II) induced by neutron and $\gamma$ irradiations

In this last section we study the luminescence activity of $\gamma$-ray and neutron induced Si-ODC(II). Our purpose is to find out possibly differences between various kind of irradiation which reflect in different homogeneous and inhomogeneous properties of Si-ODC(II) by using again the experimental and analysis approach of previous discussions.

Here we report measurements performed on three samples of the Suprasil S300 dry synthetic silica material (see section 3.2). The first one is the sample, named S300, already used in chapter 5 which shows the luminescence activity of as-grown Si-ODC(II). In all figures below, we will again report the experimental data acquired for
this sample for comparison with the new ones. The second one (hereafter named S300-\(\gamma\)) is a specimen of Suprasil S300 material treated with \(\gamma\)-rays originating from the \(^{60}\)Co source of the department of Nuclear Engineering of the University of Palermo, for a total dose of \(8.3 \times 10^6\) kGy; this radiation dose is close to the corresponding one in sample EC2 of F300 silica materials studied in section 6.1. The last sample (hereafter named S300-\(n\)) is cut from a neutron irradiated Suprasil S300 material; it was bombarded with a mean fluency of \(5 \times 10^{12}\) \(n \cdot \text{cm}^2 \cdot \text{s}^{-1}\) in the Triga Markii reactor of the Centre of Radiochemistry and Analysis for Activation in Pavia, for a total period of 9 hours. All these samples are characterized by luminescence signals of Si-ODC(II): as grown defects for S300 sample and induced ones for S300-\(\gamma\) and S300-\(n\) samples.

The measurements performed on irradiated S300-\(\gamma\) and S300-\(n\) samples are the standard laser excited time resolved luminescence ones described in previous sections. The related experimental parameters (temperature, grating, slit width, temporal width, laser energy and wavelength) are the same as those described in section 5.1 for the as-grown S300 sample.

### 6.2.1 Experimental results

In figure 6.9 we report the luminescence signals of Si-ODC(II) in the UV region for all Suprasil S300 samples acquired at the end of the laser pulse (\(t=0\)). The PL signal in the S300-\(\gamma\) sample is peaked at \(\sim 4.40\) eV and has a FWHM=0.39 eV, whereas the correspondent values for the S300-\(n\) activity are \(\sim 4.44\) eV and 0.50 eV.

Similarly to what we have found for \(\beta\)-induced defects in section 6.1.1, the line-shapes of irradiated ODCs(II) is clearly distinguishable from the as-grown one (centred at \(\sim 4.45\) eV and 0.35 eV FWHM). Indeed, the \(\gamma\) irradiated sample features a red shift of the emission peak and a wider width, as already experimental observed in the \(\beta\)-irradiated samples and in literature [46]. Although the position of the emission peak is the same as as-grown sample, the S300-\(n\) sample is clearly distinguishable thanks to a much larger FWHM. Following the analysis of previous sections, we calculate the dispersion of lifetimes as a function of emission energy (reported in figure 6.10) and the position of first moment of emission band as a function of the delay time (reported in figure 6.11 in units of the parameters \(\tau_0\)) for both irradiated samples.
Figure 6.9: Low temperature luminescence lineshape of as grown (panel-a), γ-induced (panel-b) and neutron induced (panel-c) Si-ODC(II) at $t=0$. The continuous line is the result of the fitting procedure by the theoretical model exposed in chapter 4; the dashed line is the homogeneous Poissonian line shape.
6.2. Si-ODC(II) induced by neutron and $\gamma$ irradiations

**Figure 6.10:** For as-grown (squares), $\gamma$-induced (grey circles) and neutron induced (triangles) Si-ODC(II), decay lifetime as measured at different emission energies within the emission band. The continuous line is the result of the fitting procedure by our theoretical model (see discussion).

**Figure 6.11:** For as-grown (squares), $\gamma$-induced (grey circles) and neutron induced (triangles) Si-ODC(II), difference between first moment of the emission band and first moment at $t=0$. The continuous line is the result of the fitting procedure by our theoretical model (see discussion).
6. Irradiation effects on inhomogeneous width of ODC(II)

Table 6.3: Upper section: best fitting parameters obtained by our theoretical model for all investigated samples. Lower section: Values of $\lambda$, $\sigma_{tot}$, $\hbar\omega_p$, and $H$, as calculated from best fitting parameters.

<table>
<thead>
<tr>
<th>Sample Nickname</th>
<th>$\hat{E}_0$ (±0.05) [eV]</th>
<th>$\sigma_{in}$ [meV]</th>
<th>$\sigma_{ho}$ [meV]</th>
<th>$S$ (±0.02) [eV]</th>
<th>$\gamma$ ($10^6$ eV$^{-3} \cdot s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S300</td>
<td>4.69</td>
<td>110±7</td>
<td>80±10</td>
<td>0.27</td>
<td>2.63±0.16</td>
</tr>
<tr>
<td>S300-γ</td>
<td>4.66</td>
<td>148±9</td>
<td>82±10</td>
<td>0.31</td>
<td>3.10±0.19</td>
</tr>
<tr>
<td>S300-n</td>
<td>4.69</td>
<td>155±11</td>
<td>130±16</td>
<td>0.31</td>
<td>3.00±0.17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Nickname</th>
<th>$\lambda$ (±4) (%)</th>
<th>$\sigma_{tot}$ [meV]</th>
<th>$\hbar\omega_p$ [meV]</th>
<th>$H$</th>
<th>$f$ (±0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S300</td>
<td>65</td>
<td>136±8</td>
<td>24±5</td>
<td>11±3</td>
<td>0.14</td>
</tr>
<tr>
<td>S300-γ</td>
<td>77</td>
<td>170±9</td>
<td>22±5</td>
<td>14±3</td>
<td>0.16</td>
</tr>
<tr>
<td>S300-n</td>
<td>59</td>
<td>202±12</td>
<td>54±11</td>
<td>6±2</td>
<td>0.15</td>
</tr>
</tbody>
</table>

6.2.2 Discussion

Both figures 6.10 and 6.11 are in agreement with previous discussions about the luminescence spectral dispersion of point defects in a glassy matrix and can be analyzed in the theoretical framework of chapter 4.

