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***Gamma ray induced processes of point
defect conversion in silica***

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Gamma ray induced processes of point defect conversion in silica

Introduction

Increasing attention has been paid through the last decades to the subject of point defects in amorphous materials [1]. This is due to the wide technological relevance of such materials as well as to the intrinsic interest of understanding the physics of point defects in complex solids (glasses) whose structure is characterized by high translational and orientational randomness [2]. At variance with the case of crystals, where a point defect drastically interrupts the strictly periodic structure, amorphous solids require only modest changes of their already disordered “structure” to accommodate point defects. Specifically, amorphous solids feature a high capability of accommodating impurity atoms at interstitial sites, or as (homo or heterovalent) substitutions. Flexibility of the amorphous structure plays a major role also in the processes of defect generation by external treatments (chemical treatments, particle irradiation, heating, mechanical stress,...) since lower activation free energies of defects result in higher generation efficiency. The random structure of the material has also the effect that a given defect explores various environments and this aspect has a dual importance. On the one hand this makes the defect a probe of the local amorphous structure, on the other the defect properties are influenced by the different environments.

One of the widely employed and studied amorphous materials is the vitreous silicon dioxide ($\alpha\text{-SiO}_2$) also known as amorphous silica or silica *tout court* [3-5]. Its atomic structure is particularly simple, which helps in the study of point defects. Attention has been specifically focussed on structures, electronic properties and generation mechanisms of defects in this material. In general, point defects can be usefully related to modifications of some macroscopic properties, as the appearance of optical absorption and fluorescence bands and of Electron Paramagnetic Resonance

(EPR) signals. In many cases the defect formation depends on the manufacturing procedure of the material and on later treatments.

Despite hundreds of publications available in the literature, in few cases only a univocal identification of the atomic structure of the defects and an explanation of their production mechanisms have been attained [3]. Most of the available information comes from studies of *ad hoc* prepared materials, so many questions remain unsolved. Accordingly, many of the optical features characterizing the as-grown material (that is the material prior to any treatment) are not get attributable to a specific defect having a known structure. Also, the identification of the precursor of radiation-induced defects and the exact mechanism of their generation are still debated [3].

In general, external treatments are very useful since they often allow obtaining valuable information on the atomic and electronic structure of point defects. More specifically, kinetics of change of measurable features in the course of the treatment, provide unique information and hints about the mechanisms of generation of the defect (such as conversion from another defect, process involving impurity atoms, relation with atomic diffusion,...).

In this Ph.D. thesis we report experimental studies of the effects of ionizing radiation in vitreous silica (mainly γ -ray and part β -ray). The main target is the spectroscopic characterization of induced point defects and the identification of their formation mechanisms. To this purpose we use EPR spectroscopy and obtain complementary information from optical absorption and photoluminescence measurements. This multi-technique approach proves very useful to evidence when distinct spectroscopic features can be attributed to the same defect and when correlations point out the possible existence of defect conversion.

Comparison of growth of defect concentrations as a function of the accumulated irradiation dose allows eliciting their processes of formation from the unperturbed network or of conversion of precursor defects. Correlations among native and induced defects clarify aspects of the mechanism of their generation.

Since radiation-induced defects can be destroyed by thermal treatment we use this technique as an additional way to investigate the mechanisms of defect generation. The relation between precursor and radiation-induced defect is tested through the observation of thermal back-conversion of defects in their precursors. Similarly, information on defect stability and on annihilation process kinetics could be found.

We have chosen to study silica specimens from different commercial sources for two main reasons. First, analysis and comparison of the effects of irradiation in materials from different sources allows sorting out general features from specific ones, related to a given manufacturer (in this way, hints concerning the nature of the given defects can be also obtained). Second, the “rigidity” of the industrial manufacturing process warrants the reproducibility of the basic characteristics of material from a given source. This is useful for comparing our data to those already available from current literature and for having at disposal an unlimited supply of samples to subject to different treatments in order to sort out the wanted feature or model.

This Ph.D. thesis is organized in 10 chapters. Chap.1 introduces the physical characteristics of amorphous silica and of its point defects. Chap.2 reviews the current understanding and open questions regarding defects investigated in the thesis. Chaps.3-5 concern experimental methods and materials employed. In Chaps.6-9 we report and discuss the experimental results. Finally, in Chap.10 we summarize our results and briefly discuss perspectives of future works.

A list of publications and of Conference Reports reflecting much of the work done for this Ph.D. thesis can be found in the Appendix.

Chapter 1

Point defects in amorphous silica

1.1 Physical properties of amorphous SiO_2 and of point defects

In order to introduce the concepts related to the point defects it is useful to consider first the generality of the unperturbed amorphous silica. Thermodynamic studies have shown that this material has a glass transition and a stable state at room temperature [4]. The most generally adopted structural model of a- SiO_2 is the continuous random network (CRN) [3, 6-8], which is based on the assumption that directional bonding of mixed covalent and ionic character applies both in crystalline and a- SiO_2 . In this model, short-range order dominates, with each Si atom at the center of a regular tetrahedron and four oxygen atoms at the vertexes forming O-Si-O angles of 109.5° (fig.1). Each oxygen atom binds two silicon atoms and bridges two tetrahedra. This order resembles that of most of the crystalline polymorph of SiO_2 but in the amorphous state the Si-O-Si angle (α of fig.1) presents some variability, resulting in a random orientation distribution of SiO_4 tetrahedra [9].

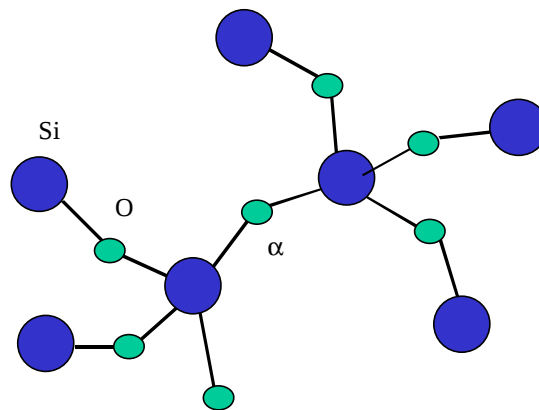


Figure 1 Fragment of amorphous silica representing the atomic dispositions and the linking between tetrahedra.

So, the amorphous matrix features a crystalline-like short-range order, due to the close similarity between the structural units SiO_4 in both matrices. As a consequence, the electron

structure and density of states are similar [10-11], yielding, also in the amorphous state, a wide energy-gap between the valence and the conduction bands (nearly 8 eV for an “ideal” a-SiO₂ matrix). This is the reason why the a-SiO₂ reproduces several macroscopic properties (e.g. the transparency in the visible and the electrical insulation) typical of α -quartz crystalline SiO₂. These properties are on the basis of many technological applications of a-SiO₂.

It is worth to note that the CRN model for the amorphous state is still debated. Other models have been constructed from old crystallite theory that depicted the amorphous as an aggregate of extremely small crystals [12-13]. Besides, other models derive from computational techniques (molecular dynamics, for example) [14] or from topological construction [3]. Nevertheless, it has been quite well established that the CRN model in which the SiO₄ tetrahedral units are randomly linked together at the corners well describes the structure of a-SiO₂ [15].

In the framework of the CRN model, point defects are defined in a straightforward way by extending the models proposed for a crystal. The embedding of defects in the amorphous state has the consequence that, even if they have a well-defined structural identity, they explore various different environments. This aspect has been evidenced by comparing defects in the crystalline and amorphous state, as for example for the E' center (see par.2.1). In general, a point defect can be visualized as a local distortion of the atomic structure caused by a bond rupture, an over or under-coordinated atom, the presence of an impurity atom (homo or heterovalent substitution, interstitial,...), etc. [16]. These defects are usually indicated as *intrinsic* when they are due to irregular arrangements of the crystal atoms (Si and O for SiO₂), and *extrinsic* when they are related to impurities (atoms differing from Si or O).

A further general classification of the point defects, useful in the following discussion, can be made on the basis of their electronic configuration: those having unpaired electrons constitute *paramagnetic* defects, and the others are the *diamagnetic* defects. Both typologies could in principle be characterized by optical activities as absorption and emission bands. Instead, only the paramagnetic defects have a further feature since they are responsible for a non-zero magnetic

moment, having unpaired electrons, and are responsible for the magnetic resonance absorption (Electron Paramagnetic Resonance, EPR, Chap.3).

Examples of the point defects are: the *vacancy* (an atom is removed from its “reticular” position), the *interstitial* (an atom is in a non-reticular position) and the *valence defect* (a bond Si-O is broken) [3, 10, 17]. In particular, among the intrinsic defects in silica we found the neutral oxygen vacancy [3, 17-20]¹: $\text{O}=\text{Si}-\text{Si}=\text{O}$, the peroxy bridge: $\text{O}=\text{Si}-\text{O}-\text{O}-\text{Si}=\text{O}$, the non-bridging oxygen²: $\text{O}=\text{Si}-\text{O}^\bullet$ (NBOHC), the tricoordinated silicon: $\text{O}=\text{Si}^\bullet$ (usually named E' center), the twofold coordinated silicon³: $\text{O}=\text{Si}^{\bullet\bullet}$. Some of these defects are pictorially reported in fig.2. It is worth to note that these defects may present several charge states due to electron or hole trapping.

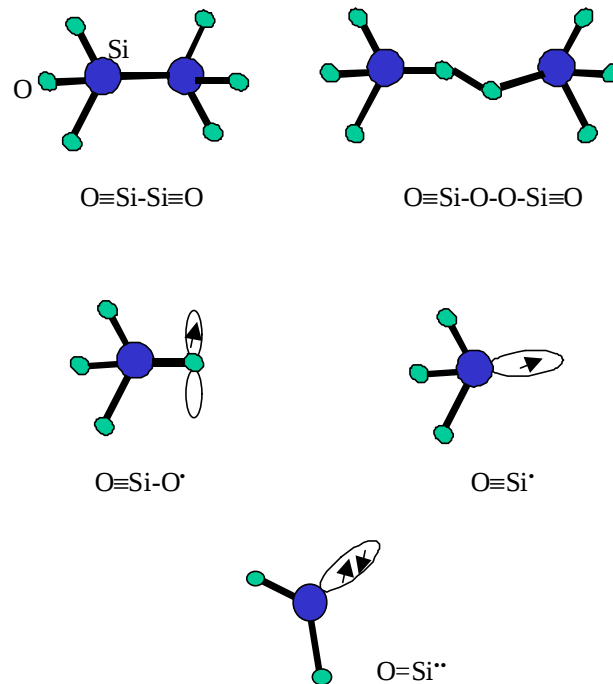


Figure 2. Fragments of amorphous silica pictorially representing various point defects. By arrows are indicated the electrons spins, inserted in pictorial orbitals.

Many extrinsic defects in amorphous silica are associated to metallic, halogen and substitutional elements trapped in the starting materials or involved in the manufacturing procedure

¹ in this and the following formulae O indicates atoms linked to the unperturbed matrix, the symbols =, ≡ indicate Si bonds with 2 or 3 of such O atoms, respectively, and the symbol – indicates a Si bonded to 1 atom.

² the symbol • represents an unpaired electron in a broken (dangling) bond.

³ the symbol •• represents a couple of non-bonded electrons.

(see Chap.5) [21]. The Germanium (Ge) is particularly important since it is homovalent to Si and it can give rise to defects with analogous structures to the intrinsic defects reported in fig.2 but with Ge substituting Si [22]. Another impurity that plays a prominent role in amorphous silica is the hydrogen. This is mainly captured during the manufacturing in the form of OH radical (from <1 part per million by weight, ppm, to ~ 1000 ppm) or bonded to Si. Its importance is due to the supposed participation in various generation processes of defects, both intrinsic and extrinsic, and to the high mobility, also at low temperatures [22-25].

Electronic states (ground and excited) of a point defect may have energy separation lower than the energy-gap (~8 eV) of the silica matrix [11]. For instance, the broken bond defects, like $\text{O}\equiv\text{Si}-\text{O}^\bullet$ or $\text{O}\equiv\text{Si}^\bullet$, are related to the (anti-bonding) localized states that should be found between the valence and the conduction band [3, 24]. As a consequence, the transitions among electronic states of the defect, induced by the electromagnetic field, give rise to absorption and emission bands with energy spanning from below ~2.0 eV, in the visible range, up to ~8 eV, in the vacuum UV (VUV) region, which explains the loss of transparency of the material. Also, the defects may trap charge, electron or hole, so they influence the insulation properties of silica. Finally, in the case of paramagnetic defects a redistribution of the electronic levels is introduced with energy separation very small (~10 μeV) and related to the presence of a magnetic field (see Chap.3), so varying the magnetic properties of the material.

As reviewed in refs.18-20, 22-25, various optical absorption and emission bands as well as EPR structures, in the case of paramagnetic defects, have been detected. From them, energy level diagrams for the defects have been derived together with, in the case of the EPR, information on the electronic orbitals and on their atomic environment (see Chap.3). However, it is very difficult to correlate such information to a particular structural model of the defect and only in few cases, following ad-hoc experiments, as e.g. for the $\text{O}\equiv\text{Si}-\text{O}^\bullet$, $\text{O}\equiv\text{Si}^\bullet$ centers, that were observed in ^{29}Si and ^{17}O isotopic enriched samples [18], a successful determination has been done.

1.2 Formation processes of point defects

At this point a basic question may be raised: which is the origin of point defects? The obvious answer is the manufacturing and the history of the material. The same traditional production of a-SiO₂, in fact, implies its rapid cooling (quenching) from a high temperature melt (~2000 K) with the ensuing formation of intrinsic defects [3, 4, 21]. Also, depending on the starting material used in the melt and on the atmosphere of the manufacturing process, some impurities may be trapped. On the basis of the traditional commercial manufacturing procedures four main typologies of high purity silica glasses have been distinguished. In general, they contain different low concentrations of metallic, OH and other impurities (see Chap.5) [21]. It is worth to note that comparison of the point defects in these four silica types may be useful to evidence if a defect is related with a particular impurity, for example containing it, or if the defect induction is favored by the impurity, as evidenced for the hydrogen [24].

Of course, post-manufacture treatments of the material can also produce defects [17]. In particular, it is known that defects may be induced or transformed after the exposure to special atmosphere, heating, drawing, as in the production of optical fibers [3, 4], exposure to particle or ionizing radiation, etc. [3, 17]. The examination of the external treatments effects has been and is still of basic importance in the physics of defects in solids since it gives useful information on their atomic structures and generation mechanisms. A given external treatment may cause the appearance, the increment or the reduction of a specific macroscopic property (e.g.: an optical absorption band, an EPR signal, etc...). The variations (growth, reduction or bleaching, thermal annealing) of these physical properties may be measured as a function of the time duration or intensity of the external treatment and often they can evidence correlation (or anti-correlation) among kinetics of the different properties.

A lot of progresses in the knowledge of defects are related to the individuation of these correlations, which may be used to clarify the different phenomenologies of the properties related to defects. In fact, some of them may be attributed to a single particular defect, as for the A-type or B-

type defects (see Chap.2). Besides, the correlations may put in evidence conversion mechanisms from a type of defect to another, as for the B-type defects and the H(II) centers (see Chap.8), giving precious information to identify their atomic structures. By this way it can be evidenced if the defects arise from the unperturbed matrix or from a preexisting defect, named *precursor*.

Since the EPR spectroscopy is able to give detailed information on the electronic orbital composition is of particular importance the case in which one can establish a link between an optical property and an EPR signal as in the case of E' centers [18, 26]. Unfortunately, a given paramagnetic center, even if well characterized, may arise from the conversion of more than one diamagnetic precursor [23-24], in this case, it is possible to resort to the different manufacturing procedures (for example, differing for the final OH content [24]). In fact, the peculiarity of the generation process (dependence on impurity, on manufacturing, ...) could explain the identity of a precursor. For example, the process may be a bond rupture followed by a structural local reorganization of the preexisting precursor and this should be evidenced as a poor dependence on the material manufacturing. At variance, a more complicated reaction may occur in which atoms must diffuse away from or toward the precursor to stabilize the defect. In these cases, some dependence on the material manufacturing and the temperature at which the defect is formed is expected. In the study of the effects of the manufacturing of the material is of fundamental importance to employ a variety of types of materials with controlled preparation and high reproducibility.

A particularly useful technique in the investigation of the mechanisms of defect generation is the irradiation of silica with beam of particles (electrons, neutrons, ions, etc.) or ionizing radiation (UV, X, γ , etc.) [3, 17, 24-25, 27-28]. Two main mechanisms are distinguished (see later):

- i) the *knock-on* processes, in which atomic displacements are caused by the direct transfer of the projectile kinetic energy;
- ii) the *radiolysis* processes, in which atomic motion or bond ruptures are caused through ionization or electron excitation.

It is worth to note that stable reticular distortions are created also with sub band gap photons, by UV lamp electron excitation to intra gap states at precursors [29] or by two-photon laser-induced processes [30-31]. Also, radiation-induced defects may arise from the trapping of an electron or hole at an unperturbed site, as in the case of the self-trapped hole [32], without any bond rupture.

The radiation induced defects include all the typologies encountered in vitreous silica, vacancy, interstitial and valence defects. So, by this method, the characterization of a wide variety of defects is possible. The kinetics of variation of the defects can be easily investigated by varying the irradiation time or intensity. As an example, when the concentration of a radiation induced defect reaches a constant value after a prolonged irradiation, the existence of a precursor can be reasonably hypothesized. In fact, the irradiation process converts the precursor until they are exhausted. Also, since some of the irradiation processes may occur only at a given energy, the selection of an appropriate beam can discriminate the reaction mechanisms.

Thermal annealing is another external treatment frequently used for the investigation of point defects. In fact, many varieties of radiation-induced defects can be destroyed on increasing the temperature, as for the case of the E' centers [18, 24]. In general, by warming an irradiated material it is possible to individuate the temperature at which a given defect is destroyed. By this way useful information related to the defect structure, as for example the strength of the molecular-bonds and the depth of the defect potential well, can be obtained. Also, the study of thermal behavior can be used to evidence the existence of correlations. For example, it is possible to establish if macroscopic properties, like optical absorption bands or EPR signals, are related to one defect when they follow the same kinetics under the action of a given thermal treatment.

Another important information obtained from the thermal treatment regards the correlation between a precursor and a defect. In fact, during the irradiation, the precursors content is reduced and the defects content is increased. If the defects are destroyed at high temperature, it is possible that they are back-transformed into the precursors, as in the case of the B-type defects and the H(II) centers, (see Chap.8). These thermally activated back-conversion processes can be used to confirm

the relationship between a defect and its precursor. Different defects should have distinct potential wells [33], so it should be possible, in principle, to anneal them selectively and put in evidence the existence of a correlation from back-conversion.

1.3 Radiation-damage processes

As the radiation induced defects will be a major concern in this work, let us gain a somewhat deeper insight into the mechanisms by which they can be created in solids. This introduction may clarify some aspects that will be considered later, starting from Chap.5.

It is possible to distinguish two classes of radiation damage processes, the knock-on and the radiolysis [3, 17, 28]. In the knock-on processes the projectile particles of the incident beam interact directly with the atoms of the material causing displacements (for example, vacancy-interstitial Frenkel pair) or site distortions. Two kinds of knock-on processes are generally considered: the elastic, that conserves the total kinetic energy, and the inelastic, in which some of the projectile kinetic energy is lost in electronic transitions (excitation, ionization,...) or nuclear reactions [3]. In order to create defects by displacements, it is necessary that the projectile gives sufficient energy to the target atom to break its bonds and to prevent that the knocked-on atom is recaptured from its neighboring atoms. The value of this energy for a given atom in the matrix is called displacement energy T_d , and it has been estimated that, in SiO_2 , $T_d^{\text{O}} \cong 10 \text{ eV}$ and $T_d^{\text{Si}} \cong 20 \text{ eV}$, for O and Si displacements, respectively, assuming an Si-O bond energy of $\sim 5 \text{ eV}$ [11, 34-36]. The environment of the knocked-on atom influences these energies and in general they are found to depend both on the topological arrangement and on the temperature.

Several types of “radiation” may produce displacements by “knock-on” collisions: fast neutrons, thermal neutrons, energetic ions, energetic electrons ($\geq 70 \text{ Kev}$ for O, $\geq 200 \text{ keV}$ for Si, [27]) and γ rays (through the generated electrons, see later). Cascades of knock-on may also occur in the case of energetic particles when they transfer a large amount of kinetic energy to the displaced atoms [37-38]. In particular, cascades has been found to be important for fast neutrons

($E > 0.1$ MeV) in which case an overall displacement efficiency 2-3 orders of magnitude greater than the primary displacement is found [3, 39-40]. In general, it has been found that up to $\sim 2 \times 10^{19}$ EPR centers/cm³ can be produced in quartz (0.05% of the total number of bridging oxygen atoms) by displacements processes [41].

In radiolytic processes the irradiation primarily changes the state of an electron but no stable ionic or atomic defects are initially formed [3, 17, 28]. The energy absorbed appears in the form of electrons in a normally empty conduction band and holes in the normally occupied valence bands, or in the form of excitons (electron-hole pairs bound to each other) at some site of the material. These excitations could be considered as a first step and are followed by other processes that lead to stable electronic states. A significant fraction of these electron-hole pairs recombine radiatively (luminescence, see Chap.3) or are separately trapped on impurities, on pre-existing defects or on radiation-induced defects, or are absorbed in non-radiative processes involving phonons. Finally, if the electron-hole pair recombines non-radiatively and its energy is focussed on an atom it may be converted into kinetic energy of the latter (as for example an ion repelled by electrostatic forces), resulting in bond ruptures or in the creation of vacancy-interstitial pairs.

The radiolysis processes (electronic excitation, ionizations and bond rupture) have been found to be predominant in electron and γ irradiation as they overcome the efficiency of the knock-on processes by at least an order of magnitude [3, 27, 42]. On the other hand, only radiolysis processes are possible when sub-band gap photons like UV are employed. It is worth to note that in the case of energetic irradiation particles a cascade of radiolysis processes could be induced since several electron-hole pairs are created by the scattered projectile [3].

The effects of the irradiation are usually quantified by the energy deposited in the material. To determine this energy it is useful to start introducing the scattering differential cross section $s_E(\mathbf{q}, T)$. Independently from the collision event (knock-on, radiolysis), $s_E(\mathbf{q}, T)$ is the probability density that a projectile particle, with incident energy E , transfers an energy from T to $T + dT$ to the

target and is deflected of an angle in the range from q to $q + dq$, with respect to its incident direction, [3, 40].

From the differential cross section it is possible to derive the energy transferred to the target per unit length $\left(-\frac{dE}{dx}\right)$. Considering that during a collision a projectile can transfer energy T , the average energy transfer over a range dr in the target material is

$$\langle T \rangle = N dr \int_0^{T_{\max}} \int_{T_{\min}} T s_E(q, T) dq dT \quad (1.1)$$

where N is the number of scattering centers per unit volume, $T_{\max}$ and $T_{\min}$ are the maximum and minimum energy transferred, respectively, and dr is small enough to account for a single collision. Therefore the average energy loss $\langle \Delta E_1 \rangle$ of a projectile over a range dr equals $-\langle T \rangle$, and the energy transferred to the target per unit length (stopping power) is⁴:

$$\left(-\frac{dE}{dx}\right) = -\frac{\langle \Delta E_1 \rangle}{dr} = N \int_0^{T_{\max}} \int_{T_{\min}} T s_E(q, T) dq dT \quad (1.2).$$

The deposited energy is called absorbed dose, or dose, and, in a target of thickness x , is given by

$$D = \frac{f \Delta t}{x} \int_0^x \left| \frac{dE}{dx} \right| dx \quad (1.3)$$

where $f \Delta t$ is the fluence of projectile particles (particles per unit area). The dose is usually measured in Gray (1 Gy = 1 Joule/1 Kg); another still diffused unit is the rad which is related to the Gray by the following conversion formula: 100 rad = 1 Gy. In general it is worth to note that not all the deposited energy gives rise to point defects as a great quantity is loosed in radiative and non-radiative processes.

⁴ It is worth to note that in the presence of composite targets, like SiO₂, the energy loss is determined, in first approximation, as the sum of the energy losses of each constituent (Si and O) weighted by their mass fractions (0.47 and 0.53 for Si and O, respectively) [43].

Among the various irradiation damage sources the γ rays are very interesting. They can act through photoelectric effect, Compton effect and pair production (electron-positron) [40] and give rise to primary electrons and a cascade of scattered energetic electrons and photons. Depending on the γ photon energy one of the above processes prevails [44], and in the case of a ^{60}Co source, having $E_\gamma = 1.25$ MeV, the Compton effect is dominant in generating the primary electron. In particular, the maximum electron energy $T_{\max} = E_\gamma[2\alpha/(1+2\alpha)]$ is 1.0 MeV (where $\alpha = E_\gamma/m_e c^2$, $m_e \equiv$ electron mass, $c \equiv$ speed of light [40]).

The electrons produced by γ rays are sufficiently energetic to induce knock-on as well as radiolysis processes. In this respect, the path of a γ ray through the matrix can be visualized as a succession of electrons, ions and excited molecules that may directly produce defects or may diffuse outside the path to react with other sites of the material.

In amorphous silica the predominant effects produced by a ^{60}Co source are due to radiolysis [3, 42]. The primary electrons, having maximum energy of 1.0 MeV, are able to produce displacement of O atoms by knock-on processes since the required energy is ~ 70 keV [27]. The calculated knock-on displacements, for a dose 100 kGy, are $\sim 5 \times 10^{15} \text{ cm}^{-3}$ from which $\sim 10^{14} \text{ cm}^{-3}$ results in stable E' centers [42, 45]. At variance, more than 10^{15} cm^{-3} stables E' centers are observed [42] for a dose of 100 kGy. This density is significantly larger than that expected if displacement due to knock-on processes were the dominant mechanism of defect creation. One can then reasonably assume that it is the energy loss by the γ ray in processes such as electron-hole-pair creation that subsequently results in defect creation.

A final interesting aspect regards the limit of very high doses of irradiation. In particular, after prolonged irradiation the physical properties (density, refractive index, elastic constants) of crystalline and amorphous SiO_2 become almost identical and, in addition, a common amorphized structure is observed [46-48]. This state is also almost independent of the irradiation process (knock-on or radiolysis), and is distinguishable from ordinary non-irradiated vitreous silica since it

has density slightly higher by 3-4 % [46]. This heavily damaged state of SiO_2 is known as *metamict state* [3] and is considered to arise through different stages involving point defects. In particular, it has been proposed that the metamictization process is a structural relaxation that is triggered by a critical defects concentration since the latter provides enough freedom to influence the atomic network connectivity [49-50]. For example, in quartz it has been supposed that point defects progressively lower the network connectivity, until the solid can no longer freely accommodate additional point defects, and a rearrangement of the damaged network takes place [51].

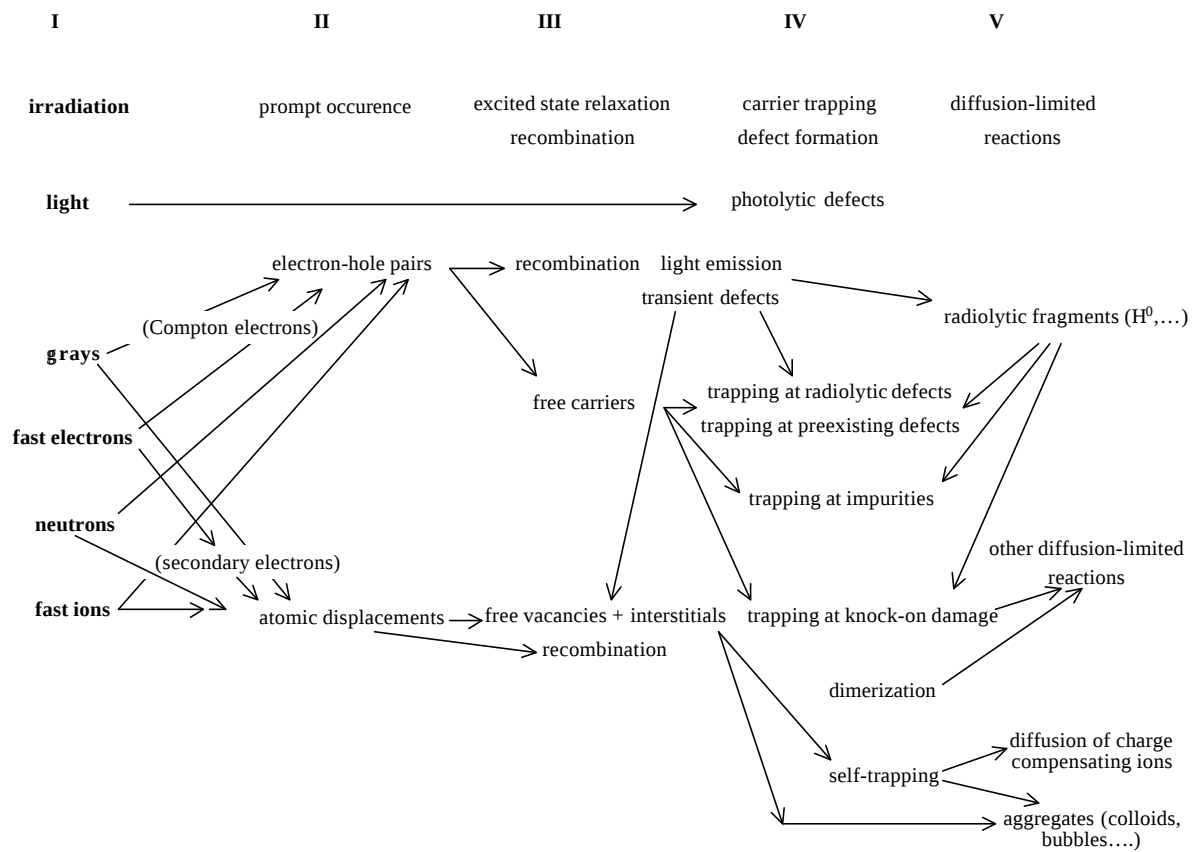


Figure 3. Schematic diagram of the most relevant radiation damage processes in glasses. Taken from ref. [3].

It is worth to note that the transition to the metamict state must be considered as a cooperative effect resulting from the presence of point defects. So, starting from a critical concentration the point defects should be considered in a different way with respect to the isolated local structural modifications. By comparison of various irradiation sources, a critical concentration

of paramagnetic point defects of the order of $10^{18}/\text{cm}^3$ has been estimated [49], this could be considered a general physical limit to the non-cooperative point defect treatment.

To conclude this section on the radiation damage processes a summary diagram of the most relevant mechanisms is reported in fig.3 [3].

Chapter 2

History and questions on radiation induced point defects

This chapter is dedicated to the introduction of the point defects investigated in this work. We will consider the experimental results from the literature important to introduce the questions regarding these point defects. In particular, we will report the principal proposed models and generation mechanisms together with the current interest in the investigated defects.

2.1 The E' centers

The most famous and studied point defect in silica is the E' center [26, 52-58]. This is a paramagnetic defect whose EPR spectrum was first observed in 1956 in irradiated α quartz and named E'₁ center [52]. The EPR studies evidenced that it comprises an unpaired electron highly localized in a silicon hybrid orbital orientated towards an oxygen position [59]. The principal evidence for this conclusion was the observation in the EPR spectrum of a pair of satellite lines, separated by ~ 40 mT, having intensity correlated to that of the E'₁ center signal and in particular 2.5% relative to the latter intensity. Since this percentage is consistent with the 4.7 % natural abundance of the ²⁹Si isotope, the pair of lines was attributed to the hyperfine interaction (usually named *strong* because of the large field distance between the lines) of the electron spin with a nearby nucleus of ²⁹Si having spin $I=1/2$ (see Chap.3).

Various structural models have been proposed [60-63]. Among them, the one proposed by Feigl, Fowler and Yip succeeded to correctly predict the electron localization and the strong hyperfine interaction due to ²⁹Si [64-65]. In this model, the E'₁ center is a spin localized at the site of a positively charged oxygen vacancy ($\text{O}=\text{Si}^{\bullet+}\text{Si}=\text{O}$, where the symbol “+” indicates the absence of an electron). This charged vacancy, having lost one electron, is subject to bond rupture [66] and the unpaired electron remains in one Si tetrahedral sp hybrid orbital extending into the O vacancy

direction, while the positively charged Si relaxes into the plane of its three oxygen neighbors (see fig.4) [64]. In spite of this success, the model failed in predicting the splitting of weak hyperfine interactions, experimentally ~ 0.8 mT [59], supposed to arise from the interaction between the unpaired electron and next nearest neighboring Si nuclear spins.

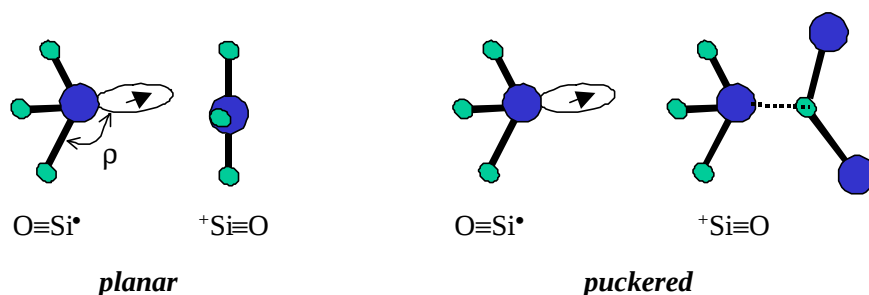


Figure 4. Amorphous silica fragments pictorially representing the E' center defect in the planar [64], left, and puckered [67], right, configurations.

A refined version hypothesized that the planar silicon actually relaxes beyond its basal oxygen plane and eventually bonds (back-bond) with another oxygen atom, fig.4 [67-70]. This model, usually referred as **puckered configuration**, confirmed the main characteristics of the previous one and agreed better with the experimental weak hyperfine interactions, which were attributed to the nuclear spins of the Si atoms bonded to the basal O atoms of $O \equiv Si^\bullet$. In this model, the relaxed silicon is poorly involved in hyperfine interactions due to its large distance from the unpaired electron.

The E' center was observed also in irradiated silica, and was designated E'_γ [54-56]. The E'_γ center was found to have the same main spectral features as the E'_1 [53, 55]. However, various new theoretical models were considered examining different bonding configurations to take into account the amorphous nature of the matrix [71-73]. Finally, the study by computer simulations of the E'_γ EPR signature [53, 55] and the investigation of the hyperfine interactions with ^{29}Si [55, 74] and ^{17}O [75], in ad-hoc enriched or depleted silica, lead to the conclusion that this center should have essentially the same atomic structure in silica and in α quartz. As a consequence, it was supposed

that also in silica the basic structure of the E'_γ center is constituted by an unpaired electron highly localized in a dangling tetrahedral sp hybrid orbital of a silicon atom bonded only to three oxygen atoms $O\equiv Si^\bullet$ [67, 70, 74]. The only slight difference with respect to the crystal is a Gaussian distribution, peaked at 110.5° with halfwidth of 0.7° , of the angle ρ (see fig.4) between the basal O atom bonds and the dangling orbital [55, 75]. Finally, also for the case of the amorphous, the more specific model for the E'_γ center has been supposed to be the positively charged oxygen vacancy in the puckered configuration [70].

Results on the annealing kinetics of radiation induced centers have suggested the existence of more than one distinct E' center in silica [24, 57, 76]. In particular, another EPR signal with line shape slightly different from that of the E'_γ , but characterized by the same strong hyperfine interaction, was identified [57]. The E'_γ and the new center can be distinguished for their different annealing kinetics and temperature [76, 77]. However, since the two centers share nearly identical ^{29}Si strong hyperfine interaction, it has been suggested that the orbital of the unpaired electron must in both cases comprise a dangling tetrahedral orbital on a single silicon bonded to three oxygens, $O\equiv Si^\bullet$. As a consequence, the new center was identified as a variant of E' center and was named E'_β [57].

The structural model for this center was tentatively constructed observing that its EPR signature evidenced a highly symmetric environment. So, it was speculated that the E'_β lack a major off-axis perturbation ahead of the orbital of the unpaired spin. It was then concluded that the E'_β can be ascribed to the effective absence of a second silicon opposite to the unpaired spin. In other words, either the dangling orbital is projecting into a small void in the glass network or the second silicon is so distant that its influence is minimal. Since the kinetic data evidenced the participation of H atoms in the generation of the E'_β , its complete structural model was suggested to comprise a threefold coordinated silicon with the unpaired electron pointing away from a vacancy whereas the other silicon is bonded to an H atom and has also relaxed away by more than 5 Å: $O\equiv Si-H$ $O\equiv Si^\bullet$

(see fig.5) [76, 18]. In this way the unpaired electron is almost in a cavity and no interaction with the other half of the vacancy is expected.

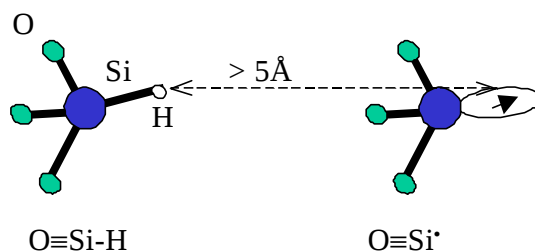


Figure 5. Amorphous silica fragment pictorially representing the E'_{β} center [24].

An interesting aspect is that this “void” character was noted also in the case of E'_{γ} center. In fact, a more symmetric environment of the E'_{γ} site was evidenced after a thermal treatment at 573 K and this evidence was interpreted suggesting that some structural relaxation of the second silicon has occurred [57]. A similar variation after thermal treatment from 400 to 700 K has been observed for E'_{γ} centers obtained in γ irradiated crushed quartz [78]. Another observation of isolated silicon dangling bond has been reported under the name “hemi E' center” or E'_s [79-80]. Also this center was suggested to arise from a threefold-coordinated Si in a neutral environment in which all the other Si and O in the vicinity have the proper coordination.

Other spectroscopic studies evidenced that an optical absorption band centered at ~ 5.8 eV have intensity correlated to that of the E' EPR signal, both in α quartz and in silica. As a consequence, this band was attributed to an optical transition among the E' center energy levels [26, 54, 81]. Assuming the model of the positively charged oxygen vacancy for the E' this absorption band was explained as a charge transfer from the silicon retaining the electron ($O\equiv Si^{\bullet}$) to the facing one ($^+Si\equiv O$) [82]. A successive calculation found that both ($O\equiv Si^{\bullet}$) and ($^+Si\equiv O$) have highly localized states near mid-gap so a transition energy of 5.8 eV is not expected [10]. The charge transfer process was further questioned as the two different E' center variants, observed in silica, have absorption bands peaked at 5.8 eV and 5.4 eV, respectively [18, 83], with too small difference

with respect to the expected big variation in the separation between the Si atoms [24]. It was then assumed that this optical transition is wholly confined within the $\text{O}\equiv\text{Si}^\bullet$ molecular group. Successively, the positively charged vacancy model and the isolated threefold-coordinated Si have been reconsidered by ab-initio calculations [84]. It has been shown that both the transition energy and the transition probability of the charged vacancy, assuming a charge transfer process, agree better than the other model with the experimental values. Recently, it has been confirmed the charge transfer process for the charged vacancy model (E'_γ) and it has been suggested that in the case of the isolated silicon dangling bond (E'_β) a transition to the conduction band could be involved [85].

Various studies have been reported on the dependence of the concentration of E'_γ centers (hereafter simply indicated as E' centers) on the radiation dose in silica, both to clarify its generation mechanism and to individuate its precursors. Both aspects are important also to get information on the effective structure of the center with the aim to clarify if its basic structure can be identified with the threefold coordinated silicon only, considering the neighboring atoms as perturbations.

It has been evidenced that the growth of E' centers at room temperature as a function of absorbed energy is very similar, no matter of the irradiation source (γ , e, X, UV) [19, 23, 86]. This fact suggests that the elemental processes are also quite similar and probably they are due to the creation of electron-hole pairs across the band gap. Three main processes of generation have been identified in samples prepared by different procedures [23, 25, 86]. In the first the E' concentration is proportional to the dose in a low-dose region and shows a saturating tendency in the high-dose region. In the second process, the E' concentration always increases with dose following a sub-linear power law: D^ν ($\nu < 1$). Finally, in the third process a linear growth of concentration without saturation is observed after a sub-linear power law growth. In general, the response to irradiation (growth rate and defects concentration) depends on the OH content and on the oxygen content of the material. The OH may affect the process through the irradiation-generated H that can be

involved in annihilation of defects [23, 24, 86, 87]. On the other hand, the oxygen content may control the concentration of over or under-coordinated Si sites that may play the role of precursors [18, 20].

The growth with saturation is usually associated to the presence of precursor defects on the assumption that they are converted at constant dose rate and proportionally to their surviving number [25]. Different interpretations have instead been given for power-law dependencies on the accumulated dose. Imai et al. [23, 86] considered the intrinsic process of generation of pairs of E' centers and of non-bridging oxygen hole centers (NBOHC): $\text{O}=\text{Si}-\text{O}^\bullet$. To explain the sublinear growth they assumed a conversion probability inversely proportional to the defect concentrations. At variance, Griscom et al. suggested a semi-empirical model based on the superposition of various saturation kinetics, that implicitly assumes a distribution of precursors [88]. Galeener et al. proposed that the sublinear growth arises from the combination of a saturation growth, due to precursors, and a linear growth due to direct activation of the unperturbed network [25]. Recently, Mashkov et al. [89] assumed the concurrence of two generation processes: the former irreversibly activates defects from the ideal network, the latter consists on reversible generation from precursors. This model succeeds to fit the experimental data over wide dose ranges, however, it relies on heuristically assuming ad-hoc non-linear conversion rates for defects.