The continuous lines in figures 6.9, 6.10 and 6.11 represent the curves calculated by our model, whereas in table 6.3 are reported the numerical values of best fit parameters ($\hat{E}_0$, $\sigma_{in}$, $\sigma_{ho}$, $S$ and $\gamma$), and of the other calculated ones ($\lambda$, $\sigma_{tot}$, $\hbar\omega_p$, and $H$).

The first important consideration is on the result about the inhomogeneous half-width: the $\sigma_{in}$ parameter clearly increases for induced Si-ODC(II), as reflected by the negative greater slopes of first moment trends in figure 6.11. This result agrees with discussions in section 6.1 where was hypothesized that the effect of $\beta$-irradiation, increasing the number of point defects and exploring possibly different precursor sites, is to enlarge the inhomogeneous statistical distribution of the homogeneous

---

4 As in previous section, here we have fixed the value of the parameter $S$ to the experimental difference between excitation energies and emission peaks, namely $S=0.31$ eV for activities related to irradiation processes.
6.2. Si-ODC(II) induced by neutron and $\gamma$ irradiations

parameter (in our analysis the zero phonon line)$^5$. The second densification-model, obviously, can not be ruled out.

As anticipated in the introduction, the doses released on S300-$\gamma$ and F300-EC2 samples are similar although the kind of irradiation is different: high energy photons against fast electrons, respectively. After comparison of the results on all homogeneous parameters in tables 6.2 and 6.3, we can conclude that these two source of damages cause very similar effects in silica and we argue that the formation of defects is due to electrons in both cases: primary and secondary electrons for $\beta$-rays, whereas Compton electrons associated with $\gamma$-rays.

Without regard on the kind of causes of damages (heavy radiations or fast particles), results exposed until now can confirm a general feature in irradiated silica: the damages created by the energy released on the matrix is responsible of an increasing of the inhomogeneous width of luminescence signals whereas the homogeneous one results quite unchanged.

Few words to describe the result obtained for the S300-$n$ sample. From table 6.3 it is possible observe that its value of $\sigma_{ho}=130\pm16$ meV is the greatest found in this work for induced Si-ODC(II), whereas the inhomogeneous half width is comparable with other one relative to the higher $\beta$-rays doses. This results can appear quite strange but it could be due to the particular process of defects’ formation during neutron bombardment. It is known that neutrons interact with the atoms of the silica matrix mainly by elastic knock-on processes which produce highly localized damages in the form of track formations on the fly directions of the neutrons. The energy released is so high that in a small volume the material results fused and after is quickly quenched because of the interaction with the cold environment [6]. The formation of defects in this heavy irradiated silica parts can be characterized by very different homogeneous features.

6.2.3 Conclusions

In this section we have studied the luminescence spectral dispersion of $\gamma$ and neutron induced Si-ODC(II). The effect of glassy heterogeneity is clearly evidenced for both kind of defects and the comparison with the as-grown and $\beta$ induced ones is done. The increase of the inhomogeneous width for all kind of induced defects is

$^5$It is worth remembering here that the comparison between results on S300 and F300 Suprasil materials is valuable, because they are both representative materials for as-grown Si-ODC(II) point defects (see section 3.2).
probably due to formation of new defects on geometrically different sites or to an
effect of densification of the material as proposed above for \( \beta \)-induced defects. The
fact that the homogeneous characteristics of these created defects are quite different
respect to the as-grown ones (a red shift of the emission peaks and an increasing of the
bandwidth), speaks for a creation process from particular precursor sites. Finally, we
observe a matching between all calculated parameters for \( \beta \) and \( \gamma \) induced defects for
the same energy dose released on the silica sample: this could indicate fast electrons
as the first cause of damage, namely primary and secondary electrons for \( \beta \)-rays and
Compton electrons for \( \gamma \)-rays.
Chapter 7

Dependence of the inhomogeneous width from excitation energy

In first section of chapter 4 we have discussed experimental results on the singlet Ge-ODC(II) luminescence band in the frame of a theoretical model which takes into account the effect of silica heterogeneity. In that case the excitation energy, which produces the PL signal, was chosen on the peak of related Ge-ODC(II) absorption band. In this chapter we investigate the same I301 sample (see section 3.2) by using different excitation energies, chosen to entirely cover the absorption band. All other experimental parameters (temperature, grating, width of slit, laser energy and temporal parameters) are kept the same as luminescence measurements described in section 4.2.1.

7.1 Experimental results

In figure 7.1 we show the optical absorption spectrum of the I301 silica sample in the ultraviolet electromagnetic region of interest. The observed OA band (centred at \(\sim 5.1 \text{ eV}\) and with FWHM \(\sim 0.4 \text{ eV}\)) is assigned to the \(S_0 \rightarrow S_1\) electronic transition of Ge-ODC(II) and, after its excitation, produces the luminescence signal already studied in chapter 4, assigned to the inverse \(S_1 \rightarrow S_0\) transition. The arrows indicate some representative energies chosen to probe entirely the absorption band of Ge-ODC(II).