Additional complexity to the question of the E' center arises since various precursors have been generally postulated in order to explain the different efficiencies of generation and growth kinetics in various materials. The obvious intrinsic precursor is the oxygen vacancy $\text{O}=\text{Si}-\text{Si}=\text{O}$. As already proposed in the first studies, the E' center arises from the trapping of a hole [64]. It has been observed that this precursor can preexist in the glass as a member of a Frenkel pair, or it can be created by the impinging radiation [24]. Successively, two kinds of this precursor have been postulated on the basis of different efficiencies of generation, one with an elongated Si-Si bond, $\text{Si}--\text{Si}$, and the other with a normal Si-Si bond [90]. Another intrinsic precursor is a strained site $\text{O}=\text{Si}-\text{O}--\text{Si}=\text{O}$, where the Si--O elongated bond is cleaved by irradiation giving rise to the pair E'

center and NBOHC: ($\text{O}\equiv\text{Si}^\bullet$) + ($\text{O}\equiv\text{Si}-\text{O}^\bullet$) [42]. However, it was subsequently observed that this process does not require a strained-bond precursor, as it occurs as well at normal sites [23, 86, 91]. Two main extrinsic precursors have been also considered. They consist of a Si atom bonded to an impurity and three oxygen: $\text{O}\equiv\text{Si}-\text{H}$ [92-94], $\text{O}\equiv\text{Si}-\text{Cl}$ [58, 83, 94]. In the irradiation process it is supposed that the bond with the impurity is broken releasing the impurity and leaving an E' center.

In conclusion, the experimental and theoretical data, both for crystal and amorphous, have not fully clarified if the E' center can be composed only of the basic structure $\text{O}\equiv\text{Si}^\bullet$ or if it is necessarily a greater molecular complex. In fact, even if in quartz the nearest Si atom and the vacancy model may be necessary, in silica this structure may be absent due to the higher structural flexibility. In this respect, the positively charged vacancy is not the only possible model for the E'_γ center in silica and, as a consequence, it can be expected that various precursor defects are effective.

Even if the creation of defects may occur from intrinsic and extrinsic precursors it has not been clarified the radiation damage process. The study of the conversion of the intrinsic defects by sub-band-gap photons evidenced that defects could be produced both by one-photon processes [29] and multi-photons processes [91], evidencing that both low energy electron-hole couples and excitons may be involved. Besides, the defect generation is influenced by the characteristic of the material, the presence of precursors, and it has been observed to depend on the OH content as well as on the oxygen content.

From all these observations some basic questions are still open:

- i) the oxygen vacancies are not the main precursors of the E' centers in amorphous silica,
- ii) many E' centers are not intrinsic defects,
- iii) a definitive proof of the E' structure needs to establish what is really faced to the unpaired electron.

2.2 The weak satellite structure of the E' centers EPR signal

A still open question regards an EPR structure satellite of the E' centers EPR spectrum observed in silica. This structure seems to be related to the E' center so it can give new hints on its atomic structure. This satellite structure has been observed for the first time by Shendrik and Yudin [71] and consists in a low intensity and poorly resolved pair of lines in the EPR spectrum centered on the E' signal and separated by 1.26 mT. This structure was observed in hydrogen containing silica glasses irradiated at 300 K by γ rays and was attributed to an hydrogen located near the E' site. Griscom [75], on the basis of observations in α -quartz [59], hypothesized its attribution to ^{29}Si hyperfine interaction. However, successive studies in ^{29}Si enriched silica lead Griscom to support the attribution to an E' center surrounded by an hydrogen atom and he suggested that this atom should be bonded as a second nearest neighbor of the E' center silicon atom ($\text{O} = \dot{\text{Si}} - \text{O} - \text{H}$) (see fig.6) [75, 95].

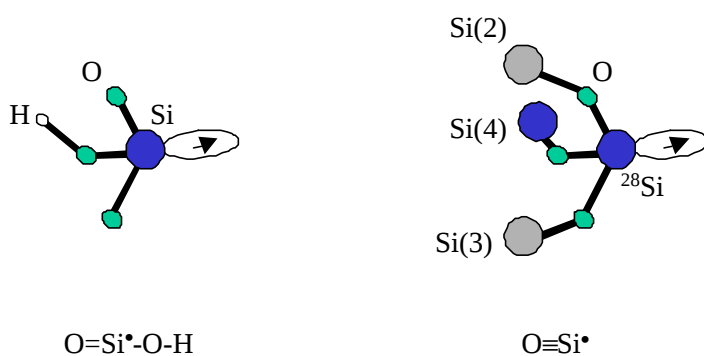


Figure 6. Amorphous silica fragments pictorially representing the models proposed for the center responsible for the weak EPR satellite structure observed near the E' centers resonance line. The H related center [75, 95], left, and the ^{29}Si related center [99], right. The Si(2) and Si(3) are in back-bond positions whereas Si(4) is equatorial.

This structural model was also used to explain the irradiation induced satellite structure of E' center in SIMOX (separation by implantation of oxygen) buried oxides silica treated in hydrogen atmosphere [96]. However, studies on hydrogen treated synthetic silica optical fibers suggested that the satellite structure could arise from a defect pair consisting of an E' center faced by an H

terminated non-bridging oxygen ($H - O - Si \equiv O$) [97]. A refinement of this study [98] evidenced that the satellite structure features a low thermal stability being removed by a thermal treatment at ~ 400 K. So, it was argued that it could be attributed to a H atom linked through Van der Waals forces to certain E' centers. Finally, recent calculations [70, 99] and the study of ^{29}Si doped silica samples [99] showed an EPR structure with features practically identical to those reported in ref.71. In particular, in ref.99 the weak satellite structure was found in all the simulations taking into account a hyperfine interaction (see Chap.3) of the electron of the E' center with second neighbor ^{29}Si atoms. It was also evidenced that this interaction should arise only when ^{29}Si atoms are linked to the basal O atoms in the E' center and their bonds are in the opposite direction with respect to the direction of the unpaired electron orbital, the Si(2) and Si(3) atoms in fig.6. It was then supposed that this hyperfine interaction is the origin of the weak satellite structure and the name **back-bond configuration** was adopted for the atomic disposition of fig.6, in analogy with α -quartz [63]. The authors also evidenced that their model introduced some constraints on the medium range order of the E' centers and also in their post-irradiation structural relaxation at a given site [99].

This summary of literature data evidences that the definitive attribution of a structural model to the weak satellite structure is still lacking. In fact, there is at least a dichotomy of models, one attributing the spectral feature to a site containing H but in a position not completely clarified, and the other related to the presence of ^{29}Si , a natural component of SiO_2 . In each case it seems that a strong relation to the E' center should exist since both models involve the basic structure of the E' center. This aspect is relevant since it can give new information on the structure of the E' center and also on the existence of particular structural configurations necessary to their generation.

The mechanism of generation of the weak satellite structure has not been investigated sufficiently, and in our opinion this should shed light on its nature. Since both the E' center and the weak satellite structure are induced by γ irradiation it is useful to investigate by this experimental approach their relation. Besides, other insight in understanding the nature of the defect related to the

satellite structure may arise by comparing the features of the latter and the E' center in a variety of materials differing for their manufacturing. Our experiments on this aspect are described in Chap.7.

2.3 The 11.8 mT EPR doublet and the B-type activity

Among the EPR spectral structures observed after irradiation of silica, a pair of lines with magnetic field separation of 11.8 mT (hereafter referred as “11.8 mT doublet”) is of great current interest because its generation process seems to involve H impurities and the oxygen deficient centers (ODC). The ODC are induced during the manufacturing process in almost all the silica types and have been extensively studied [18, 20, 22]. In addition, the defect originating the 11.8 mT doublet probably involves the Ge impurity but its structural model needs to be verified. This aspect is relevant because Ge is a homovalent substitute for Si and, besides being a natural impurity, it is widely used in doping silica for optical uses (especially in fibers) since it changes the refractive index and gives rise to enhanced photosensitivity (fiber gratings [4]). For these reasons the understanding of the Ge related defects is interesting from a basic as well as from a technological point of view.

The history of the 11.8 mT doublet is interlaced with that of the ODC and a relevant result reported in this Ph.D. thesis, is the experimental evidence of the conversion from an ODC, related to the optical B-type activity (see later), to the defect responsible for the 11.8 mT doublet. Such conversion enabled us to assign a structural model to both defects. So, in this paragraph we outline the histories of both the 11.8 mT doublet and of the optical B-type activity.

In one of the first observations reported in literature, the 11.8 mT EPR doublet was revealed in γ irradiated silica glasses containing Al^{3+} impurities as contaminant. Also, the doublet intensity was found to be proportional to the OH groups content. It was then hypothesized that the center responsible for this EPR signature consisted of a hole localized on a hydroxyl group bound to an aluminum impurity: $\text{Al-O}^{\oplus}\text{-H}$ (where the symbol $\oplus$ refers to the hole) [100].

Successively, the doublet was observed in γ irradiated Al-free natural silica treated in hydrogen or deuterium atmosphere and in Ge doped silica [101]. The hydrogen-deuterium exchange evidenced that the pair of EPR lines could be a doublet related to H. In fact, two spectral lines were observed in samples enriched with H ($I=1/2$) whereas three lines were observed in samples enriched with deuterium ($I=1$). In addition, on the basis of the g-values (see Chap.3) found in these materials, the attribution of the 11.8 mT doublet to a hole-centers was questioned. At variance, it was suggested a structural model with an electron trapped at a hydrogen-compensated substitutional Ge impurity [101].

The attribution of the 11.8 mT doublet to a Ge related center was further supported from the direct experimental observation of the doublet in γ irradiated pure GeO_2 obtained by the Vapor Axial Deposition (VAD) technique [102]. After that, the observation of the doublet also in hydrogen treated GeO_2 surfaces, obtained by mechanical fracture of solids, evidenced that the structural model could be constituted by an unpaired electron of a germanium atom bonded to two oxygen and one hydrogen: $\text{O}=\text{Ge}^\bullet\text{-H}$ (see fig.7).

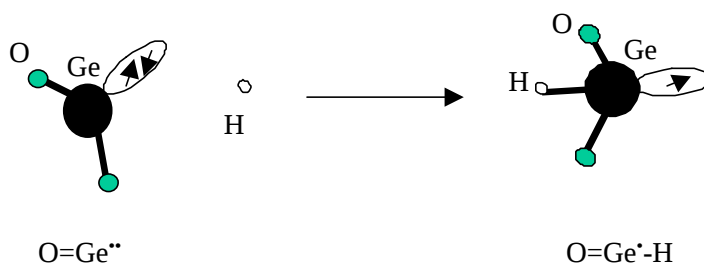
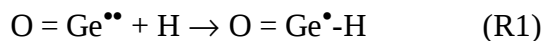


Figure 7. Amorphous silica fragments pictorially representing the conversion from the two-fold coordinated Ge center to the H(II) center with the participation of atomic H [103].

This center was named H(II) and was also suggested the generation reaction from a *two-fold* coordinated germanium (germilene center, GLPC, fig.7) [103]:



where the $O = Ge^{\bullet\bullet}$ was suggested to be a Ge atom bonded to two oxygens through two of the three sp^2 hybridized orbital and having the remaining orbital filled by two electrons as a lone pair. It is worth to note that the hypothesized reaction implies the conversion from a diamagnetic ODC to a paramagnetic one and should be evidenced by optical and EPR measurements.

Successively, in ref.104 the H(II) center was observed in as grown Ge-doped silica fibers after thermal H_2 treatment and the doublet intensity was also observed to grow after γ irradiation. Those authors assumed a reaction mechanism as in R1 to act but only after hydrogen treatment. At variance, in ref.105 the H(II) center induced with KrF laser irradiation at 5.0 eV was supposed to have as a precursor the Ge(2) center, an E' -Ge center similar to the E' -Si (see fig.4) but with Ge substituting the Si atom and with two next-nearest-neighboring germanium ions [106]. Recently, the H(II) model for the defect responsible of the 11.8 mT doublet has been supported also by theoretical calculations [107]. However, a definitive experimental proof of this structure is still lacking.

On the other hand, the history of the B-type activity evidences various contradictory aspects especially with regards to its transformation process [20, 22, 92, 108, 109]. A detailed study of the optical properties of oxygen-deficient Ge-doped silica revealed the presence of an optical activity, characterized by an absorption band at 5.15 eV ($B_{2\beta}$ band) and two related emission bands at ~ 4.2 eV (α_E band) and ~ 3.1 eV (β band) [110-113]. This overall activity was named B-type activity and was accurately characterized and distinguished from the A-type activity (see later), related to the absorption band centered at 5.06 eV (see later) [111, 114, 115]. An almost general result is that the B-type activity observed in Ge doped silica has intensity that is much greater than in other silica types. As a consequence, one of the most diffused assumptions is that the B-type activity arises from a germanium-oxygen-deficient defect even if the structure of the center is still questioned.

One of the structural models proposed for the B-active defect attributed it to the GLPC on the basis of the study of stationary and transient luminescence [114, 116]. This model was based also on the possible conversion from the two-fold coordinated germanium into the H(II) center as

suggested in reaction R1, and it was suggested that this conversion could be activated in irradiation processes [116]. At variance, other studies of natural and Ge-doped silica attributed the $B_{2\beta}$ band to a Ge divacancy, this is a fourfold coordinated Ge with two bonds with two oxygens and the other two bonds with Si or Ge atoms: $T = Ge = O$ (where T can be Si or Ge) [105]. In addition to these experimental observations various theoretical calculations and models have also been done but also in this case contrasting results regarding the GLPC and the vacancy model are reported that do not definitively attribute a structural model to the B-type active center [107, 109, 117, 118].

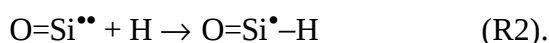
Contrasting observations were reported also in relation to the irradiation effects on the B-activity studied to find further information on its structural model. In ref.114 it was reported that the B-type activity is unaffected by illumination with UV-lamp (500 W Hg/Xe) whereas in ref.119 a reduction was observed under illumination with UV Hg discharge lamp, with ensuing creation of $E'-Si$ and $E'-Ge$ centers. At variance, γ irradiation at 77 K of natural silica evidenced that the $B_{2\beta}$ band is reduced (*bleached*) and that a successive isochronal annealing from 77 K up to ~600 K induced the growth of the H(II) center and an anticorrelated decrease of the $B_{2\beta}$ band. This observation was assumed to support the conversion in R1 on the basis of thermal diffusion of H atoms [120]. Further support to the latter reaction has been evidenced in ref.121 where the reduction of B-type activity was related to the generation of H(II) center after KrF laser irradiation in H_2 loaded Ge-doped silica. At variance in refs.122-124 the B-type activity was observed to be reduced in a correlated manner to the appearance of germanium related paramagnetic centers (GEC) different from the H(II) in Ge doped silica irradiated with KrF and XeCl laser at 4.0 eV. Analogous observations were reported in refs.125-126 where the B-type activity reduction was observed also under UV lamp (300 W Hg/Xe) irradiation and a conversion from the GLPC to the Ge- E' center was postulated in the presence of H_2 molecules.

The conflicting results summarized above evidence the complexity of the question regarding the ODC responsible for the optical B-activity. A definitive structural model for this defect is still lacking. In addition, it is observed that this activity is affected both by UV and by γ -irradiation and

it seems that a conversion to an EPR center is activated. This coincidence is very useful since it is possible to make an investigation utilizing both the optical and EPR techniques to characterize the involved defects. The most relevant part of this Ph.D. thesis is just the characterization of the effects of irradiation, mainly with γ rays, on the B-type activity by the combined use of optical and EPR measurements.

2.4 The 7.4 mT EPR doublet and the optical A-type activity

Another relevant structure in the EPR spectrum of γ -irradiated silica is a doublet of lines centered around the E' signal with magnetic field separation of 7.4 mT. This structure has been observed by various researchers and appears not only after irradiation [95, 101, 127] but also after particular treatments involving hydrogen [103, 97, 128]. The defect responsible for this EPR doublet is named H(I) and is supposed to be a variant of the E' center and to have structural similarities with the H(II) center. Its appearance has been related to the transformation of ODCs by an H atom trapping. In particular, the twofold coordinated Si has been proposed as the precursor defect that transforms to a paramagnetic center by bonding an H atom and leaving an unpaired electron [103, 129]:



The model on the right side of the reaction is usually identified as H(I) center and the hyperfine interaction between the unpaired electron and the H nucleus ($I = 1/2$) is postulated to originate the doublet of EPR lines. This model, supported by experimental observation [95] and by theoretical calculation [107], is now widely accepted.

A less definitive conclusion regards the mechanism of generation of the center under irradiation and, in particular, very little work has been done regarding its growth kinetics [77]. Moreover, we observe that the reaction R2 resembles the R1 with Si substituting for Ge. Also in this case a conversion from a diamagnetic to a paramagnetic center is postulated. In particular, such conversion regards a diamagnetic defect that is involved in the current debate on the structural

model for the center originating one of the most diffused optical activity in oxygen deficient natural and synthetic silica. This optical activity is usually reported as A-type activity [110, 111, 115]. It is characterized by an absorption band at ~ 5 eV, known as $B_{2\alpha}$, and two related emissions at ~ 4.3 eV and ~ 2.7 eV named α_i and γ bands, respectively [114, 116, 130-132], the latter activated only at high temperatures [133]. However there are some open questions regarding the defect responsible for this activity.

This activity is attributed by some authors to a neutral oxygen vacancy, $O\equiv T-Si\equiv O$ (where T should be Si or Ge), on the basis of the observed UV bleaching effect with the ensuing generation of E' centers [114, 134]. At variance, other authors proposed the twofold coordinated silicon, as shown on the left side of R2, basing on the study of optical polarization studies [135] and assumed that reaction R2 may result also after irradiation. Recently, it has been reported that an optical activity having all the characteristics of the A-activity can be induced by room temperature γ irradiation in bulk silica [136]. Since this activity is indistinguishable from the previous one it was attributed to the same species of defects and for distinction reasons the predominant emission at ~ 4.4 eV was named α_R band.

On the postulated reaction R2 it seems interesting to study the effects of the γ irradiation both on the optical A-type activity and the EPR H(I) center. In fact, this study should give new information on the generation process of H(I) and on the relation with the optical center. In addition, evidences on the model proposed for the A-type activity should be gained by EPR study. Since the relevance of the hydrogen atoms in the generation of point defects in silica has been evidenced in various papers [137], and these atoms are involved in reaction R2, it seems interesting to compare the irradiation effects in materials differing for the OH content.

Chapter 3

Experimental methods

3.1 Electron Paramagnetic Resonance

In this work we will investigate the effects of γ irradiation of vitreous silica. Among the effects of this treatment is the damaging of the matrix with the trapping of odd electrons with unpaired spin angular momentum in some site. To the latter is associated a permanent magnetic dipole that is the origin of the paramagnetism of the substance and is detectable by the Electron Paramagnetic Resonance (EPR) effect. This powerful spectroscopic technique usually yields a lot of information on the electronic ground state of the active center and this is the reason why it is widely applied to characterize point defects in solids. In view of the wide use done of this technique in this work a brief introduction to the paramagnetic resonance is necessary to correctly explain the experimental data.

3.1.1 Introductory aspects

The magnetic moment $\mathbf{m}$ of an electron is related to its total angular momentum $\mathbf{J}\hbar$, where $\hbar$ is the Planck constant 1.054589×10^{-34} J.sec, by the formula

$$\mathbf{m} = -\frac{g|e|\hbar}{2mc} \mathbf{J} = -g\mathbf{bJ} \quad (3.1)$$

where $\mathbf{b} = 9.27408 \times 10^{-27}$ J/mT is the Bohr magneton and g is the spectroscopic splitting factor, an adimensional quantity equal to 2.0023 for a free electron (e , m are the electron charge and mass respectively and c is the speed of light) [138-140]. This magnetic moment is the origin of the interaction with a static magnetic field, $\mathbf{B}$, which is described by the Zeeman Hamiltonian:

$$H = -\mathbf{m} \cdot \mathbf{B} = g\mathbf{bJ} \cdot \mathbf{B} \quad (3.2).$$

The Zeeman eigenenergies are related to the $2J + 1$ eigenvalues m of the J_z component of $\mathbf{J}$ parallel to $\mathbf{B}$, supposed to be in the direction z :

$$E_m = g\mathbf{B}m \quad (3.3)$$

and $(2J + 1)$ evenly spaced energy levels, separated by $g\mathbf{B}$, appear. An oscillating magnetic field $\mathbf{B}_1$, with frequency ω and direction perpendicular to $\mathbf{B}$ induces transitions between the split energy levels if its frequency ω equals the Larmor frequency $\omega_0 = g\mathbf{B}/\hbar$. Such transitions have a resonant character and correspond to the absorption of a quantum of energy $\hbar\omega$ from the electromagnetic field associated to $\mathbf{B}_1$, with the simultaneous variation of the direction of $\mathbf{J}$, with the selection rule $\Delta m = 1$. As better discussed in what follows, from measurements of B and ω it is possible to determine g . This latter quantity contains the relevant information on the electronic state of the paramagnetic center. For example when $B \approx 350$ mT and $(\omega/2\pi) \approx 9.8$ GHz then $g \approx 2.0$. It is interesting to note that since B establishes the splitting of the energy levels, the resonance condition $\omega = \omega_0$ can be obtained by varying the amplitude of B . An EPR spectrum consists just in the detection of the power absorbed from a paramagnetic system when the magnetic field is varied through the resonance condition.

The case of a paramagnetic ion embedded in an environment of atoms or molecules, as in a diamagnetic solid system, is different from that of the free electron. This is evidenced for example for transition metal ions that have the quenching of orbital angular momentum in the ground state [138, 140]. In addition, the splitting between the electronic levels concerned in a resonance transition may depend on the direction of the external static magnetic field with respect to the local symmetry axes. This effect is explained by the crystal field theory and is due to the admixture of electron orbital angular momentum into the spin ground state [138, 140]. It arises from the spin-orbit coupling in which the electron spin magnetic moment is affected by the magnetic field at the electron position caused by its orbital motion around the charged nucleus. This interaction causes the dependence of the Zeeman eigenenergies on the direction of B and is usually considered by

replacing the isotropic g -value with a g -tensor that takes into account the spatial anisotropy. It is worth to note that g is characteristic of the paramagnetic species and the crystal. In particular g gives structural information on the paramagnetic center, as it is function of the electronic orbital geometry and that of its surroundings. Consideration of the spin-orbit coupling perturbation to higher order introduces new terms in the spin Hamiltonian (fine structure) that are relevant for $S > 1/2$.

Up to now, the mutual interaction between the magnetic dipoles and their interaction with the thermal bath has been omitted in the dynamics of the spins. A heuristic way of considering these interactions has been introduced by Felix Bloch in his phenomenological equations of motion for the macroscopic magnetization of the sample [138-140]. He introduced two different relaxation times: T_1 to take into account the interaction of the spin with the thermal bath (the lattice vibrations) and T_2 to take into account the spin-spin dipolar interactions. The solution of the Bloch equations consists in a Lorentzian absorption line shape centered at the resonance condition $\omega = \omega_0$, with a width given by $1/T_2$ (homogeneous line shape). In the Bloch model, the time T_1 controls the saturation effect of the EPR absorption (see Chap.4).

Another effect of paramagnetic particles embedding is the redistribution of the electronic energy levels caused by the interactions with the surrounding atoms. As an example, the local crystalline fields at different sites of a system may be not equal giving rise to different g tensors. So various energy levels splitting arise for a given paramagnetic species in different spatial positions and as a consequence different resonance frequencies appear causing an inhomogeneous broadening of the absorption line.

Finally, a further reorganization of the electronic spin levels may arise from the interaction between the electronic magnetic dipole and the nuclear magnetic dipole of the same paramagnetic atom or of the neighboring ones. This is the *hyperfine interaction*, and it strongly depends on the electronic orbital so it is particularly useful in the determination of its properties. Moreover, since

various chemical elements differs for their nuclear spin, often the hyperfine interaction enables to identify which element is in the neighborhood of the electron spin.

The structure of the EPR absorption spectrum can be interpreted using the effective spin Hamiltonian:

$$H = b\mathbf{S} \cdot \hat{\mathbf{g}} \cdot \mathbf{B} + \mathbf{S} \cdot \hat{\mathbf{A}} \cdot \mathbf{I} \quad (3.4)$$

where $\mathbf{S}$ represents the effective spin of the spin center (it is a fictitious spin which describes the magnetic properties of the ground state [138]), $\mathbf{g}$ is a tensor, $\mathbf{I}$ is the nuclear spin angular momentum and $\mathbf{A}$ is the hyperfine interaction tensor including both isotropic and anisotropic contributions (see later). The first term arises from the electronic *Zeeman* interaction, the second, as just said, from the hyperfine interaction. Further terms of the Hamiltonian involving the spin, quadratic or higher order in $\mathbf{S}$, have been neglected as they are not relevant for the following discussion. Moreover, in what follows we will confine our discussion to an effective spin $S = 1/2$.

3.1.2 The Zeeman term of the spin Hamiltonian and the $\mathbf{g}$ tensor

The first term in eq.(3.4) involves the tensor $\mathbf{g}$. To introduce the effects of such a tensor on the EPR spectrum, we consider a spin $S = 1/2$ in a single crystal. We use a reference frame with x , y , z axes not necessarily coincident with the crystallographic ones. The direction of the static magnetic field $\mathbf{B}$ is specified by the direction cosines $\cos q_x$, $\cos q_y$, $\cos q_z$ with respect to x , y , z axes.

The Zeeman term of the Hamiltonian then becomes

$$H_{Zeeman} = b \begin{vmatrix} S_x & S_y & S_z \end{vmatrix} \cdot \hat{\mathbf{g}} \cdot \begin{vmatrix} \cos q_x \\ \cos q_y \\ \cos q_z \end{vmatrix} B \quad (3.5)$$

where

$$\hat{\mathbf{g}} = \begin{vmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{vmatrix} \quad (3.6)$$

and we can say that the spin is subjected to an effective magnetic field vector

$$\mathbf{B}_{\text{eff}} = \hat{g} \cdot \begin{pmatrix} \cos q_x \\ \cos q_y \\ \cos q_z \end{pmatrix} B \quad (3.7)$$

which depends on the particular direction in which B is pointed and on the g tensor peculiarities.

Now, we can write the Hamiltonian as

$$H_{\text{Zeeman}} = b\mathbf{S} \cdot \mathbf{B}_{\text{eff}} \quad (3.8)$$

and its eigenvalues as

$$(E_{\text{Zeeman}})_m = bB_{\text{eff}} m \quad (3.9).$$

The splitting of the energy levels depends, through B_{eff} , on the orientation of B with respect to the x , y , z , axes as stated by eq.(3.7). This implies that the resonance magnetic field in a single crystal is a function of the particular direction of the external field.

Since B_{eff} depends also on g , the experimental determination of the resonance fields of a paramagnetic crystal for various orientations of the applied static magnetic field B with respect to the crystal axes, is a way to determine the g tensor components. Once these components are found it is possible to diagonalize the g tensor and establish its principal axes, gaining information on the geometry of the center and on its orientation in the single crystal [141].

3.1.3 The powder line shape

When the paramagnetic substance is a powder or an amorphous solid the orientations of the crystal axes with respect to an external reference frame are random. So, even if for each paramagnetic species we can define a g tensor, with respect to the crystal axes, we must consider the distribution of these axes orientations with respect to an external reference frame. A distribution of the resonance fields appears for any arbitrary orientation of the static magnetic field. In addition, depending on the symmetry of the g tensor, it is possible that different spin center orientations give the same resonance field. This degeneration causes that for certain resonance fields a larger number

of spins absorb energy than for other resonance fields. This effect results in the asymmetric absorption line shapes and this inhomogeneous line is characteristic of paramagnetic species in amorphous or powder materials.

When the g tensor is referred to its principal axes, it has the diagonal form

$$\hat{g} = \begin{vmatrix} g_1 & 0 & 0 \\ 0 & g_2 & 0 \\ 0 & 0 & g_3 \end{vmatrix} \quad (3.10).$$

where g_1, g_2, g_3 are the principal values of the tensor. In a reference frame with axes coincident with the g tensor principal axes, the Zeeman Hamiltonian becomes [141]

$$H_{Zeeman} = b(S_1 g_1 \cos q_1 + S_2 g_2 \cos q_2 + S_3 g_3 \cos q_3)B \quad (3.11)$$

with eigenvalues

$$(E_{Zeeman})_m = m b B \sqrt{(g_1 \cos q_1)^2 + (g_2 \cos q_2)^2 + (g_3 \cos q_3)^2} \quad (3.12).$$

From (3.12) we find that the energy splitting between two adjacent levels is given by

$$\Delta E = b B \sqrt{(g_1 \cos q_1)^2 + (g_2 \cos q_2)^2 + (g_3 \cos q_3)^2} \quad (3.13).$$

The resonance condition is given by $\Delta E = \hbar \omega$.

The amplitude of the absorption depends on the number of spin centers whose g tensor principal axes coincide with the reference frame chosen, that is on the probability to find a spin with such an orientation. Moreover, at variance to the crystal case, it is evident that varying the amplitude of the static field, but leaving its direction fixed, we can find other spins with the same energy splitting ΔE but with a different orientation (q_1, q_2, q_3). So, scanning the magnetic field amplitude we scan the distribution of the orientation of the spin centers in powder or glass matrix.

The resulting absorption line shape in amorphous and powder matrices has been calculated theoretically, even by numerical methods [53, 142-144]. On the basis of these results, one can infer the principal values g_1, g_2, g_3 from the field positions of the maximum signal, the zero cross and the minimum, respectively, in the EPR derivative spectrum (see fig.8). However, in the powder that is

formed by micro-crystals, the crystallographic orientation of the g tensor cannot be determined. A typical powder-like EPR experimental spectrum for $S = 1/2$ spin centers is outlined in fig.8 both for the derivative (fig.8a) and the absorption spectra (fig.8b). In this figure, the positions of the principal g values are reported in the derivative spectrum, evidencing how they can be determined experimentally. Moreover, one can deduce the symmetry properties of the center. As an example, we note that if two of these principal values coincide one can deduce that the center has axial symmetry.

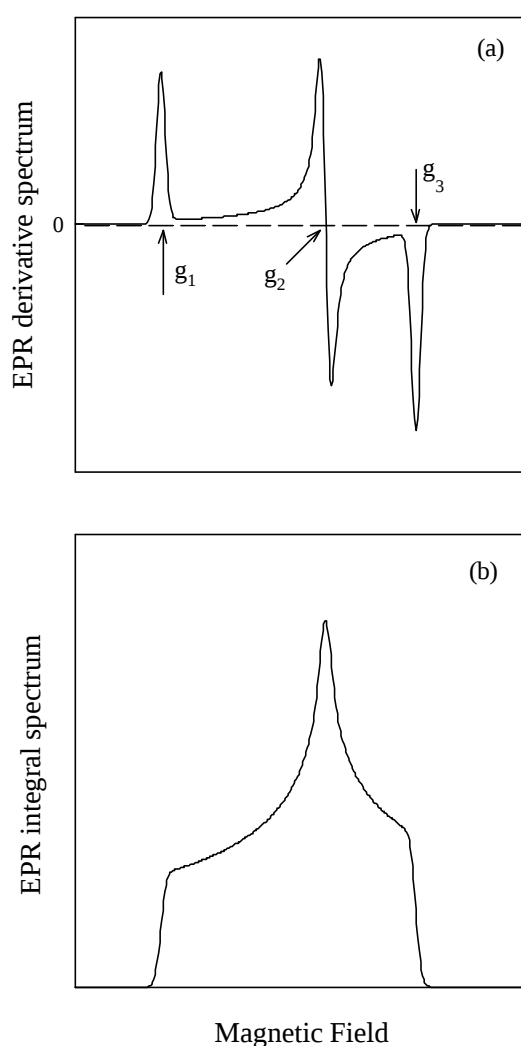


Figure 8. Typical EPR signal for amorphous or powder materials; (a) derivative spectrum, (b) integral spectrum. The principal g tensor values are evidenced

3.1.4 The hyperfine interaction

The second term in eq.(3.4) arises from the electron-nuclear hyperfine interaction. This interaction may involve either the electron and the nuclear spins of a given atom or the electron spin of an atom and one or more nuclear spins of neighboring atoms. The hyperfine interaction has two contributions, the former (isotropic) is the Fermi contact term and measures the s character of the electronic orbital, the latter (anisotropic) is the magnetic dipolar interaction between the electron and the nuclear spins [138-139]. The tensor A in eq.(3.4) includes both contributions and is represented by a 3 x 3 symmetric matrix in a generic reference frame

$$\hat{A} = \begin{vmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{xy} & A_{yy} & A_{yz} \\ A_{xz} & A_{yz} & A_{zz} \end{vmatrix} \quad (3.14).$$

It is worth to note that in general the principal axes of this tensor differ from those of the g tensor. In fact, the g tensor principal axes depend mainly on the charge distribution (crystal field) around the electron, whereas the A tensor principal axes depend on the nuclear spin distribution.

To illustrate the effects of the hyperfine interaction on the EPR spectra, we shall firstly consider here the case of an electron spin $S = 1/2$ interacting with a nuclear spin I , embedded in a crystalline matrix. We assume that the principal axes of the A tensor coincide with that of g and that the static magnetic field B is parallel to one of A principal axes, in particular to the z -axis. Under these simplifications the Hamiltonian is

$$H = bS_z g_{zz} B + A_x I_x S_x + A_y I_y S_y + A_z I_z S_z \quad (3.15).$$

Assuming that the Zeeman term is much larger than the hyperfine terms, to the zero order in perturbation theory we have only the Zeeman Hamiltonian

$$H = bS_z g_{zz} B \quad (3.16).$$

The eigenstates of H are the eigenfunctions of S_z : $|m_S\rangle$, with eigenenergies

$$E_{m_S} = b g_{zz} B m_S \quad (3.17).$$

Each eigenstate $|m_S\rangle$ has associated $(2I + 1)$ nuclear spin eigenstates of the component I_z , having eigenvalues m_I . So, the complete system state is $|m_S, m_I\rangle$ with degenerate energy (3.17).

To the first order of perturbation theory, only the hyperfine interaction term containing S_z in eq.(3.15) should be considered [139]

$$H = bS_z g_{zz} B + A_z I_z S_z \quad (3.18)$$

so, we find:

$$E_{m_S m_I} = b g_{zz} B m_S + A_z m_S m_I \quad (3.19)$$

and each Zeeman energy level is split into $(2I + 1)$ equally spaced levels.

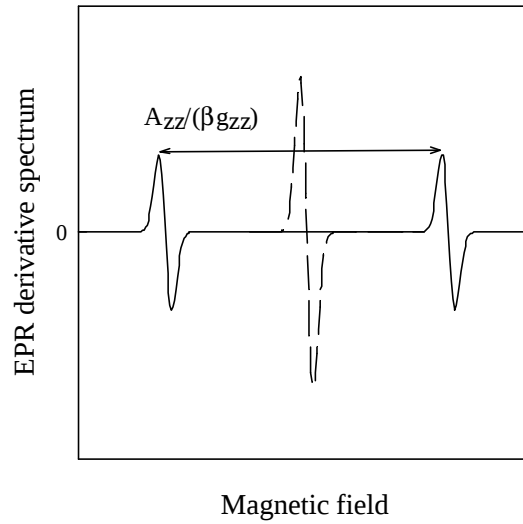


Figure 9 Typical EPR derivative spectrum for an electron spin $S = \frac{1}{2}$ interacting with a nuclear spin $I = \frac{1}{2}$. The relation between the line field splitting and the hyperfine constant is evidenced. The dashed line is the Zeeman resonance that would be observed in absence of hyperfine interaction.

The microwave magnetic field induces transitions between the energy levels with $\Delta m_S = 1$ and $\Delta m_I = 0$. The resonance condition is:

$$\hbar \omega = b g_{zz} B + A_z m_I \quad (3.20).$$

We note that for each m_I we have a different resonance field so that $(2I + 1)$ lines appear in the absorption spectrum (see fig.9). In this approximation, the lines are centered on the resonance field

of the Zeeman interaction, $B = \frac{\hbar \omega}{bg_{zz}}$, that corresponds to the absorption line that would be observed if no magnetic nucleus were present. Moreover, the splitting of adjacent lines ($\Delta m_I = 1$) in the spectrum is constant and equal to $\frac{A_z}{bg_{zz}}$ in magnetic field units ($\frac{A_z}{\hbar}$, in frequency units). As a consequence, the value of the hyperfine interaction can be inferred from the experimental spectrum.

As an example, in fig.9 we report the typical EPR derivative spectrum that is observed for a spin system with electron spin $S = 1/2$ and nuclear spin $I = 1/2$, in this case two resonance lines are observed with magnetic field separation $\frac{A_z}{bg_{zz}}$.

Even if the procedure reported is approximate, it is frequently valid when working with strong magnetic fields. For example, for a magnetic field 330 mT and $g = 2.0023$, the electron Zeeman energy is $\sim 10^{-24}$ J and we can use the previous approximation for hyperfine energy up to 10^{-25} J (corresponding to $A \sim 10$ mT or less). For hyperfine energy less than 10^{-26} J ($A \sim 1$ mT) the nuclear Zeeman interaction, neglected in the present approximation, must be considered.

As for the g tensor, the components of the A tensor may be found in a single crystal by varying the orientation of the applied static field with respect to the crystal axes and measuring the splitting of the hyperfine lines. At variance, for powder and amorphous solids, where the spin centers are randomly oriented, only the principal value of A tensor may be derived from the EPR resonance spectrum as seen in the case of g .

3.1.5 Determination of the hyperfine interaction with second order perturbation theory

As shown in the previous paragraph, the hyperfine interaction introduces satellite absorption lines in the EPR spectrum of an electron spin. In the approximation used, the hyperfine lines have equidistant resonance fields separation due to the equal spacing of the energy levels. However, the

calculation up to the second order of perturbation theory evidences an unequal energy separation of the hyperfine levels.

In view of the results reported in this thesis, we consider this effect for an electron spin $S = 1/2$ and a nuclear spin $I = 1/2$ [138-140]. We assume that the g and A tensors have axial symmetry and have the same principal axes. So, using these axes, we have

$$\mathbf{B} = B(l, m, n) \quad \hat{g} = \begin{vmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & g_{\parallel} \end{vmatrix} \quad \hat{A} = \begin{vmatrix} A_{\perp} & 0 & 0 \\ 0 & A_{\perp} & 0 \\ 0 & 0 & A_{\parallel} \end{vmatrix} \quad (3.21)$$

where B is the static magnetic field amplitude, l, m, n its direction cosines with respect to the principal axes; $g_{\perp}, g_{\parallel}$ are the principal values of the g tensor and $A_{\perp}, A_{\parallel}$ those of the A tensor. We obtain the following resonance fields corrected to the second order of the perturbation theory for the two expected absorption lines

$$B_L = \frac{\hbar\omega}{gb} - \frac{K}{2gb} - \frac{1}{4gb\hbar\omega} \left(n^2(l^2 + m^2) \frac{g_{\parallel}^2 g_{\perp}^2 (A_{\parallel}^2 - A_{\perp}^2)^2}{2g^4 K^2} \right) + \\ - \frac{1}{8gb\hbar\omega K^2} A_{\perp}^2 (A_{\parallel}^2 + K^2) \quad (3.22)$$

$$B_H = \frac{\hbar\omega}{gb} + \frac{K}{2gb} - \frac{1}{4gb\hbar\omega} \left(n^2(l^2 + m^2) \frac{g_{\parallel}^2 g_{\perp}^2 (A_{\parallel}^2 - A_{\perp}^2)^2}{2g^4 K^2} \right) + \\ - \frac{1}{8gb\hbar\omega K^2} A_{\perp}^2 (A_{\parallel}^2 + K^2) \quad (3.23)$$

$$\text{where} \quad g = \sqrt{g_{\perp}^2(l^2 + m^2) + g_{\parallel}^2 n^2} \quad (3.24)$$

$$\text{and} \quad K = \frac{\sqrt{g_{\perp}^2 A_{\perp}^2 (l^2 + m^2) + g_{\parallel}^2 A_{\parallel}^2 n^2}}{\sqrt{g_{\perp}^2 (l^2 + m^2) + g_{\parallel}^2 n^2}} \quad (3.25).$$

It can be noted that the two fields B_L and B_H have different distances from the resonance field of the electron spin without hyperfine interaction, $B = \frac{\hbar\omega}{gb}$ (central line). In other words, the hyperfine absorption lines have asymmetric field position with respect to the central line. This is due to the

presence of the third and fourth terms in eqs. (3.22), (3.23) introduced by the second order perturbation calculation. This effect is relevant when it is necessary to compare the spectral position of the unperturbed center with that inferred from the hyperfine structures. It is worth to note that in the case $S = 1/2$ and $I = 1/2$, and under the approximation made, the field splitting ($B_H - B_L$) between the hyperfine lines is related to the hyperfine tensor also with the second order perturbation correction. As a consequence, the experimental determination of this distance is still a good way to characterize the A tensor.