In figure 7.2 are shown the normalized spectra of three representative luminescence signals excited at different energies (4.86, 5.17, 5.51 eV), on the low energy
7. Dependence of the inhomogeneous width from excitation energy

Figure 7.1: Optical absorption band of Ge-ODC(II) in the I301 silica sample. The arrows indicate some of the excitation energies used to study the dependence of the related luminescence signal.

We observe spectroscopic differences between all these PL bands: low energy excitation produces narrower PL band (FWHM=0.40±0.04 eV) centred at 4.33±0.02 eV; as observed in section 4.2.1, excitation on absorption peak gives a PL band centred at 4.39±0.02 eV and with a FWHM=0.44±0.04 eV; finally excitation on high energy side produces a wider band (FWHM=0.57±0.04 eV) centred at 4.31±0.02 eV.

Guided by the analysis performed in previous chapters we have thus extracted from each time resolved luminescence measurements the dispersion of lifetimes as a function of emission energies. In figure 7.3 we report the lifetime dispersion related to different excitations, as indicated in the right part of each panel. These data clearly show a dispersion of lifetimes for all excitation energies, even if the dependence is quite similar for all graphs as can be evidenced by comparison with all dashed lines which indicate the lifetime dispersion of the uppermost panel ($E_{ex}=4.86$ eV). All important information about the inhomogeneity effects are also contained in the behaviour of the first moment $M_1(t)$ as a function of delay time. In figure 7.4 we report the values [$M_1(t) - M_1(0)$], that is the difference between first moment at a general time delay $t$ and initial first moment at $t=0$ as a function of the time delay.
Figure 7.2: Normalized data of luminescence signals excited at three different energies: 4.86 eV (dark grey triangles), 5.17 eV (light grey circles) and 5.51 eV (white circles). The continuous lines are the result of the fitting procedure by our theoretical model (see discussion).

The horizontal axis is expressed in units of the lifetime $\tau_0$, defined as the lifetime measured at the peak of luminescence band $E_{\text{peak}}$. Values of the parameters $\tau_0$ and $E_{\text{peak}}$ for representative excitation energies $E_{\text{ex}}$ are reported in table 7.1. Figure 7.4 shows for all curves a red shift of the first moments with slopes negatively increasing for different excitation energies, from 4.77 to 5.51 eV.

### 7.2 Discussion

In previous chapters we have used the most probable transition energy (peak of the absorption band) to excite the luminescence in all silica samples. This choice permits the excitation of the major part of defects and thus the analysis of data with our theoretical model gives the possibility of estimation of the most representative inhomogeneous width of the entire ensemble of defects. On the other hand, the use of the “central” excitation energy does not ensure to probe the whole statistical
7. Dependence of the inhomogeneous width from excitation energy

**Figure 7.3**: Lifetime of luminescence of Ge-ODC(II) in the I301 silica sample as a function of the emission energy inside the PL band. Each panel represents measurement performed at different excitation energies (indicated in the right parts of the panels). The continuous lines are the result of the fitting procedure by our theoretical model and, for comparison purpose, the dashed lines repeat the fitting curve of the uppermost panel.

**Table 7.1**: Excitation energy investigated, relative emission energy peak and central lifetime $\tau_0$ for luminescence of Ge-ODC(II) in the I301 silica sample.

<table>
<thead>
<tr>
<th>$E_{ex}$ [eV]</th>
<th>$E_{peak}$ (±0.02) [eV]</th>
<th>$\tau_0$ (±0.2) [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.77</td>
<td>4.27</td>
<td>8.5</td>
</tr>
<tr>
<td>4.86</td>
<td>4.33</td>
<td>8.6</td>
</tr>
<tr>
<td>5.02</td>
<td>4.37</td>
<td>8.4</td>
</tr>
<tr>
<td>5.17</td>
<td>4.39</td>
<td>8.4</td>
</tr>
<tr>
<td>5.39</td>
<td>4.35</td>
<td>8.5</td>
</tr>
<tr>
<td>5.51</td>
<td>4.31</td>
<td>8.9</td>
</tr>
</tbody>
</table>
7.2. Discussion

Figure 7.4: Difference between first moment at a time delay $t$ and initial first moment at $t=0$ as a function of the time delay for the indicated excitation energies. The continuous line is the result of the fitting procedure by our theoretical model (see discussion).

distribution of the ensemble of ODC(II) point defects\(^1\) and the choice of different narrow excitation energies\(^2\), covering the entire absorption band, guarantees that we can excite selectively different subset of all point defects in the sample. The values of the $\sigma_{en}$ of these subset of defects can be thought as an “effective inhomogeneous width” representative of the studied part of ODC(II). As expected from previous measurements (see chapter 4) we found here a dispersion of lifetimes and a correspondent red-shift of first moments for all excitation energies used (luminescence spectral dispersion).

These experimental results can be analyzed in the framework of the model discussed in previous chapters, but we again stress that our result should be interpreted in a qualitative way considering that our theoretical analysis in principle was not thought to analyze different excitation energies and actually some objections can be made. Only for sake of clarity we repeat that the homogeneous parameters considered undistributed are the half Stokes shift $S$ (here fixed to 0.38 eV), the homogeneous half-width $\sigma_{ho}$ and the parameter $\gamma$, whereas the homogeneous parameter which has

\(^1\)In our system the homogeneous half width $\sigma_{ho}$ is sensible smaller than the inhomogeneous one, thus defects far more of $\sigma_{ho}$ from the energy of absorption peak are not excited.

\(^2\)For this kind of experiment the availability of a tunable laser source is fundamental.
7. Dependence of the inhomogeneous width from excitation energy

Table 7.2: Upper section: best fitting parameters obtained by our theoretical model for the investigated excitation energies in the I301 silica sample. Lower section: Values of $\lambda$, $\sigma_{tot}$, $\hbar\omega_p$, $H$, and $f$, as calculated from best fitting parameters for each excitation energy.