3.1.6 The glass line shape

Until now, we have considered the powder and amorphous absolutely equivalent from a spectral point of view. This is true only in a first approximation. In fact, a peculiarity of amorphous state with respect to crystalline and powder states is the “freedom” in the structural parameters of the matrix. As an example, bond lengths and bond angles are not strictly fixed. As a consequence, in the amorphous materials a distribution of the parameters characterizing a given spin center is encountered. Such distribution adds inhomogeneity to the spectral features of the particular paramagnet that are reflected in the final appearance of the spectra. It is observed, however, that the generality of the spectra are like the powder case, so the main spectroscopic parameters, like the principal g values and the hyperfine splitting, can be directly determined from the experimental spectrum. However, fine aspects of the spectra, relevant also from a structural point of view, can be determined only by fitting procedures taking into account the distribution of parameters introduced by the amorphous nature. Such effects have been investigated by ad-hoc fitting procedure starting from the spin-Hamiltonian and introducing distribution of the g tensor values or the A tensor values, and have been widely employed to characterize EPR spectra in amorphous [57, 145-146]. However, we will not consider this aspect further in this Ph.D. thesis.

3.2 Optical spectroscopy

Point defects are investigated in this work also by optical techniques for evidencing correlations between optical activities and EPR signals. These correlations will be used to support structural models and to get hints on the generation mechanisms of defects, for example, when a conversion from a diamagnetic precursor is hypothesized. Here the main aspects of the optical measurements used in this thesis are briefly reported for reference in the following discussion.

3.2.1 Absorption

As noted in Chapter 1, the presence of a point defect in a material introduces new electronic energy levels that belong neither to the valence band nor to the conduction band. These levels could be found in the gap of forbidden energies and, as a consequence, electronic excitation between them can be induced by electromagnetic radiation with energy less than the band gap. Such transitions give rise to absorption bands that in principle should have Lorentzian line shape. However, in the case of electronic system embedded in solids the interactions with the atomic vibrations and the inhomogeneities of the local structure, especially in amorphous, lead to absorption bands that can be approximated by gaussian shapes.

The absorption effect is evidenced by measurements in which radiation, with energy varied continuously in a chosen interval, is made to traverse a sample and then is revealed. In accordance to the Bouguer-Lambert-Beer's empiric law the intensity I (energy per unit of area and unit of time) of radiation emerging from the sample is related to the incident intensity I_0 by the macroscopic formula [147-148]:

$$I(E) = I_0(E) e^{-\alpha(E)d} \quad (3.26)$$

where $\alpha(E)$ is the *absorption coefficient* at the photon energy E and d is the sample thickness passed by the radiation. The absorption coefficient expresses the inverse of the length traversed by the light before it is attenuated by a factor $1/e$, and is usually measured in cm^{-1} . Often, the adimensional

quantity $A(E) = \text{Log}_{10}[I_0(E)/I(E)]$ is reported, this is called *absorbance*. It represents an absolute measure of the absorption intensity and it is related to the absorption coefficient by the formula

$$\alpha(E) = 2.303 A(E)/d \quad (3.27).$$

To relate the experimental quantities to the theory we consider two non-degenerate electronic states y_i and y_f of the defects with energies $E_i < E_f$. In the radiation-matter interaction an atomic system can be considered as an electric dipole with moment $\mathbf{M} = \sum_i e_i \mathbf{r}_i$, where e_i are the electron charges and $\mathbf{r}_i$ their positions. Then, according to the quantum mechanics theory, the probability that the electromagnetic radiation induces an electronic transition between the levels E_i and E_f is proportional to the Einstein coefficient for absorption [149-150]

$$B_{if} = \frac{2p}{3\hbar^2 c} |\mathbf{M}^{\hat{f}}|^2 \quad (3.28)$$

where c is the speed of light and $\mathbf{M}^{\hat{f}}$ is the electric dipole matrix element, $\int y_f^* \mathbf{M} y_i d\mathbf{t}$, in which y^* is the complex conjugate of the wave function and $d\mathbf{t}$ is a volume element (see eq.(3.33) for further details on the y). The integrated absorption coefficient is related to the Einstein coefficient B_{if} and to $\mathbf{M}^{\hat{f}}$ by the formula

$$\int \alpha(E) dE = \frac{NB_{if} \hbar \omega_{\hat{f}}}{c} = \frac{2p \omega_{\hat{f}}}{3\hbar c^2} N |\mathbf{M}^{\hat{f}}|^2 \quad (3.29)$$

where N is the number of atoms per unit volume in the state y_i , and $\omega_{\hat{f}} = (E_f - E_i)/\hbar$ is the Bohr frequency. The important result of eq.(3.29) is that the absorption intensity experimentally measured can give useful information on $|\mathbf{M}^{\hat{f}}|$ and, possibly, on the wave functions of the states involved in the electronic transition.

A relevant quantity usually employed to compare the intensities of the absorption bands is the *oscillator strength* f of the electronic transition. This is a dimensionless quantity defined as the ratio between the integrated absorption over an experimental band peaked at $\omega_{\hat{f}}$ and the theoretical absorption calculated approximating the atomic system as a charged harmonic oscillator with

frequency ω_{fi} [148-149]. It can be shown that the oscillator strength for the transition $y_i \rightarrow y_f$ is given by [148-150]

$$f = \frac{2m\omega_{fi}}{3\hbar e^2} |\mathbf{M}^{fi}|^2 \quad (3.30)$$

where m is the electron mass and in this formula $\mathbf{M}^{fi}$ is the dipole matrix element of the real transition. The oscillator strength is a parameter related to the selection rules of the electronic transition by $\mathbf{M}^{fi}$ and its determination can give information on the electronic orbitals involved. In particular, the influence of the symmetry properties or the spin multiplicity of the states involved in the transition establish the value of $\mathbf{M}^{fi}$ and, as a consequence, if a given transition is possible or not. For example, $f \approx 1$ is signature of a strongly allowed electric dipole transition whereas $f \ll 1$ characterizes a forbidden transition [148-149]. We note that for the majority of the electronic transition considered in the present thesis $f \approx 0.1$ that corresponds to a dipole allowed transition.

A quantitative relation between f and the experimental quantity $\alpha_{\max}$ is given by the Smakula's formula [151]:

$$N f = 0.87 \times 10^{17} n \alpha_{\max} \Delta / (n^2 + 2)^2 \text{ (eV}^{-1} \text{ cm}^{-2}) \quad (3.31)$$

where N is expressed in cm^{-3} , n is the glass refractive index, $\alpha_{\max}$ (cm^{-1}) is the absorption band height and Δ (eV) the Full-Width at Half-Maximum of the absorption band. This formula has been derived under the assumption of gaussian absorption bands as expected in glasses due to the intrinsic inhomogeneities. It enables to derive the concentration of absorbing centers once that the oscillator strength is known or, conversely, the oscillator strength from the concentration.

Another used quantity for the absorption effect is the cross section $\sigma(E)$. This is the total probability of absorption for a given absorbing species, it is measured in cm^2 and is related to the absorption coefficient by the formula

$$\alpha(E) = N\sigma(E) \quad (3.32).$$

The cross section can be related to the oscillator strength by means of the eq.(3.31), in this respect both quantities may be interchanged to characterize an optically active center when its absorption coefficient has been measured.

In this Ph.D. thesis, optical absorption measurements will be employed to reveal the presence of point defects. The optical absorption bands present in the material will be measured, and the effects of external treatments on these bands will be considered in order to study the kinetics of variation of the related defects. The variations of these optical features will be compared with the variations of some EPR signals, searching for eventual correlations. In this case the estimation of defect concentration from EPR measurements (see later) can be employed to derive the oscillator strength of the related bands.

3.2.2 Emission

Useful information on the energy level structure of a point defect in a solid can be obtained also through the emission measurements. It is known that after absorption process the excited electron reaches its ground state by a combination of radiative and non-radiative (phonon assisted) processes [147-148, 152]. In order to qualitatively explain these processes it is useful to consider the Jablonski energy levels diagram reported in fig.10 [152].

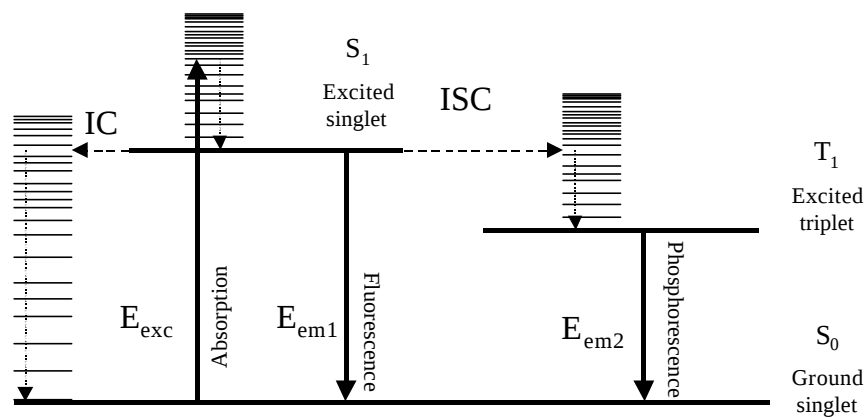


Figure 10. Energy levels (Jablonski) diagram illustrating possible electronic processes following absorption of a photon. The combs represent vibrational states. The continuous arrows represent processes that involve photons, the dashed arrows represent processes that do not involve photons and the other are vibrational relaxations. ISC is the intersystem crossing, singlet-triplet conversion, and IC is the singlet-singlet internal conversion [152].

In the case of a point defect in an insulating matrix these levels represent electronic states in the gap between the valence and the conduction bands. We now consider how these levels could arise and their relation to observable quantities.

According to the Born-Oppenheimer approximation [150, 152] the total wave function of polyatomic molecules, applicable also to point defects, can be factored into a product of nuclear (vibrational) y_v and electronic y_{es} wave functions as follows

$$y = y_v y_{es} \quad (3.33)$$

where y_{es} comprises orbital and spin angular wave functions. The electric dipole moment can be calculated using the (3.33) and it can be shown that dipole transitions are favored when the total spin of the electronic system does not change [152]. Besides, in the electronic excitation process it is possible a transition from the ground to an excited nuclear vibrational state. This is explained by the Franck-Condon factor, $\int (y_v)_f^* (y_v)_i dt_{nuclear}$, arising from the overlap of nuclear vibrational wave functions in the calculation of the dipole moment elements of matrix [152]. The simplified effect of this factor is summarized in the Franck-Condon principle that states that since electronic transition is faster (10^{-15} sec) than the nuclear motion (10^{-13} sec) the nuclei have unchanged position and momentum immediately after the transition. As a consequence, the system should go in those $(y_v)_f$ of the excited electronic state that give maximum product $(y_v)_f^* (y_v)_i$. These excitations arise when the excited electron causes an atomic geometric rearrangement in the molecule by electron-phonon coupling [147-148, 152].

In fig.10, the most common energy levels diagram is reported. The ground state, S_0 , is a spin singlet which has two electrons in the same orbital state but with opposite spin orientation ($S_{tot} = 0$). The two excited states refer to the two electrons occupying different orbital states with opposite spin orientation, singlet S_1 , or with the same spin orientation, triplet T_1 ($S_{tot} = 1$). Superimposed to these levels are reported the energy levels due to the nuclear vibrational motions related to y_v and represented by the combs in the figure.

The absorption process stimulated by photons at energy E_{exc} causes the singlet to singlet transition $S_0 \rightarrow S_1$ (spin-allowed) and in general also some vibrational excitation according to the Franck-Condon principle. After a rapid *vibrational relaxation*, that requires 10^{-11} – 10^{-9} sec [152], the system is in the ground vibrational level of the excited state S_1 . From this state the system can return to S_0 by several paths as shown in fig.10.

The radiative process of *fluorescence* is due to the spin-allowed transition $S_1 \rightarrow S_0$. This is characterized by very rapid reduction of the emission intensity within 10^{-4} – 10^{-8} sec (lifetime) [152]. It is worth to note that in general the peak energy of this emission band, E_{em1} , is lower than that of the absorption band E_{exc} (Stokes shift). This effect is partly due to the deactivation of the vibrational excitation in the S_1 state. In addition, applying again the Franck-Condon principle a radiative transition from S_1 to excited vibrational state in S_0 is possible, causing further reduction of E_{em1} with respect to E_{exc} .

The nonradiative process of *intersystem crossing* (ISC) causes the system conversion from the singlet excited state, S_1 , to the vibrational excited triplet state, T_1 [147-148, 152]. After the system relaxes to the vibrational ground state a triplet-singlet radiative transition, $T_1 \rightarrow S_0$, may occur, giving rise to *phosphorescence*. The phosphorescence emission is related to a spin-forbidden transition since there is a spin change, and usually is characterized by relatively long lifetime (10^{-4} – 10^2 sec). The phosphorescence emission has a band peaked at energy, E_{em2} , lower than the absorption energy and in general also lower than E_{em1} due to the various internal conversion processes that excite vibrations.

Other nonradiative processes reported in fig.10 are due to internal conversions and bring the system into the vibrational excited S_0 state without emission of photons. These processes, in some systems, may be competitive with respect to the radiative processes and, as a consequence, prevent the observation of emission.

In general it is assumed that the emission processes, generally indicated as *photoluminescence* (PL), are related to the absorption, so that the emission intensity can be written

as

$$I_{PL}(E_{em}, E_{exc}) \propto y I_0(E_{exc}) (1 - e^{-\alpha(E_{exc})d}) \quad (3.34)$$

where y is a factor related to the efficiency of the emission process, $I_0(E_{exc})$ is the intensity of the incident radiation at energy E_{exc} , $\alpha(E_{exc})$ is the absorption coefficient and d is the radiation path length. When the $\alpha(E_{exc})$ is sufficiently low, the emission intensity is simply proportional to the absorption coefficient

$$I_{PL}(E_{em}, E_{exc}) \propto y I_0(E_{exc}) \alpha(E_{exc}) d \quad (3.35)$$

It is then possible to determine the absorption spectrum related to a given emitting species by monitoring its emission at a fixed energy while scanning E_{exc} and maintaining $I_0(E_{exc})$ constant. This spectrum is called *excitation spectrum* and it is expected to reproduce the corresponding absorption line.

In amorphous systems, where inhomogeneities are relevant, both fluorescence and phosphorescence are characterized in general by gaussian bands, as the absorption, but the peak energies are lower than absorption energy and with different FWHM. The emission measurements are of great importance in the study of point defects. First, they enable to further characterize the electronic levels besides absorption. Also, it often happens that the absorption bands of different defects overlap partially and cannot be fully resolved. In such cases the study of the related emission bands, if present, may be decisive to separate the optical features, for example by the excitation spectra. In addition other information may be gained from the temporal (relaxation times) study of the emission.

In this Ph.D. thesis we will employ photoluminescence (PL) measurements to complement the absorption measurements and further investigate the presence of point defects. In particular, the PL measurements will be relevant in some cases in which the absorption spectra are the overlap of unresolved bands. As in the case of optical measurements the effect of external treatments on the samples will be followed by investigation of the effects on the PL bands. A comparison among

optical absorption, emission and EPR measurements will be carried out to evidence the existence of correlations.

3.3 Neutron activation

In order to establish the consistency of the structural models proposed for some point defects with the presence of residual Ge impurities in the structure, we tried to determine the content of this impurity in the investigated materials, by neutron activation measurements. We will describe briefly and qualitatively the principles of these measurements.

These measurements are destructive. The samples are bombarded with fast neutrons in a nuclear reactor. The nuclei of silica matrix and of the impurities become unstable isotopes by trapping neutrons. The ensuing radioactive decay processes are characterized by radiation emissions (mainly γ and X-rays) at given energies peculiar of the unstable nucleus. These emissions are measured and examined to determine the presence and concentration of the various elements.

In particular, the decay of a given radiation intensity as a function of time is measured after the bombardment. This intensity is related to the concentration of the excited nuclei that is given by the decay formula

$$N(t)=N(0)e^{-t/\tau} \quad (3.36)$$

where $N(0)$ is the starting concentration of excited nuclei and τ is their lifetime. Using the expression (3.36) the concentration $N(0)$ of a given activated element can be determined. In the formula (3.36) the lifetime τ is known for the various elements and it is related to the half-life time $t_{1/2}$ by the formula

$$\tau = (t_{1/2})/\ln 2 \quad (3.37).$$

In the case of the germanium determination, two nuclear decays can be revealed after the bombardment



with energy emission at 264.6 KeV, and half-life $t_{1/2} = 79$ min,



with energy emissions at 215.5, 264.5, 416.4 KeV, and half-life $t_{1/2} = 11.3$ hours.

Such measurements have high sensitivity and enable to detect concentrations of ≥ 0.7 ppm (part per million) by weight of a given element.

3.4 Electron Spin Echo

The EPR measurements can be employed to determine the concentration of the paramagnetic species present in a given sample. To this aim it is necessary to find a reference signal and relate its EPR spectrum intensity to the concentration of spin centers. Such spin concentration can be determined by the spin echo technique as will be shortly explained in what follows.

As reported in the par.3.1.1, the electron spin resonance arises when a spin system is subjected to an oscillating magnetic field $\mathbf{B}_1$ at frequency ω equal to the Larmor frequency $\omega_0 = g\mathbf{b}B/\hbar$. In general, a continuous-wave field $\mathbf{B}_1$ is applied but it is also possible to use pulsed fields.

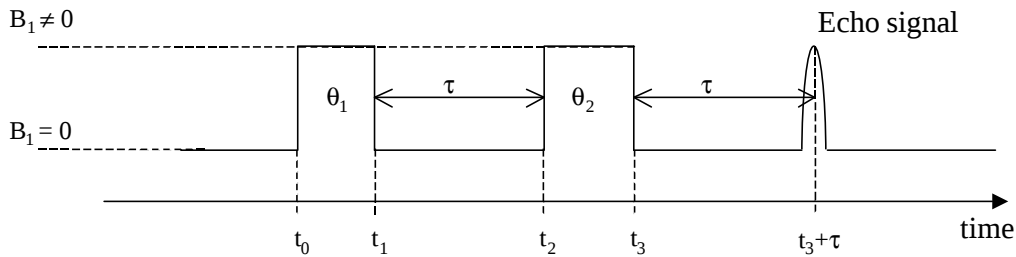


Figure 11. Schematic representation of the spin echo phenomenon. B_1 is the oscillating field amplitude, τ is the delay time between field pulses and θ_i are the pulse areas.

Hahn [153] discovered and explained the spin echo phenomenon in inhomogeneous two-level spin systems by applying a proper sequence of two pulses of field. This is pictorially reported in fig.11 where the first pulse is applied at t_0 and the second pulse at t_2 , waiting for a delay τ to elapse between the pulses. It was observed that if the delay τ is shorter than the relaxation time T_1 ,

and the two pulses have proper length a signal is emitted from the spin system at a time τ after the second pulse. Such signal is the spin echo and it is observed in inhomogeneous electron spin systems. Its origin is explained by assuming a coherent dephasing of the spins resonating at slightly different frequencies due to inhomogeneities [139, 153].

Detailed experimental and theoretical studies [154-157] of the spin echo phenomenon evidenced that its intensity depends on B_1 , the length of the two field pulses and on their time distance τ . In particular, a good generally applicable formula for the spin echo intensity is [154, 155]

$$I_{\text{ESE}}(\tau) \propto \langle \sin \theta_1 \sin^2(\theta_2) \rangle e^{-2b\tau} \quad (3.40)$$

where $\theta_1 = \frac{gbB_1}{\hbar}(t_1 - t_0)$, $\theta_2 = \frac{gbB_1}{\hbar}(t_3 - t_2)$, $\langle \rangle$ denotes an averaging over the resonance line [154], supposed to be composed of a convolution of Lorentzian with weights $g(B)$ that is the line shape of the paramagnetic species, and b is given by

$$b = b_0 + b_{\text{ID}} \langle \sin^2(\theta_2) \rangle \quad (3.41).$$

It can be shown that b_0 and b_{ID} arise from different spin-spin interaction processes [154-155] and that

$$b_{\text{ID}} = 8.2 \cdot 10^{-13} C \quad (3.42)$$

where C is the spin concentration in spins/cm³. These formulae evidence that by measuring the spin echo decay time as a function of θ_2 it is possible to determine by a best fit procedure the parameters b_0 and b_{ID} in (3.41) and then the spin concentration from (3.42). This procedure is very useful for an absolute determination of the spin concentration [155, 157].

The spin echo measurements were used in this work to determine the E' center concentration. It was used a standard EPR spectrometer to determine the E' center line shape and a second harmonic spectrometer [158] for the time resolved measurements to detect the spin echo of the E' signal and to study its decay features [159].

Chapter 4

Experimental set-ups

This chapter summarizes the properties of the instruments employed in this thesis work with detailed description of the main experimental parameters. Greater accuracy is dedicated to the EPR instrumentation since this is the principal measurement technique employed.

4.1 The EPR spectrometer

In a typical magnetic resonance experiment a static, B , and an oscillating magnetic field, $B_1 \cos \omega t$, perpendicular to each other simultaneously stimulate the paramagnetic sample. The system magnetization $\mathbf{M}$ absorbs energy per unity of volume from the electromagnetic field at an average rate A given by [138]:

$$A(\omega_0, \omega) = \frac{\omega}{2p} \int_0^{2p} \mathbf{B}_1 \cdot \frac{d\mathbf{M}}{dt} dt = \frac{1}{2} \omega c'' B_1^2 \propto \frac{NB_1^2}{1 + T_2^2 (\omega_0 - \omega)^2 + g^2 B_1^2 T_1 T_2} \quad (4.1)$$

where c'' is the imaginary part of the system magnetic susceptibility, N is the spin concentration per unit volume, $\omega_0 = g\hbar B_0/\hbar = gB_0$ is the resonance (Larmor) frequency and T_1 , T_2 are the longitudinal and transversal relaxation times, respectively, accounting for the spin-lattice and spin-spin interactions [138-140]. According to eq.(4.1), for $g^2 B_1^2 T_1 T_2 \ll 1$, the absorption is proportional to the square amplitude of the oscillating field. Usually, this low-power condition is fulfilled and when absorption is measured as a function of $B_0 = \omega_0/g$, at fixed frequency ω , as in typical EPR measurements, a lorentzian resonance line shape is detected:

$$A(\omega_0) = A(B_0) \propto \frac{NB_1^2}{1 + T_2^2 \left(\frac{g\hbar B_0}{\hbar} - \omega \right)^2} \quad (4.2)$$

it has maximum at $B_0 = \omega/g$ (*resonance field*), Half-Width at Half-Maximum $\Delta B_{1/2} = 1/(gT_2)$ and area proportional to the concentration of absorbing centers.

In the case of an inhomogeneous spin system, as in the powders or amorphous as discussed in Chap.3 [53, 141-144], a distribution of the resonance fields, B_0 , is present. For example, in the case of eq.(3.13), the different relative orientations of the external field and the g tensor axes yield different resonance values

$$B_0 = \frac{\hbar \omega}{bg(B_0)} \quad (4.3)$$

where now we have introduced

$$g(B_0) = \sqrt{(g_1 \cos q_{1,0})^2 + (g_2 \cos q_{2,0})^2 + (g_3 \cos q_{3,0})^2} \quad (4.4)$$

to stress the relation between the amplitude of the resonance field and its direction with respect to the g tensor axes.

As a consequence of this distribution of B_0 , it is necessary to consider in the determination of the absorption intensity and line shape a weighting factor for the number of spins $dN(B_0)$ with resonance field $B < B_0 < B + dB$. The absorption intensity at a specific resonance field, B_0 , in the low-power condition, is then given by [53, 141-143]

$$A(B_0) \propto \int_{B_{\min}}^{B_{\max}} \frac{NB_1^2}{1 + T_2^2 \left(\frac{g(B)bB}{\hbar} - \frac{g(B_0)bB_0}{\hbar} \right)^2} f(B) dB \quad (4.5)$$

where $f(B)$ is a distribution function, determined from eq.(4.3), and counting how many different relative orientations (q_1, q_2, q_3) give the same resonance field B [142], and $B_{\min}$, $B_{\max}$ are the minimum and maximum resonance fields expected from eq.(4.3). A typical absorption line, calculated from eq.(4.5), is reported in fig.8 (Chap.3) for a spin 1/2. Additional complexity arises in the amorphous systems in which distribution of the g tensor principal values and axes should also be considered. It is usual to simulate this effect by overlapping absorption lines (4.5) obtained for different sets of g tensors and adequately weighted [57].

Now we describe the operating principles of our spectrometer in view of the discussion of the experimental results.

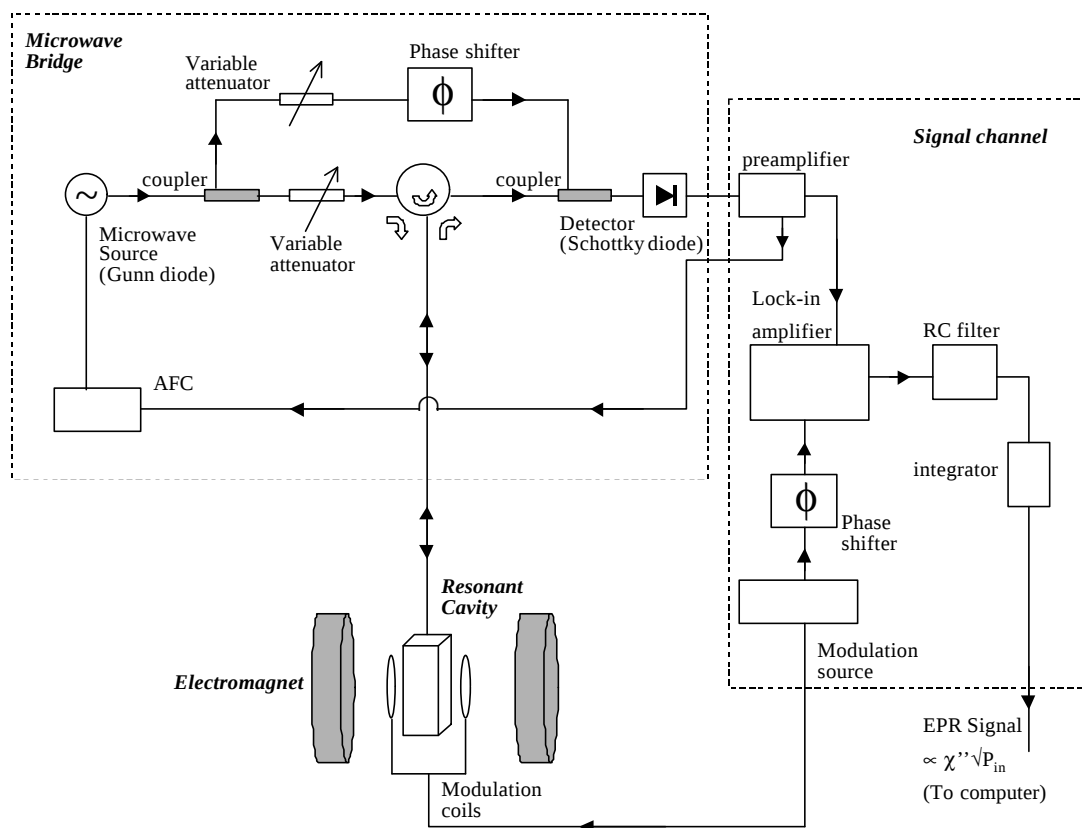


Figure 12. Block scheme of the EPR reflection spectrometer.

In general, it is difficult to change and control accurately the frequency of the electromagnetic field, so typical EPR spectrometers operate at fixed frequency and vary the static magnetic field amplitude B . The spectrometer here employed is a Bruker EMX and works at the microwave frequency 9.8 GHz. Its block diagram is reported in fig.12 evidencing the main sections: the resonant cavity, the electromagnet, the microwave-bridge and the signal channel.

The spectrometer reveals the magnetic resonance absorption by detecting the microwave power reflected from the resonant cavity when the field B is varied around the resonance value. The reflected power depends mainly on two factors, the energy absorbed by the cavity due to the electric losses on its walls and the energy absorbed by the paramagnetic sample put inside the cavity [141]. In particular, the latter is related to the resonance absorption. In fact, when the magnetic field B satisfies the magnetic resonance condition, $\omega = g\mu_B B_0/\hbar = g\mu_B B_0$, for a paramagnetic species, the

absorption from the sample increases causing a change in the reflected power level. This variation is then detected as a voltage signal from suitable circuitry that is described in the following.

In particular, it is possible to show that the variation $|\Delta E_r|$ of the reflected voltage at the magnetic resonance is [141]

$$\frac{|\Delta E_r|}{E} = \frac{c'' h Q}{2} \quad (4.6)$$

where E is the voltage incident on the cavity, that depends on the input power $E \propto \sqrt{P_{in}} \propto B_1$ [141]; η is the filling factor,

$$h = \frac{\int_{V_{sample}} B_1^2 dV}{\int_{V_{cavity}} B_1^2 dV} \quad (4.7)$$

that depends on the geometry of the cavity and of the sample, V refers to the volumes of the cavity or of the sample; Q is the loaded cavity quality factor in absence of magnetic resonance absorption

$$Q = \frac{2p(\text{stored energy})}{\text{energy dissipated per cycle}} \quad (4.8).$$

It depends on the energy leakage not due to magnetic resonance absorption and is related to the unloaded cavity quality factor Q_0 , to the cavity coupling to the microwave line and, eventually, to the dielectric or conductivity losses in the sample [141].

To optimize the sensitivity, the spectrometer is regulated so that when the microwave source is tuned to the cavity frequency the power reflected from the cavity is as low as possible, without lessening the cavity quality factor. This condition is named *critical coupling* and it is obtained by regulating the coupling iris between the microwave line and the cavity [141].

The peculiarities of the various parts of the spectrometer clarify better its functions and the parameters that are involved in a measurement.

The **resonance cavity** is a metallic box in which, due to its size and shape (usually rectangular or cylindrical), particular frequencies and spatial distributions of the oscillating electric

and magnetic fields can be realized. These distributions are named resonance modes. The here employed cavity is rectangular with resonance frequency at ~ 9.8 GHz and principal resonance mode TE_{102} [141]. It has a quality factor $Q_0 = 6000$ enabling high sensitivity in accordance to eq.(4.6). The samples are inserted in the geometrical center of the cavity where the TE_{102} magnetic field amplitude is maximum and the electric field zero, enhancing the filling factor (4.7) and the sensitivity.

The cavity is inserted at the center, C, of the gap between the poles of an **electromagnet** with static field, B, directed perpendicular to the oscillating field B_1 . The electromagnet poles are cylindrical and are separated by 62 mm. The field B can be varied up to 10 T in steps of 10^{-4} mT and with absolute accuracy of $\sim 8 \times 10^{-2}$ mT. In addition, B is homogeneous within 10^{-3} mT in a rectangular volume $\Delta x = 5$ mm, $\Delta y = 22$ mm, $\Delta z = 10$ mm centered at C, where z is the pole to pole direction, y is the vertical direction and x is perpendicular to the yz plane. This gives typical field homogeneity on the volume (see Chap.5) of the investigated samples of 2.5×10^{-5} mT.

The central part of the spectrometer is the **microwave bridge** that is composed of various elements. The first is a Gunn diode *microwave source* at frequency $\nu = \omega/2\pi \sim 9.8$ GHz and power 200 mW. This source is coupled to the cavity by waveguides, couplers and an iris. The microwave frequency is locked to the cavity resonance frequency by the Automatic Frequency Control (AFC) system [141]. The latter is a frequency modulation type [141] working at 76.8 KHz. The microwave power arriving to the cavity can be attenuated over a range of 60 dB, with a minimum step of 1 dB. This characteristic allows to adequately fulfill the condition $g^2 B_1^2 T_1 T_2 \ll 1$ to obtain a reliable measurement of the true EPR line shape.

The signal reflected from the cavity is revealed by a Schottky barrier diode working in the linear region [141]. As reported in eq.(4.6), the linear detector current is proportional to the square root of the input power. To ensure that the diode works within its linear regime, some extra power tapped from the source and correctly phased is superimposed to the signal from the cavity.

The revealed signal is elaborated by the **signal channel** that employs a lock-in detection system as further improvement of the instrumental sensibility. This detection is realized by superimposing a low frequency oscillating field: $\frac{1}{2} B_m \sin(\omega_m t)$, named *modulation field*, to the static field B . As a consequence, the paramagnetic resonance response and the signal reflected from the cavity are amplitude modulated at the frequency ω_m . So, by using a phase sensitive amplifier (lock-in), the spectrometer selects the signal at ω_m and gives a rectified voltage output [141].

The amplitude and frequency of the modulation field should satisfy some constraints to avoid line shape distortions in the revealed spectrum [141]. In particular, the amplitude should be less than the peak-to-peak field distance ΔB_{pp} in the derivative spectrum (see later), and usually is set in the range $B_m \leq 0.4 \Delta B_{pp}$ [141]. As regards the frequency, it should be $\omega_m < \frac{gb\Delta B_{pp}}{\hbar}$ to avoid the appearance of sideband resonance lines separated by $\frac{\hbar\omega_m}{gb}$ and in a range B_m around the resonance field [141]. This condition is usually satisfied by choosing a modulation frequency $\omega_m = 2\pi \times 100$ KHz, that prevents the sidebands appearance for $\Delta B_{pp} \geq 3.6 \times 10^{-2}$ mT.

The detected signal could be magnified by varying the gain of the lock-in amplifier by a factor up to 4×10^6 . To improve the signal to noise ratio a RC circuit filters the lock-in amplifier output. The RC time constant (T_{const}) can be regulated in the range $0.01 \text{ msec} \div 5.24 \text{ sec}$, to cut noise frequency higher than $1/T_{const}$. However, to avoid distortion of the line shape it is necessary that T_{const} be adequately regulated with respect to the scan speed [141]

$$T_{const} \leq 0.1 \frac{\Delta B_{pp}}{\Delta B_{sweep}} T_{sweep} \quad (4.9)$$

where ΔB_{sweep} , T_{sweep} are the interval of magnetic field scanned and the scan time.

Finally, an integrating Analog to Digital Converter is employed to digitize the analog EPR signal. This A/D converter is characterized by a conversion time T_{conv} which can be set in the range $0.32 \text{ msec} \div 2.62 \text{ sec}$.

An intrinsic feature of the lock-in detection is that the modulation of B produces a signal proportional to the slope (first derivative) of the real absorption curve [141]. This explains why usual EPR spectra are in the first derivative form $\frac{dA}{dB}$. This form is advantageous to individuate inflection points and maximum position of the absorption line shape which is very useful in the resolution of partially overlapping absorption lines. All the EPR spectra reported in this thesis are first derivative, as usual in EPR works.

To conclude this section, we summarize the parameters that can be regulated in a spectrometer in a more schematic way since they usually differ in the detection of distinct paramagnetic species. These parameters are:

input microwave power: P_{in} ;

modulation field frequency: ω_m ;

modulation field amplitude: B_m ;

RC filter time constant: T_{const} ;

receiver gain;

conversion time: T_{conv} ;

all these parameters should opportunely be set for each EPR signal in order to avoid distortions. A good review of the procedures followed for these settings is reported in ref.141.

4.1.1 Saturation effects

Among the various instrumental settings previously reported the input microwave power is of particular experimental relevance. In fact, as evidenced in eq.(4.1), it is necessary to work under the condition $g^2 B_1^2 T_1 T_2 \ll 1$ to reveal a resonance absorption that can be easily related to the concentration of the paramagnetic centers. Also, if this condition is not satisfied the intensity of the absorption reaches a constant value and the line shape is also broadened when P_{in} is excessively increased, as can be seen from eq.(4.1). These distortions affect the exact determination of the g

tensor values, as explained in Chap.3, from examination of the experimental resonance line. So the wrong regulation of P_{in} compromise two relevant information of EPR measurements.

The origin of these distortions is related to the spin-lattice relaxation processes (see par.3.1.1). In particular, they arise when the spin relaxation rate is not fast enough to balance the rate of excitation by the microwave field [138]. This regime is usually indicated as *saturation*. The saturation is a peculiarity of a given paramagnetic species and is related to the specific solid system, since it depends on the relaxation times T_1 , T_2 . So, the study of the saturation properties of the resonance lines can be useful to distinguish different paramagnetic centers.

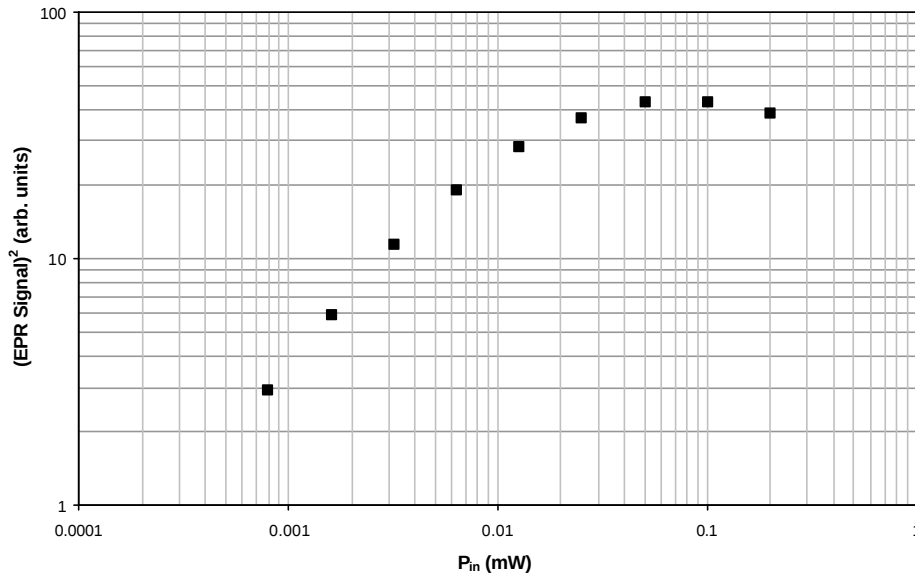


Figure 13. Typical behavior of the EPR signal as a function of the impinging microwaves power.

An experimental procedure has been followed to identify the microwave saturation properties of a given resonance line. It consists in detecting the EPR signal as a function of P_{in} . As reported in the previous paragraph the EPR signal is given by $|\Delta E_r| \propto c'' \sqrt{P_{in}}$. So, in the non-saturation regime, $g^2 B_1^2 T_1 T_2 \ll 1$, the squared EPR signal is proportional to P_{in} , since χ'' depends only on B, whereas at higher power the proportionality is lost. By plotting $(\Delta E_r)^2$ as a function of P_{in} , as reported in fig.13, the non-saturated regime is identified as a linear region, this is followed by a distortion regime that typically ends with a constant value of (ΔE_r) before stronger distortions

cause the signal to drop to zero. This procedure has been employed to distinguish the various EPR signals, individuated in the irradiated samples, besides that to find the suitable power to estimate the paramagnetic center g values and concentration.

4.1.2 Spin concentration

Once the linear regime of an EPR signal has been determined, it is possible to evaluate the spin concentration by measuring the area under the absorption curve by doubly integrating the revealed signal with respect to B (the EPR spectrum is proportional to the first derivative of the absorption).

Usually, the spin concentration is determined by comparing the investigated signal with a reference sample, with known number of paramagnetic centers. In the present work, the determination of the spin concentration has been made by this comparison technique but using as reference one of the resonance signal induced by γ irradiation in all silica samples. This signal is due to the E' -Si center [26, 52-58]. The spin concentration of the latter has been determined preliminarily by the spin echo technique described in par.3.3.

Once the E' centers concentration was determined, their concentration/area ratio has been estimated for reference. In particular, it was found that the area normalized by $\sqrt{P_{in}} (mW)^{1/2}$, B_m (mT), T_{conv} (msec), receiver gain and sample weight (gr) gives the concentration:

$$\text{concentration} = (\text{normalized area}) \times (3 \pm 0.3) \times 10^{15} \text{ centers/cm}^3 \quad (4.10)$$

The latter relation has been used for the determination of the other paramagnetic species concentration starting from their normalized area. The method used should be enough accurate since, by using the same sample for the reference and for the unknown signal, there is less indetermination due to filling factors and other coupling problems [141]. As a final remark, from the reproducibility of the EPR measurements, a typical error of 10 % of the registered spectrum

intensity has been estimated. As a consequence, we attribute this error to all the EPR intensity measurements reported in the following discussions.

4.2 Optical measurements

Besides the EPR measurements the samples were investigated by optical measurements in order to evidence correlations among optical and paramagnetic activities. These correlations are particularly relevant to get hints for the defect structure and to clarify the generation mechanisms of defects, for example, when a conversion from a precursor may be hypothesized. Here the main features of the optical measurements used in this thesis are shortly reported for reference in the following discussion.

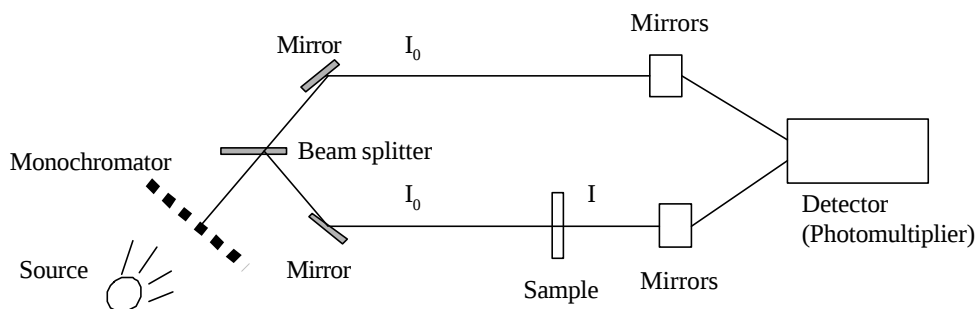


Figure 14. Simplified block scheme of the double-beam spectrophotometer employed for optical absorption measurements.