<table>
<thead>
<tr>
<th>$E_{ex}$ [eV]</th>
<th>$E_0$ (±0.05) [eV]</th>
<th>$\sigma_{in}$ [meV]</th>
<th>$\sigma_{ho}$ [meV]</th>
<th>$S$ (±0.02) [eV]</th>
<th>$\gamma$ (±0.09) [10^6 eV^{-3} s^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.77</td>
<td>4.60</td>
<td>110±7</td>
<td>120±16</td>
<td>0.38</td>
<td>1.56</td>
</tr>
<tr>
<td>4.86</td>
<td>4.64</td>
<td>125±8</td>
<td>111±14</td>
<td>0.38</td>
<td>1.49</td>
</tr>
<tr>
<td>5.02</td>
<td>4.69</td>
<td>154±9</td>
<td>94±12</td>
<td>0.38</td>
<td>1.46</td>
</tr>
<tr>
<td>5.17</td>
<td>4.70</td>
<td>177±10</td>
<td>93±12</td>
<td>0.38</td>
<td>1.41</td>
</tr>
<tr>
<td>5.39</td>
<td>4.65</td>
<td>208±12</td>
<td>85±11</td>
<td>0.38</td>
<td>1.45</td>
</tr>
<tr>
<td>5.51</td>
<td>4.61</td>
<td>234±14</td>
<td>59±8</td>
<td>0.38</td>
<td>1.42</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$E_{ex}$ [eV]</th>
<th>$\lambda$ (%)</th>
<th>$\sigma_{tot}$ [meV]</th>
<th>$\hbar\omega_p$ [meV]</th>
<th>$H$</th>
<th>$f$ (±0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.77</td>
<td>46±3</td>
<td>163±8</td>
<td>38±10</td>
<td>10±3</td>
<td>0.08</td>
</tr>
<tr>
<td>4.86</td>
<td>56±3</td>
<td>168±8</td>
<td>32±8</td>
<td>12±3</td>
<td>0.08</td>
</tr>
<tr>
<td>5.02</td>
<td>73±4</td>
<td>181±9</td>
<td>24±6</td>
<td>16±5</td>
<td>0.08</td>
</tr>
<tr>
<td>5.17</td>
<td>78±5</td>
<td>200±10</td>
<td>23±6</td>
<td>17±5</td>
<td>0.07</td>
</tr>
<tr>
<td>5.39</td>
<td>86±5</td>
<td>225±11</td>
<td>19±5</td>
<td>20±6</td>
<td>0.08</td>
</tr>
<tr>
<td>5.51</td>
<td>94±6</td>
<td>241±12</td>
<td>10±3</td>
<td>42±12</td>
<td>0.07</td>
</tr>
</tbody>
</table>

to take into account the heterogeneity effect of silica matrix, is the zero phonon energy $E_0$ which was distributed with a gaussian shape centred at $\hat{E}_0$ and with a homogeneous half-width $\sigma_{ho}$. On this basis, we can write an expression of the PL emitted by the ensemble of colour centres in the amorphous solid and one can numerically integrate it in order to simulate the time-resolved PL spectra, $L_s(E,t)$, as a function of the four parameters $\hat{E}_0, \sigma_{in}, \sigma_{ho}$ and $\gamma$. From $L_s(E,t)$, can be easily calculated the lifetime decay $\tau_s(E)$ and the kinetics of the values $[M_1s(t) - M_1s(0)]$, by using the same procedure applied to the experimental data. The upper part of table 7.2 resumes the best parameters obtained by best fitting of experimental data with the curves obtained by numerical integration for most representative investigated excitation energies.

In table 7.2 are also indicated the Huang-Rhys factor $H = S^2/\sigma_{ho}^2$, the vibrational frequency $\hbar\omega_p = \sigma_{ho}^2/S$, the total half-width (from $\sigma_{tot}^2 = \sigma_{in}^2 + \sigma_{ho}^2$) and the parameter
7.2. Discussion

Figure 7.5: Panel-a: homogeneous half width (grey squares), inhomogeneous (white triangles) and total one (black circles) as a function of excitation energies. Panel-b: parameter $\lambda$ as a function of excitation energies in I301 samples.

$\lambda = \sigma_{in}^2/\sigma_{tot}^2$ which estimates the degree of inhomogeneity.

In figure 7.5-a we report the homogeneous, inhomogeneous and total half widths as a function of the investigated excitation energies. In panel-b we show the dependence from the excitation energy of the parameter $\lambda$. From figure 7.5 two main considerations related to excitations on the two sides of the OA band, can be done: firstly, the homogeneous half width of ODC(II) varies from $\sim 120$ meV to $\sim 50$ meV; we can tentatively rationalize this results hypothesizing a microscopic mapping between geometrical features of point defect’s environment and their homogeneous optical properties:

$$E_{em} = f(\theta, d_{Si-O})$$
$$\sigma_{ho} = g(\theta, d_{Si-O})$$

where $\theta$ and $d_{Si-O}$ represent the O-Si-O angle and the Si-O distance, respectively,
of the defects excited selectively by varying the energy $E_{ex}$. Surely, only quantum-mechanical calculation can find out the correct functional links of $f$ and $g$ in equations 7.1 and thus the consequence functional dependence $\sigma_{ho} = h(E_{ex})$ shown by experimental data in figure 7.5.