4.2.1 The absorption spectrometer

The optical absorption measurements were carried out in the UV range with a JASCO V570 spectrophotometer working in the NIR-VIS-UV. Its simplified block scheme is reported in fig.14. The light source for UV range measurements is a deuterium discharge tube operating in the wavelength range 190-350 nm (3.5-6.5 eV). The wavelength of the impinging light is selected by a monochromator employing a Czerny-Turner mount plane grating with 1200 lines/mm. The light is then split into two paths one passing through the sample and the other used as reference. At the end of these paths the light is detected by a photomultiplier tube. The spectrophotometer measures the

sample absorbance (Abs) from which the absorption coefficient can be determined, once the sample thickness is known (see eq.(3.27)).

All the measurements reported in this thesis were carried out in the range 190-300 nm (4.1-6.5 eV) by steps of 0.5 nm with a detection spectral bandwidth 2 nm, scan speed 10 nm/min and averaging value data for ~ 4 sec at each data point.

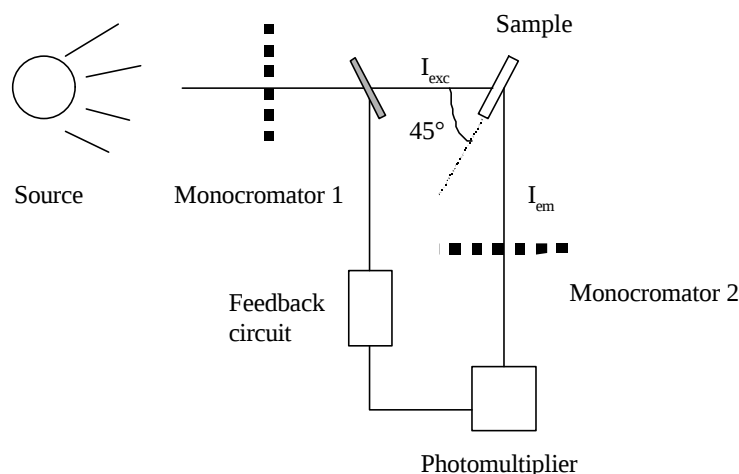


Figure 15. Schematic block scheme of the spectrofluorometer with the sample mount in the 45° back-scattering geometry.

4.2.2 The photoluminescence spectrometer

The photoluminescence (PL) measurements were carried out in the VIS-UV range using a JASCO FP-770 spectrofluorometer. A simplified block scheme of the instrument is depicted in fig.15. The light source is a 150 W Xenon arc lamp operating in the wavelength range 220-750 nm (1.7-5.6 eV). The spectral bandwidth of excitation and emission lights can be varied from 1.5 to 20 nm by two monochromators, M1 and M2. The emitted light is then detected by a photomultiplier. In order to avoid differences in the emission due to the intensity inhomogeneity of the source lamp a feedback circuit is used to adequately regulate the overall photomultiplier gain. This circuit employs a Rhodamine B quantum counter to obtain a wavelength-independent reference signal.

The set-up of the spectrometer in the emission measurements, reported in fig.15, is the 45° back-scattering configuration. In this configuration, the excitation radiation impinges on the glass

sample at 45° from its surface and in a direction at 90° from the detection direction. Such disposition prevents that the excitation radiation is revealed from the detector except from the very low intensity scattered contribution.

In the PL emission measurements the light excitation wavelength and bandwidth are fixed by M1. At the same time M2 spans an emission wavelength range with fixed bandwidth. PL emission measurements are not absolute since they are single beam and only relative intensity comparison in a spectrum can be made. For this reason, it is necessary to correct the spectra for the instrumental response to avoid distortion at different wavelength. This is done by an instrumental procedure in which the sample is substituted by a MgO diffuser plate and a scan is executed revealing the emission at the same wavelength λ as the excitation. This kind of spectra represents the spectral response of the detector since fluctuations in the excitation light are compensated by the feedback circuit. The correction function $R(\lambda)$ determined in this way has been used to scale all the emission spectra.

PL excitation measurements (PLE) have been carried out detecting the emission at fixed wavelength and bandwidth in M2 while the excitation wavelength was varied maintaining fixed the bandwidth in M1. These spectra need no correction since the feedback circuit realizes real time compensation for differences in excitation intensity.

The accuracy of the emission intensity was evaluated to be within 10 %. This error has been determined by the reproducibility of a given measure and is attributed to variations in the mounting geometry. This, in fact, causes different reflection and scattering of light influencing the excitation light intensity on each emitting optical center.

Chapter 5

Materials and treatments

This chapter is devoted to describe the materials employed in this thesis and the treatments to which the samples were subjected. The principal details are reported to individuate those parameters relevant for the discussion of the experimental results.

5.1 Materials

As reported in Chapters 1-2, in the study of the processes that cause point defects in silica glasses the material manufacturing is of great relevance. In fact, the mechanisms of defect generation are strongly conditioned by the presence of impurity atoms and the very preparation technique is often believed to affect these mechanisms [3, 18, 21, 23, 33, 114]. In particular, we refer to the temperature and atmosphere under which the different materials are produced.

The presence of impurities is relevant because it gives origin to native defects appearing in the “as grown” material before any external treatment. In addition, the impurities may be involved as intermediary in the generation of point defects or, most relevant, as perturbation of sites giving rise to precursors. All these features condition the sensibility of the various materials to the post-manufacturing treatments.

For these reasons the comparison of materials produced following different procedures is particularly relevant in the study of point defects. In particular, it should be evidenced the different resistance to the irradiation and the existence of correlation between the generation of particular defects and the peculiarity of the material and also their correlation with the presence of certain impurities.

The samples used in this thesis are of commercial origin. This choice is related to the rigidity of the industrial manufacturing and the tested high reproducibility of the material characteristics. The materials can be classified on the basis of the convention introduced in refs.21,

160. In particular, four typologies of silica are distinguished on the basis of the main manufacturing features (some details are protected by the producer) and the concentration of the most diffused impurity, the OH group, believed to be bonded to a Si atom, $\text{O}=\text{Si}-\text{OH}$ (see fig.6 for example), normally bonded to three other oxygen:

Type I (natural dry): fusion of quartz powder by electric arc in a crucible in vacuum or inert gas atmosphere at low pressure. $[\text{OH}] < 30$ ppm (by weight, $\sim 10^{18}$ centers/cm³); other impurities, usually less than 10 ppm.

Type II (natural wet): flame fusion of quartz powder in water vapor atmosphere. $[\text{OH}] 150 \div 400$ ppm; other impurities less than the starting material because some of them are volatilized in the flame.

Type III (Synthetic wet): hydrolysis of pure silicon compounds, usually SiCl_4 , injected in gas-phase into a hydrogen/oxygen flame. Actually, the process is an oxidation, since the compound is transformed in the flame into fused drops of SiO_2 . $[\text{OH}] \geq 100$ ppm; other impurities content negligible since the starting material contains much less impurities than the natural quartz.

Type IV (Synthetic dry): Reaction of O_2 with SiCl_4 in water-free-plasma. $[\text{OH}] < 1$ ppm; other relevant impurity: $[\text{Cl}] \sim 100$ ppm.

TABLE 1. Sample list (nickname), type [21-160], and nominal OH content

Silica Sample	Type	[OH] ppm by weight; (cm ⁻³)
Infrasil 301 (I301) ¹	Natural dry (I)	≤ 8 ; (5.6×10^{17})
Pursil 453 (P453) ²	Natural dry (I)	< 5 ; (3.5×10^{17})
Puopsil A (QPA) ²	Natural dry (I)	15; (10^{18})
Silica EQ 906 (EQ906) ²	Natural dry (I)	20; (1.4×10^{18})
Silica EQ 912 (EQ912) ²	Natural dry (I)	15; (10^{18})
Vitreosil (VTS) ³	Natural wet (II)	150; (10^{19})
Herasil 1 (H1) ¹	Natural wet (II)	150; (10^{19})
Herasil 3 (H3) ¹	Natural wet (II)	150; (10^{19})
Homosil (HM) ¹	Natural wet (II)	150; (10^{19})
Suprasil 1 (S1) ¹	Synthetic wet (III)	1000; (7×10^{19})
Suprasil 311 (S311) ¹	Synthetic wet (III)	200; (1.4×10^{19})
Corning Substrate (CSB) ⁴	Synthetic wet (III)	800-1000; ($5.6-7 \times 10^{19}$)
Corning 7940 (CNG5F) ⁴	Synthetic wet (III)	800-1000; ($5.6-7 \times 10^{19}$)
Suprasil 300 (S300) ¹	Synthetic dry (IV)	< 1 ; (7×10^{16})

Supplied by: ¹Heraeus [161], ²Quartz & Silice [162], ³TSL [163], ⁴Corning [164].

In summary, it is observed that, apart from the OH groups introduced in the manufacturing process, the natural silica contains impurities belonging to the employed quartz, whereas the synthetic silica have less impurities but trap residues of the halogen used in the synthesis.

A full list of the samples here used is reported in Table 1 specifying the type, the OH content and the manufacturer. In parenthesis is reported the nickname adopted. We have verified the OH content by IR absorption measurements by detecting the band at 2720 nm attributed to the OH stretching vibrational mode of Si-OH, and we found fair agreement with the nominal values.

We have also investigated the Ge content of our silica samples, in view of its relevance in the study of the optical B-activity. This content has been determined with the neutron activation technique reported in par.3.3, and the results are summarized in Table 2 where the experimental weight ratio Ge/SiO₂ is shown together with the deduced Ge concentration.

TABLE 2. Neutron activation measurement results. Sample list, weight ratio Ge/SiO₂ and Ge concentration

Sample	Ge/SiO ₂ (ng/mg)	[Ge] (10 ¹⁶ cm ⁻³)
H1	0.93	1.6
QPA	0.78	1.5
EQ906	0.73	1.4
Other in Table 1	< 0.5	<0.8

The samples, received in the shape of slabs having sizes 50 x 5 x 1 mm³, were cut in pieces of sizes 2 x 5 x 1 mm³ (used in spin echo measurements), and 5 x 5 x 1 mm³. Unless otherwise specified, all the results are reported for the latter size. In the following, to simplify reference to the various materials, the notation adopted is (nickname)/(dose), where the dose is reported in kGy for simplicity (10 kGy = 1 Mrad).

We finally report that all the samples, also after the cut procedure, present no EPR signal before irradiation. Also, all the native optical activities were found to be highly reproducible in samples of the same manufacturing but coming from different stocks.

5.2 Treatments

In this section we report the irradiation procedures employed in this thesis and the thermal treatments. We note that for each material all the irradiation were carried out in different pieces so, unless otherwise specified, series of irradiated samples were obtained. The results reported for each irradiation type refer to these series of samples.

5.2.1 g-irradiation

Our study of point defects induced by ionizing radiation was performed principally by exposing the samples to γ -rays in a source of ^{60}Co [the irradiation was carried out in the irradiator IGS-3 of the Department of Nuclear Engineering, University of Palermo]. γ -rays emitted by ^{60}Co have energies 1.17 MeV and 1.33 MeV (mean energy 1.25 MeV). In the irradiator the dose rate was ~ 4 kGy/hour; this value is peculiar of SiO_2 because, as reported in par.1.3, the energy deposited depends on the atomic weight of the target material. Unless otherwise specified, the irradiation was carried out at room temperature, in normal atmosphere, and in the dose range from 5 Gy up to 10^7 Gy.

For some experiments (described in Chap.8) γ irradiation was performed at $T = 77$ K. In this case the samples were immersed in liquid nitrogen. In principle, the presence of the liquid in the path of the γ -rays could attenuate their deposited energy influencing the estimation of the dose accumulated in the samples. To investigate this effect we made test irradiation with the container filled with water at room temperature. In fact, since the liquid nitrogen density relative to water is 0.81, they are considered to have almost the same attenuation effect. We have verified that the irradiation into water is comparable with the irradiation with the empty container with differences less than 10%. As a consequence, we can assume that the same dose rate is effective at 77 K and at room temperature.

5.2.2 b-irradiation

Irradiation with electrons of 2.5 MeV and current 20 μA was carried out in a Van de Graff accelerator [irradiation was performed at LSI laboratory, Palaiseau, France] [165]. The dose range investigated was $1.2 \times 10^6 \div 5 \times 10^9$ Gy, at the dose rate 20 kGy/sec (SiO_2) and at $T = 350$ K. Moreover, only for this irradiation the sample size was $5 \times 5 \times 0.5 \text{ mm}^3$, where the thickness was 0.5 mm for irradiation homogeneity reasons and to avoid charge trapping and consequent current leakage.

Another set of electron irradiation was performed in a lower dose range. This electron irradiation was carried out with a pulsed linear accelerator (LINAC) with beam energy of 5 MeV, pulse length 4 μsec , repetition frequency 10 Hz [irradiation was performed at ENEA, Centro Ricerche, Frascati (Italy)] and at room temperature [166-167]. For these experiments, only two doses were considered: 2×10^4 Gy (with 2860 pulses) and 2×10^5 Gy (with 28600 pulses), each one determined by comparison with a standard of hexahydroxil pararosaniline nitride. We note that the first dose was the minimum available in the source.

5.2.3 neutron bombardment

Neutron irradiation were performed in the core of nuclear reactor or with thermal neutrons [irradiation was carried out at “Centro di studio per la radiochimica ed analisi per attivazione” C.N.R. Pavia (Italy) with the TRIGA MARK II reactor]. A first session was executed during the neutron activation measurements (see par.3.3) and was carried out inside the core of the reactor employing two neutron fluence rates $\Delta\phi/\Delta t$:

$$\begin{aligned} (\Delta\phi/\Delta t)_1 &= 10^{12} \text{ n}/(\text{cm}^2 \cdot \text{sec}) && \text{for 4 hours} \\ (\Delta\phi/\Delta t)_2 &= 8 \times 10^{12} \text{ n}/(\text{cm}^2 \cdot \text{sec}) && \text{for 5 hours} \end{aligned}$$

and an overall irradiation flux of $[N]_1 = 1.6 \times 10^{17} \text{ n}/\text{cm}^2$ was estimated. For comparison reasons, a second irradiation session was carried out in other pieces of the material for a very short time (~ 10 sec) at $(\Delta\phi/\Delta t)_2$ yielding to an overall neutron flux $[N]_2 \sim 8 \times 10^{13} \text{ n}/\text{cm}^2$.

Finally, another neutron irradiation was performed using thermal neutrons outside the reactor core. In this case the fluence rate was $(\Delta\phi/\Delta t)_3 = 10^{10} \text{ n}/(\text{cm}^2\cdot\text{sec})$. Two irradiation fluxes were accumulated: $[N]_3 = 3.6 \times 10^{13} \text{ n}/\text{cm}^2$ and $[N]_4 = 8.6 \times 10^{14} \text{ n}/\text{cm}^2$.

5.2.4 Thermal treatments of the irradiated samples

After the irradiation some samples were thermally treated to investigate the stability of the radiation-induced centers. These treatments were performed in an electric furnace equipped with an internal thermometric sensor and a feedback electronic circuit to stabilize the temperature within $\pm 3 \text{ K}$.

In each thermal cycle, after the furnace had reached the pre set temperature, the sample was placed inside the furnace. It is worth to note that immediately after the sample insertion the temperature variation observed was not relevant for the overall treatment (maximum variation of -5K balanced within 2-3 min). After the end of the thermal cycle the sample was removed from the furnace and was returned to room temperature at normal atmosphere. After thermalization to room temperature the sample was monitored by OA, PL and EPR measurements.

Two thermal treatment sequences were executed. They can be distinguished according to usual nomenclature [77]. The *isochronal treatment* is the sequence of thermal treatments $\theta(T_i, t)$ each with constant time interval, t , but at different temperatures, T_i . The *isothermal treatment* is the sequence of treatments $\theta(T, t_i)$ with fixed temperature, T , but for a sequence of time intervals, t_i .

Our isochronal treatments were performed using a time interval of 25 min and at temperatures in the range 330-430 K by steps of 10 K. Isothermal treatments (at temperatures $T = 350, 370$ and 390 K) were carried out with time intervals from 10 to 50 minutes up to an overall duration of 200 min.

Chapter 6

Experimental results: The E' centers

The paramagnetic defects induced by γ irradiation are the main concern of this thesis work. We will investigate the defects induced by γ irradiation reporting both their main EPR spectral features and the study of their growth kinetics as a function of the irradiation dose. The open problems of all the investigated centers have been already outlined in Chap.2. In this chapter we report our experimental results on the E'-Si center, hereafter referred to as E' center.

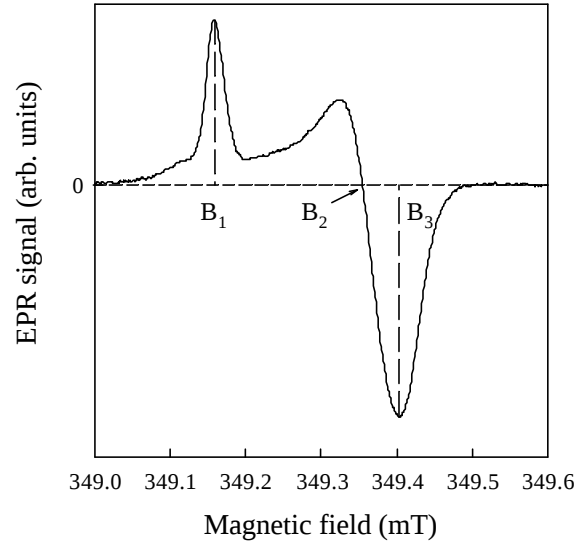


Figure 16. Typical EPR spectrum of the E' center as detected in the sample I301/5000. The magnetic field positions relative to the principal values of the g tensor are evidenced.

6.1 EPR properties

The typical EPR spectrum of the E' center observed in highly irradiated silica (≥ 500 kGy) is shown in fig.16, as measured in the sample I301/5000 using $P_m = 8 \times 10^{-4}$ mW, $\omega_m = 100$ kHz, $B_m = 0.01$ mT. This center has the characteristic resonance line of a paramagnetic site having a slightly asymmetric g-value tensor in an amorphous material [56]. To characterize the observed resonance line we determined the g tensor principal values. In particular, as explained in par.3.1.3

and evidenced in fig.16, we determined the field positions B_i relative to the principal g values in our spectrum. We also measured the microwave frequency ω during the EPR measurement employing a precision microwave counter. To estimate the g tensor values we used $g_i = \hbar\omega/\beta B_i$, and we found: $g_1 = 2.0028$, $g_2 = 2.0017$ and $g_3 = 2.0014$. The differences of these principal g values are in good agreement with those reported in literature for the E'_γ center [57, 58] so it can be concluded that we are observing this E' variant.

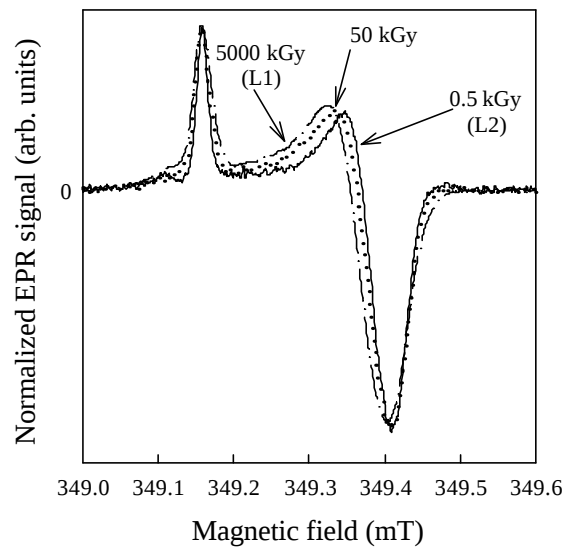


Figure 17. Normalized EPR spectra in the sample I301 γ irradiated at doses: 0.5 kGy (continuous line), 50 kGy (dotted), 5000 kGy (dash-dotted). The original spectra were shifted in magnetic field to overlap the peaks at ~ 349.2 mT, in order to enable comparison. All the spectra were acquired with $P_{in} = 8 \times 10^{-4}$ mW, $\omega_m = 100$ kHz and $B_m = 0.01$ mT.

The reported resonance line is typical of all the irradiated silica types investigated for doses higher than 500 kGy, and we will call this line shape L_1 . At variance, as reported in fig.17 for the sample I301/5000, I301/50 and I301/0.5, slightly different line shapes were observed after lower irradiation doses. In particular, a different line shape (L_2) with $g_1 = 2.0029$, $g_2 = 2.0017$ and $g_3 = 2.0015$, was observed at very low doses when the signal begins to be detectable. The same line shape was observed in all the materials except for S1 and S311 in which only L_1 was detected. As reported in fig.17, the line shape gradually changes from L_1 to L_2 on increasing the irradiation dose.