The second consideration is about the inhomogeneous half width $\sigma_{in}$, which increases strongly from $\sim 110$ to $\sim 270$ meV. Remembering that the homogeneous absorption lineshape of a single point defect is naturally asymmetric towards high energies (see theoretical chapter 2), and considering the experimental results on the homogeneous half width, we can tentatively explain this result on the $\sigma_{in}$: for lower excitation energies we are stimulating a few sub-bands ($\sigma_{in}=110$ meV) of half width $\sigma_{ho}=120$ meV. Increasing the excitation energy the sub-bands involved are more (and thus the $\sigma_{in}$ is greater) because are probed new resonant homogeneous packets (with smaller half width $\sigma_{ho}$) plus the previous already excited ones, whose high energy wings fall again on the laser energy.

Until now we have supposed that the half Stokes shift $S$ of the transition (half difference between absorption peak and emission one) was fixed, or using different words, that the absorption and emission bands are rigidly linked. In this hypothesis when the excitation energy is increased, it is consequently expected that the emission peak increases. Thus, because of the mirror symmetry discussed in section 2.2, the zero phonon line should follow the linear relation:

$$E_0 = E_{ex} - S.$$  \hspace{1cm} (7.2)

If we consider different sub-bands related to different defects, the relation (7.2) still holds using the mean parameter $\tilde{E}_0$ instead of $E_0$. In figure 7.6 we report the values of the mean zero phonon line $\tilde{E}_0$ as a function of the investigated excitation energies, together with (dashed line) the expected trend described by relation 7.2.

Observing the experimental points on $\tilde{E}_0$ in the left side of figure 7.6 we note that, for increasing $E_{ex}$, the slope of their increase is lower than that of the dashed line. Taking into account the asymmetric homogeneous sub-bands we can tentatively justify this behaviour, indeed, the packets in resonance by their high energy wings, work as an inertia for the mean parameter $\tilde{E}_0$ which can not immediately follow the value associated with central resonant packets.

On the other side, the sudden decreasing behaviour observed for the mean zero phonon line in the high energy side of figure 7.6 can not be explained in the simplified scheme of this work. As already pointed out for the behaviour of homogeneous half width, this unexpected trend of $\tilde{E}_0$ could be tentatively explained performing
quantum-mechanical calculations which map the geometrical feature to spectroscopic ones. From the macroscopic viewpoint it is important to note that results on the parameter $\tilde{E}_0$, considering that the parameter $S$ is fixed, reflect a similar dependence of the emission peaks of bands excited at different energies. Thus, results shown in figure 7.6 can be interpreted in a scheme where the low energy emission region were excited both from low energy absorption packets and high energy ones. This result can be obtained breaking the rigid link between OA and PL sub-bands, namely increasing the parameters $S$ as a function of excitation energies. More in general, a possibility can be to rewrite our theoretical model inserting directly into the equations the dependence from exciting energy and, if necessary, using a suitable functional dependence of the homogenous parameters of the investigated system from $E_{ex}$. We can surely conclude that more refinements of our model are needed to understand the results exposed in this chapter.

### 7.3 Conclusions

In this chapter we have studied the luminescence of Ge-ODC(II) varying the excitation energy inside the related absorption band. We have evidenced that the spectral dispersion of luminescence, namely the distribution of lifetimes and the
red-shift of first moment of the luminescence bands can be revealed for all exciting energies, confirming the presence of heterogeneity of the glassy matrix. These results were analyzed in the frame of our theoretical model enlightening a dependence of the half widths $\sigma_m$ and $\sigma_{ho}$ from the excitation energy, consistently with the idea that different homogeneous sub-bands are selectively excited by the narrow laser source. Finally, results on the mean zero phonon energy (or on the emission peaks) indicate that our model should be refined to take into account the effect of different excitation energies related to the stimulation of all different point defects inside the silica matrix.
Conclusions

In this last chapter we briefly review all remarkable results found in this PhD thesis and after we discuss the possible perspectives.

Modeling the heterogeneity in silica

We have investigated the inhomogeneous properties of point defects in a glassy matrix via mapping by time-resolved PL the dependence of the radiative decay lifetime on emission energy. We have proposed a theoretical model, based on an extension of the standard theory of the optical properties of point defects, incorporating a statistical distribution of the zero phonon line to account for the effects of the non-equivalent environments probed by each point defect in an amorphous matrix as opposed to a crystalline one. This model enlightens a direct connection between the dispersion of the radiative decay lifetime within a luminescence band as a function of emission energy and the inhomogeneous properties of defects in a glassy environment.

To confirm our predictions we have experimentally studied by time-resolved luminescence the extrinsic (Ge-related) oxygen deficient centres in amorphous silicon dioxide. Both the triplet and the singlet PL of the defect feature a dispersion of decay lifetimes within the emission band and a temporal red shift of its first moment. Comparison with the luminescence of aggregates of F-centres in a crystalline sample of LiF and defects in crystalline sample of sapphire confirms that these effects are peculiar of centres embedded in disordered solids.

On the whole, our results suggest luminescence spectral dispersion to be a general optical property which allows to clearly discriminate the behaviour of defects embedded in amorphous solids from crystalline solids. At least, this appears to be true for oxides. Also, it is worth stressing that the lifetime of a PL band of defects in a solid is widely regarded as a strong fingerprint of the defect, which can be used
to unambiguously recognize it by time-resolved PL measurements. It is worth noting that, without taking care of lifetime dispersion effects evidenced here, lifetime differences as large as \( \sim 30\% \) in amorphous systems can wrongly be inferred as signatures of different defects.

Moreover, we find that the degree of inhomogeneity experienced by the triplet luminescence band is appreciably less than by the singlet band indicating that the dispersion of homogeneous features in silica is probed by a specific electronic transition and is not a characteristic of the type of defect only.

Our model is able to fit all experimental data and to provide an estimate of the ratio \( \lambda = \sigma^2_{\text{m}} / \sigma^2_{\text{tot}} \) between the inhomogeneous and the total width. Finally, our approach allowed us to determine the homogeneous parameters of ODCs: homogeneous width, oscillator strength, Huang-Rhys factor and the mean frequency of the vibrational local modes.

**Isoelectronic series of ODC(II)**

We have studied by time-resolved luminescence the defects belonging to the isoelectronic series of oxygen deficient centres in amorphous silicon dioxide. The dispersion of the emission lineshape is used as a probe to quantitatively evaluate the influence of inhomogeneous effects on the optical properties of the defects. We also provided for Si-ODC(II), Ge-ODC(II), Sn-ODC(II) an estimate of the inhomogeneous and homogeneous widths, on the grounds of the theoretical model discussed above that satisfactorily reproduces all experimental data based again on the same two simple assumptions: homogeneous optical properties governed by coupling with a single “mean” vibrational mode, and a Gaussian distribution of the zero phonon energy accounting for structural heterogeneity. The degree of inhomogeneity of the defects turns out to grow regularly with the atomic weight of the central atom, while the variations of the homogeneous properties are weaker. We interpret these findings as progressive greater distortion of silica matrix in the local environment of the weighter point defects. Along with the homogeneous width, we estimate also the other homogeneous parameters of oxygen deficient centres: oscillator strength, Huang-Rhys factor and mean vibrational frequency of the electron-phonon interactions.
Effects of irradiation

We have studied by time-resolved luminescence the intrinsic oxygen deficient centers Si-ODC(II) observed in as-grown synthetic amorphous silicon dioxide, and the same defects induced in the same material by β-irradiation at different doses. The singlet PL of all these defects features the luminescence spectral dispersion, that is the dispersion of decay lifetimes within the emission band and the temporal red shift of the first moment of the band. We again, using the theoretical frame discussed above, analyze these experimental findings modeling the effects induced by disorder in silica. We observe clear differences between the spectroscopic features of the two types of Si-ODC(II), as-grown and induced ones. Also, we demonstrate that the degree of inhomogeneity experienced by the induced defects increases with growing irradiation dose and is greater than that experienced by the as-grown centers. These results point to a frame where β-induced ODC(II) are slightly different from the as-grown ones, likely due to their different formation and stabilization mechanisms. As the irradiation dose increases, the progressive inhomogeneous broadening of the PL band can be due either to the generated defects being able to explore a broader set of geometrical configurations within the silica matrix, or to a global transformation of the host which reflects in a change of the distribution of geometrical parameters and, in turn, to a different distribution of zero phonon energy. These second model is further corroborated by previous experimental findings on densification of silica under irradiation and by the experimental trend observed here for the variation of the inhomogeneous half width with the dose, which is in good agreement with similar result on hyperfine splitting of other point defects, the E’γ centres, even they are sensible to local variations of the host.

We have also studied the luminescence spectral dispersion of γ and neutron induced Si-ODC(II). The effect of glassy heterogeneity is clearly evidenced for both kind of defects and the comparison with the as-grown and β induced ones is done. The increase of the inhomogeneous width for all kind of induced defects is probably due to formation of new defects on geometrically different sites or to an effect of densification of the material as proposed above for β-induced defects. The fact that the homogeneous characteristics of these created defects are quite different respect to the as-grown ones (a red shift of the emission peaks and an increasing of the bandwidth), speaks for a creation process from particular precursor sites. Finally, we observe a matching between all calculated parameters for β and γ induced defects for the same energy dose released on the silica sample: this could indicate fast electrons
as the first cause of damage, namely primary and secondary electrons for $\beta$-rays and Compton electrons for $\gamma$-rays.

**Dependence of the inhomogeneous width from excitation energy**

We have studied the luminescence of Ge-ODC(II) varying the excitation energy inside the related absorption band. We have evidenced that the luminescence spectral dispersion can be revealed for all excitation energies, confirming the presence of heterogeneity of the glassy matrix. These results were analyzed in the frame of our theoretical model enlightening a dependence of the half widths $\sigma_{in}$ and $\sigma_{ho}$ from the excitation energy, consistently with the idea that different homogeneous sub-bands are selectively excited by the narrow laser source.

**Perspectives**

Here we are going to discuss some hints for future works on the exposed topics.

From a general viewpoint our model should be applicable to a wide set of physical systems, if are satisfied the following main hypotheses: description as a molecular system, presence of an inhomogeneous broadened luminescence band, the absence of non radiative de-excitation channels from the considered excited state. For example could be very interesting to study the luminescence signals coming from other glass systems, from the size distribution of nano-materials and from proteins which are intimately characterized by a conformational heterogeneity which guarantees their biological functionality. In particular, a strong confirm of our model could be given by the study of a glassy system where also the hole burning technique is applicable (system with homogeneous width narrower respect to the inhomogeneous broadening, see section 1.3) in order to have a separate estimation of the two contributions to the bandwidth.

From the viewpoint of irradiation and induced defects discussed in chapter 5 it could be interesting to study the luminescence spectral dispersion as a function of preparation history of various samples (i.e. with different maximum temperatures in a sol-gel synthesis), trying to find out a correlation between homogenous features of defects and growing methods.
Moreover, can be useful repeat our analysis on homogeneous/inhomogeneous features in dependence of increasing temperature in a thermal annealing experiments, that is checking if the decreasing of defects’ concentration is followed by a change in the inhomogeneous properties and providing a way to discriminate between the two interpretation models. Indeed, one could try to anneal, at a temperature not high enough to reverse the densification effect, a portion of the induced population of defects. If the densification-related model is correct, the inhomogeneous width associated with the defects surviving the annealing should not change, because it is mainly determined by local structural properties not affected by the treatment.

Experimental results shown in this PhD research work were interpreted using a model based on the hypothesis of gaussian distribution for the homogeneous parameter zero phonon energy. The model well fits the experimental findings except for the lineshape of Sn-ODC(II) (see section 5) and for the lineshape of highly irradiated F300 sample (see section 6.1). Both of these samples are characterized by a high degree of inhomogeneity probed by the $\lambda$ parameter, respectively 90% and 80%, and this fact could be the reason for this bad agreement between experimental points and theoretical curves. We can argue, indeed, that the particular silica matrix of both samples (grown with sol-gel technique for the first sample and heavily modified by fast electrons for the second one) can be analyzed in the frame of a theoretical model which uses a non-gaussian distribution of one homogeneous parameter. One possible hints for future refining of our results is to try different distributions (maybe asymmetric ones) or to extract it a posteriori from experimental data.

As already concluded in chapter 7 the results on the mean zero phonon energy (or on the emission peaks) indicate that our model should be refined to take into account the effect of different excitation energies related to the stimulation of all different point defects inside the silica matrix.

In chapter 4 we have studied the slow luminescence bands of germanium and tin related ODC(II). The extension of this analysis to the slow luminescence related to intrinsic Si-ODC(II) could be useful to give more generality to the results of less heterogeneity probed by the triplet-singlet slow transition respect to the single-singlet fast ones. Moreover, as we done in chapter 5, could be also important to verify the presence of a general trend following the weight of the central atoms (Si, Ge and Sn).
Bibliography


[2] G. Pacchioni, L. Skuja and D. L. Griscom (Eds.), *Defects in SiO$_2$ and Related Dielectrics: Science and Technology*, Kluwer Academic Publishers, USA (2000). 1.1, 1.2.2, 1.2.2, 1.3, 1.4, 2, 2.1, 2.1, 2.1, 2.2, 2.2, 2.2, 2.2, 2.2, 2.2, 4.2.2, 6.1.2


[18] L. Skuja, “Optically active oxygen-defciency-related centers in amorphous silicon dioxide”, *Journal of Non-Crystalline Solids*, 239 (1998), 16. 1.2, 1.2.1, 1.2.2, 1.2.2, 1.4, 3.2, 4.2.1, 4.2.2, 4.2.2, 4.3.2, 5.1, 5.2, 6.1.2


[22] S. Agnello, R. Boscaino, M. Cannas, A. Cannizzo, F. M. Gelardi, S. Grandi and M. Leone, “Temperature and excitation energy dependence of decay processes of luminescence in Ge-doped silica”, Physical Review B, 68. 1.2.1, 4.2.1, 4.2.2, 4.3, 4.3.2, 5.1


[28] V. Radtsig, Kinetics and Catalysis, 20 (1979), 456. 1.2.2

[29] V. Radtsig and A. Bobyshev, “Twofold Coordinated Si and Ge Atoms and Hydrogen Paramagnetic Centers in Amorphous SiO2 and GeO2”, Physica Status Solidi (b), 133 (1986), 621. 1.2.2


[31] L. Skuja, “Isoelectronic series of twofold coordinated Si, Ge, and Sn atoms in glassy SiO2: a luminescence study”, Journal of Non-Crystalline Solids, 149 (1992), 77. 1.2.2, 1.2.2, 3.2

121


[34] C. Jones and D. Embree, “Correlations of the 4.77 - 4.28 eV luminescence band in silicon dioxide with the oxygen vacancy”, *Journal of Applied Physics*, **47** (1976), 5365. 1.2.2


[66] M. Nogami, “Persistent spectral hole burning of Sm$^{2+}$ and Eu$^{3+}$ ions in sol-gel derived glasses”, *Journal of Non-Crystalline Solids*, **259** (1999), 170. 1.3


[73] W. B. Fowler and D. L. Dexter, “Relation between absorption and emission probabilities in luminescent centers in ionic solids”, *Physical Review*, **128** (1962), 2154. 2.1, 2.1, 2, 3


[76] T. Förster, “Fluoreszenz Organischer Verbindungen”, *Vandenhoeck und Ruprecht, Göttingen*, **158**. 2.2

[77] Opotek Inc., “Tunable laser system”, 2233 Faraday Ave, Suite E, Carlsbad, CA 92008, USA. 3.1.1
Bibliography


[81] Princeton Instruments, “Roper Scientific, Inc.”, *3660 Quakerbridge Road, Trenton, NJ 08619 USA*. 3.1.2


[84] Heraeus Quartzglas, *Hanau, Germany, catalog POL-0/102/E*. 3.1.3


[88] A. Mackay, 7509 North Broadway P.O. Box 'G' Red Hook, New York 12571-0046, USA. 3.2, 4.3


[90] L. Vaccaro, “Electronic and vibrational properties of the Non Bridging Oxygen Hole Center in the bulk and at the surface of silica”, *PhD Thesis* (2009), Dipartimento di Scienze Fisiche ed Astronomiche, Universitá degli Studi di Palermo (Italy). 4.1


[94] L. Nuccio, “Diffusion of small molecules in amorphous SiO$_2$: effects on the properties of the material and on its point defects”, *PhD Thesis* (2009), Dipartimento di Scienze Fisiche ed Astronomiche, Università degli Studi di Palermo (Italy). 4.2.2

[95] F. L. Galeener, A. J. Leadbetter and M. W. Stringfellow, “Comparison of the neutron, Raman, and infrared vibrational spectra of vitreous SiO$_2$, GeO$_2$, and BeF$_2$”, *Physical Review B*, 27. 4.2.2, 5.2


Bibliography


[106] B. Evans, “Optical transmission in undoped crystalline $\alpha$-$\text{Al}_2\text{O}_3$ grown by several techniques”, *Journal of Applied Physics*, 70 (1991), 3995. 4.3.1

[107] G. Pacchioni and R. Ferrario, “Optical transitions and EPR properties of two-coordinated Si, Ge, Sn and related H(I), H(II), and H(III) centers in pure and doped silica from ab initio calculations”, *Physical Review B*, 58 (1998), 6090. 5.2


Scientific activity

Publications


Communication to congress: talk


Communications to congresses: posters


Attended schools

- Probing the Nanoworld: Microscopies, Scattering and Spectroscopies of the Solid State, 12–23 March 2007, Julich Germany.
- Research with Neutron and Synchrotron Radiation, 5–9 March 2007, Sportheim Planneralm Styria, Austria.

Attended courses

- Raman spectroscopy applied to amorphous systems, Palermo 2007.
- Punctual and extended defects in amorphous materials, Palermo 2006.
Report on the thesis of Mr. Michele d'Amico entitled “Conformational heterogeneity in silica: homogeneous and inhomogeneous linewidths of Oxygen Deficient Centres”

The study of amorphous materials has gained much momentum in recent years due to their widespread applications, but also because they represent good model systems for understanding some fundamental aspects of protein dynamics.

In his thesis, Mr. D'Amico investigated the heterogeneity in silica using time-resolved photoluminescence spectroscopy, and showed that fluorescence is a more sensitive probe of heterogeneity than phosphorescence. By modelling the inhomogeneity in terms of a statistical distribution of zero-phonon lines, he could establish a direct link between inhomogeneity and radiative decay. He also carried out a comparative study on Ge-doped silica and F-centres aggregates in crystalline LiF, and confirmed that the lifetime decay is specific to centres embedded in disordered solids, and can be used to distinguish defects in amorphous versus crystalline solids.

This study was also carried out for defects of the isoelectronic series of oxygen-deficient centres in amorphous silicon dioxide. The degree of inhomogeneity was found to grow with the atomic weight of the central atom, presumably due to a progressively larger distortion of the silica matrix. The effect of irradiation was also investigated using β-, γ- and neutron irradiation and is compared between these three. Overall, the characteristics of the irradiation induced defects are different from the case of as-grown solids, speaking for a creation process from specific sites, which deserves looking into in detail for potential engineering applications.

Mr. D'Amico's thesis represents a thorough and detailed investigation of inhomogeneous effects in amorphous solids. The thesis is clearly written and the results are nicely borne out by the used models. Finally, the conclusions are clear and well presented. I therefore approve Mr. D'Amico’s thesis without reserves.

Lausanne, January 27th, 2009

Professor Majed CHERGUI
Acknowledgments

It seems to me very difficult to find the right words to thank all the people who, explicitly or not, have helped me to realize the present work. I would try, and I apologize with the people I could forget.

I acknowledge the financial support received from the project “P.O.R. Regione Sicilia, Misura 3.15, Sottoazione C.”

I think that the formation acquired during a PhD course is fundamental for the scientific independence of a researcher, and for this reason I acknowledge Prof. Maurizio Leone for trusting me and giving me freedom in laboratory work. I also thank him a lot for his role of tutor not only as a scientific guide but also for the advice regarding my future. The joint discussion with the members of the research group in Solid State Physics played a fundamental role for me. Thus, I want to remember individually all of them, the professors Roberto Boscaio, Franco Gelardi and Marco Cannas, the doctors Simone Agnello, Fabrizio Messina, Gianpiero Buscarino, Laura Nuccio, Eleonora Vella, Giovanna Navarra, Antonino Alessi, Lavinia Vaccaro and Gianfranco Vaccaro. In particular, I want to acknowledge Fabrizio who shared with me the last two years in laboratory: the frequent pleasant conversations with him gave me depth of thought and confidence in myself. It is a pleasure for me to thank Dr. Rosa Maria Montereali for having kindly sent us the irradiated LiF sample and Prof. Aurelio Agliolo Gallitto for the sapphire sample. I also thank Prof. Antonio Cupane, for carefully proofreading my thesis and for discussing with me about my research work from a different point of view. I would like to express my appreciation for the work of Prof. Natale Robba, the coordinator of the PhD activities until December 2008. I am also grateful to Prof. Majed Chergui who has reviewed this work giving the report shown above. I thank B. Boizot, S. Guillos and V. Metayer for taking care of the β ray irradiation at the “Ecole Polytechnique” of Palaiseau, E. Calderaro and
A. Parlato of the “Dip. di Ingegneria Nucleare” of Palermo for γ ray irradiation and the “Centro di Studio per la Radiochimica ed Analisi per Attivazione” of Pavia for the neutron irradiation. Finally, I acknowledge the technical assistance received by Mr. G. Lapis, Mr. G. Napoli, and Mr. G. Tricomi.

I surely have to repeat a thank to Eleonora and Laura who have been (and are) for me dear friends, everyday. A grateful and warm embrace to Giorgio and Marco for their friendship, hoping that it will get stronger and stronger. A special thought is reserved to Vito, who has shared with me the merit and defects of our room, switching between study and laugh. My greetings go to the other colleagues who have become special friends of mine: Bruno, Matteo, Salvo, Saro and Valeria.

My special thanks go to my loved family for the constant help and the careful up-bringing they have always given me, which have surely contributed to the achievement of the results in my work: thanks to my mother, my father, my sister and to my niece Sara, who makes us happy and united.

And, last but not least, I want to recognize the fundamental role of my emotional happiness during the last years in completing my work. Thus, I would give back this debt in the future with ever unchanged fidelity and love to Alessandra, a present which the fate placed by chance before my eyes during a nice evening of Spanish music.

Michele