Further characterization of the E' center was carried out studying the signal dependence on the microwave power. In fig.18, we report the squared double integral of the EPR line (normalized to the maximum double integral) as a function of P_{in} . The samples I301/5000 and I301/0.5 were chosen as representative of the line shapes L_1 and L_2 , respectively. As evidenced in the figure, the region of linear dependence on the microwave power is shifted in the two samples, in particular the I301/0.5 reaches the saturation value at a lower power than the I301/5000. These properties point out differences in the coupling with the lattice vibrations of the spin centers in the two samples. These aspects will be discussed later in this chapter.

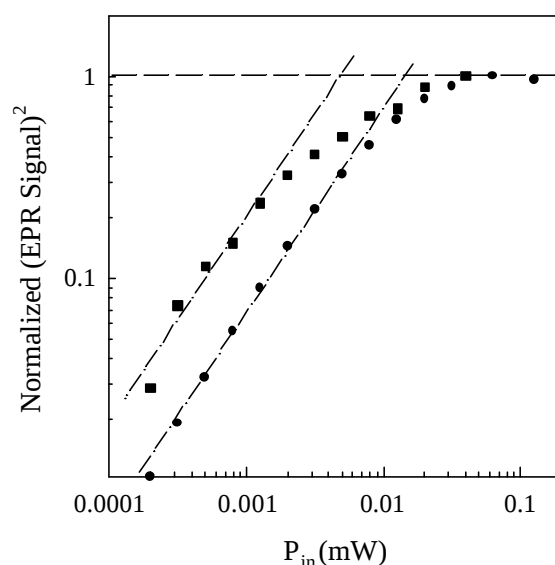


Figure 18. Dependence of the normalized double integral of the E' centers signal on P_{in} , in the samples I301/0.5 (squares) and I301/5000 (circles). The linear dependence is evidenced by the dash-dotted lines.

6.2 Growth kinetics induced by irradiation

We found that the E' centers can be induced by γ -irradiation in all the materials listed in Table 1 (Chap.5) in the dose range $0.1 \div 10^4$ kGy. We verified that pieces from different production stocks for each material gave the same results proving the high reproducibility of the material features. The characteristics of the growth by irradiation of E' centers, relevant for our study, are summarized in fig.19a, where the data reported refer to the series of samples EQ906 (we recall that

a different piece is employed for each irradiation dose). This growth shows that the concentration increases on increasing the irradiation dose and tends to an asymptotic value at high doses. As shown in fig.19 for the samples H1, S300 and S1, growth by irradiation with the same qualitative features are observed in all the investigated materials, even if with different initial rate and different final concentration values. As shown in fig.19, the synthetic wet material (S1, fig.19d) is found to be more resistant to irradiation than the others. In particular, the E' centers concentration reaches an asymptotic value at doses higher than in other materials by at least two orders of magnitude.

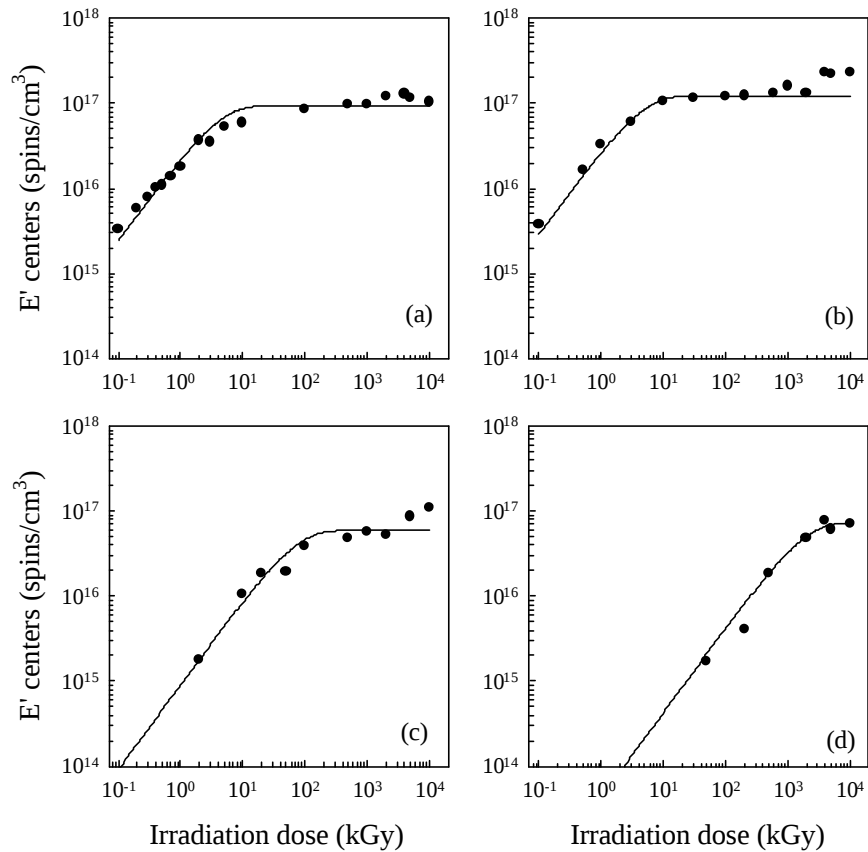


Figure 19. E' centers concentration dependence on γ irradiation dose. (a) Natural dry silica EQ906; (b) natural wet silica H1; (c) synthetic dry silica S300; synthetic wet silica S1. Each point refers to a different sample of the same material. The continuous lines are the best-fit curves with the simple exponential growth law $N(D) = N_{\text{sat}}(1 - e^{-kD})$.

The E' centers concentration dependence on dose in all the investigated materials has a typical exponential growth that in first approximation can be described by the law

$$N(D) = N_{\text{sat}}(1 - e^{-kD}) \quad (6.1)$$

where D is the accumulated dose, $N(D)$ is the centers concentration after a dose D , N_{sat} is the asymptotic *saturation concentration* of the centers and k is the production rate constant. In order to compare more quantitatively the results of the irradiation and to obtain orders of magnitude for the relevant parameters of the growth kinetics we made a fitting of the data with the law (6.1). Best-fit parameters are listed in Table 3, and plotted in fig.20 in a pictorial map of the various samples. We consider only those samples for which the approximation of eq.(6.1) is good (correlation coefficient ≥ 0.96), moreover errors in the best-fit parameters are not considered for our limited purpose of discussing on orders of magnitude.

TABLE 3. Best fit parameters of the E' centers growth kinetics in γ -irradiated samples with the simple exponential law $N(D) = N_{\text{sat}}(1 - e^{-kD})$.

Sample	type	N_{sat} (10^{17} spins/cm ³)	k (10^{-2} /kGy)	$1/k$ (kGy)
I301	Natural dry	2.8	8	13
EQ906	Natural dry	0.94	26	4
EQ912	Natural dry	1.7	10	10
QPA	Natural dry	2.2	5	20
H1	Natural wet	1.2	24	4
H3	Natural wet	2.1	0.2	500
S1	Synthetic wet	0.7	0.06	1600
S311	Synthetic wet	0.30	0.03	3000
S300	Synthetic dry	0.60	2	50

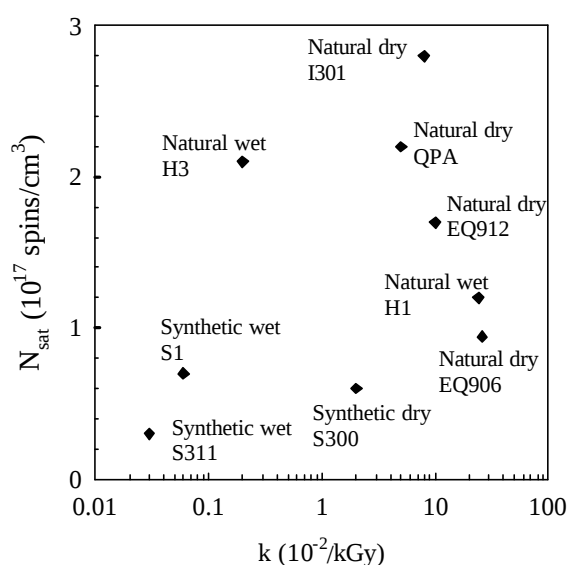


Figure 20. Map of the saturation concentration, N_{sat} , and production rate constant, k , of the E' centers in various γ -irradiated silica materials.

N_{sat} ranges from 3×10^{16} spins/cm³ up to 2.8×10^{17} spins/cm³ covering an order of magnitude. k varies from 3×10^{-4} kGy⁻¹ up to 2.6×10^{-1} kGy⁻¹ with an overall variation of three orders of magnitude. As evidenced in fig.20, the points representative of the various materials are almost uniformly mixed in the graph. So, we cannot identify typical dependence of the mechanism of E' centers production on the material apart from the already observed enhanced stiffness of the synthetic wet materials.

The generation process of E' centers was further investigated by electron irradiation (β -rays), which allows to explore the effect of doses higher than by γ -rays. As a consequence, it could be possible to investigate in greater detail the effects on materials that are more radiation resistant, like the synthetic wet. The irradiation was carried out in the natural dry samples EQ906, EQ912, QPA and P453 and in the synthetic wet CNG5F and CSB.

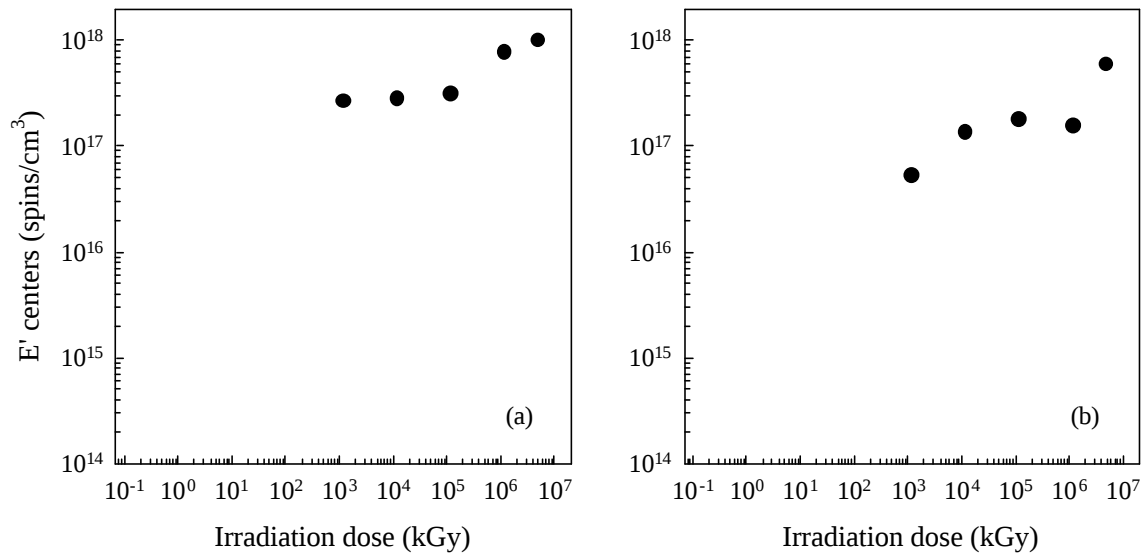


Figure 21. E' centers concentration dependence on β irradiation dose as detected in the natural dry silica EQ906 (a) and the synthetic wet silica CSB (b). Each point refers to a different sample of the same material.

The β irradiation generated the E' centers in all the investigated materials starting from the lowest irradiation dose of 1200 kGy. The EPR line shape of these centers reproduce the line shape L_1 detected after high γ -doses and shown in fig.16. As reported in fig.21a for the EQ906 sample, the

growth by irradiation of the E' centers shows that their concentration is constant for all the investigated β irradiation doses from 1200 kGy up to $\sim 10^5$ kGy whereas at higher doses it increases without saturation. This same dependence on dose was found in other natural samples. In particular, the concentration is constant up to $\sim 10^5$ kGy and then increases again at higher doses. A summary of the growth kinetics parameters is reported in Table 4, where we show the asymptotic concentration value N_{sat} , determined experimentally, and the maximum concentration registered.

TABLE 4. Parameters of the E' center growth kinetics in β -irradiated samples.

Sample	type	N_{sat} (10^{17} spins/cm ³)	Max concentration (10^{17} spins/cm ³)
EQ906	Natural dry	2.7	10
EQ912	Natural dry	2.7	16
QPA	Natural dry	5.0	13
P453	Natural dry	0.7	9.5
CSB	Synthetic wet	1.6	6
CNG5F	Synthetic wet	0.67	4

In samples of EQ906, QPA and P453 we measured a concentration of E' centers after β -irradiation higher than after γ -irradiation, at the same dose level. Moreover, in all the natural samples, the maximum concentration of spin centers is $\sim 10^{18}$ spins/cm³, much higher than after γ -irradiation.

The growth by irradiation of the synthetic wet sample CSB is reported in fig.21b. It is shown that the number of the E' centers increases on increasing the dose up to $\sim 10^4$ kGy where it reaches an asymptotic value. On further increasing the dose, over 10^6 kGy, the number of E' centers grows again without apparent saturation in the investigated range of doses. A similar dependence was observed in the other synthetic material, CNG5F. The maximum concentration of E' centers in the synthetic samples was $\geq 4 \times 10^{17}$ spins/cm³, lower than in natural materials but always higher than after γ -irradiation.

6.3 Discussion

The results reported above evidence that the E' centers generated by γ -rays have a typical growth by irradiation in which the concentration of the centers increases on increasing the irradiation dose and then tends to an asymptotic value, we call this growth *saturation kinetics* (fig.19). This kinetics is observed in all the investigated materials. Also, the results obtained after β -irradiation are consistent with this kind of kinetics. In fact, in natural silica the concentration of E' centers is already saturated at the lowest β irradiation dose (fig.21a) whereas in synthetic silica the concentration first increases and then saturates on increasing the β -irradiation dose (fig.21b). This feature is a confirmation of the saturation observed with γ irradiation but occurring only at very high doses $\sim 10^4$ kGy. The similarity of the growth by irradiation under γ and β -rays suggests that the same mechanism of defect generation is effective.

This characteristic saturation kinetics is indicative of a process of generation of defects from precursors, which are present in the matrix before irradiation. In fact, the precursors are progressively converted to E' centers by irradiation and, when the precursor concentration is exhausted, a saturation appears in the E' concentration [25, 86-89]. The simplest growth law that can describe this process is reported in eq.(6.1), and we employed it to fit the data and obtain orders of magnitude for the E' saturation concentration, N_{sat} , and the production rate k (Table 3 and fig.20). N_{sat} depends on the particular material, it is minimum in the synthetic wet materials, 3×10^{16} spins/cm³, one order of magnitude lower than in some natural samples. Also, poor variability of N_{sat} is found among the various natural samples. For example, among the natural dry N_{sat} changes from 1 to 3×10^{17} spins/cm³. These differences suggest that the number of precursors depend poorly on the material.

Another interesting aspect of the growth kinetics is the high variability of k . This parameter changes by three orders of magnitude from the synthetic wet samples, $k \sim 3 \times 10^{-4}$ kGy⁻¹, to the natural samples, $k \sim 10^{-1}$ kGy⁻¹. Also, among the natural samples there is a strong variability as

observed comparing the natural wet materials H1, $k \sim 2 \times 10^{-1} \text{ kGy}^{-1}$, and H3, $k \sim 2 \times 10^{-3} \text{ kGy}^{-1}$. We note that the parameter k is related to the probability of conversion of the single precursor [89]. So, since we observe that k changes in the various materials, it can be suggested that different precursors are present.

It was already reported that various precursors of the E' centers are possible both of intrinsic [24, 90, 42] and extrinsic [58, 83, 92-94] type. Also, these precursors may be activated in the same materials concurrently [88, 89]. These aspects add complexity to the interpretation of the mechanisms of generation of the E' centers. This complexity requires growth laws less simple than the single exponential of eq.(6.1). However, we note that the information and deduction attained with our approximation are sufficiently reliable to individuate the main features of the generation process.

Further information on the E' centers generation by irradiation can be obtained considering the line shape. As reported in fig.17, E' centers have the line shape L_2 at low irradiation doses and the line shape L_1 at high doses, in all the materials except the S1 and S311 in which only L_1 is observed. A gradual variation between the two line shapes is observed on increasing the irradiation dose. By detailed examination of the g values we note that the difference between the values g_2 and g_3 in L_2 is smaller than in L_1 , which suggests a more symmetric environment for the center with the EPR line shape L_2 . In addition, we observe that when the E' centers have the line shape L_2 they also have a microwave power dependence different from the case when they have the line shape L_1 (fig.18). In particular for L_2 the EPR signal linear dependence on the microwave power extends at lower powers than for L_1 . These features suggest a variation in the spin-lattice interaction of the spin centers associated to L_2 and L_1 that can be related to differences in the atomic environment of these defects.

The previous results lead to the conclusion that two slightly different typologies of E' centers are observed. We note that if we neglect the samples S1 and S311, the line shape variation of the E' centers with irradiation dose was observed in all the investigated materials. So, the effect

seems to be independent from the material and the “gross features” of the precursor, as for example its atomic composition. It is then possible that this effect is “peculiar” of the mechanism of generation of the defect and could be attributed to its environment. In other words, the environment of the precursor is important in its overall conversion for example contributing to the site relaxation as expected in the process of generation of the E'_{γ} (fig.4, par.2.1).

As reported in par.2.1, it is known that the variants of E' centers, E'_{γ} and E'_{β} , differ because the latter has an EPR signature that evidences a highly symmetric environment [57]. In addition, the proposed model for the E'_{β} suggests that this center may be related to a cavity ahead of the unpaired electron [24]. This, in fact, could explain the more symmetric line shape. Further, it has been observed that after thermal treatments E'_{γ} centers evolve to a more symmetric environment [57, 78] and this effect was attributed to a structural relaxation of the second silicon (see fig.4, Chap.2).

On the basis of our experimental observations and the above reported literature data, we can speculate on the differences in the line shapes observed at low and high doses of irradiation. In particular, it is possible that the first centers that are converted are those with a more elastic environment so that the unpaired electron has more voids ahead. Obviously, this refinement should not necessarily distinguish the “gross features” of the precursor since it depends only on the environment. This could explain why we do not observe a strong dependence of the line shape evolution on the material even if different precursors have been supposed on the basis of the variation of k values. Moreover, it could explain also why only L_1 is observed in the synthetic wet materials. In fact, these materials are subjected to high irradiation doses and the kind of centers induced could arise already from precursors with a stiffer environment.

Chapter 7

Experimental results: Weak hyperfine interaction of E' centers

In this chapter we will consider the weak satellite structure of the E' centers EPR signal. In par.2.2 we have introduced the current interest of this EPR feature and the open questions regarding its structural model. The main EPR spectroscopic properties of the structure observed in our samples will be here reported. In addition, we have measured the growth of the signal as a function of the dose in γ and β irradiated silica and we will compare it with the growth of the E' centers in order to evidence analogies and differences and to discuss the relationship between this center and the center responsible for the weak satellite structure.

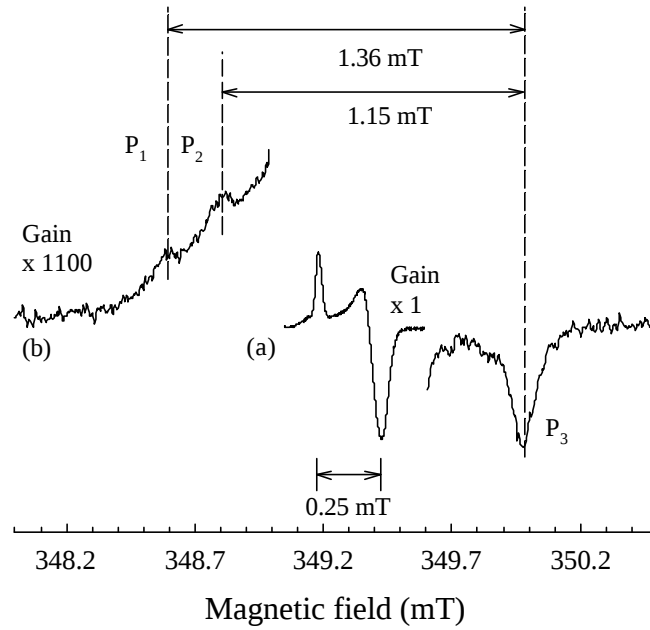


Figure 22. EPR spectra of the E'_γ centers (a) and the weak satellite structure (b) as detected in the sample I301/5000. The relative magnification of the two spectra is evidenced.

7.1 EPR properties

A typical EPR spectrum with the weak satellite signal of the E' centers resonance line is reported in fig.22, as revealed in the sample I301/5000. We employed a magnetic field scan of 3 mT around the resonance field of the E' centers and used $P_m = 50 \mu W$, $B_m = 0.07$ mT, $\omega_m = 100$ kHz.

As reported in fig.22b, the weak satellite signal overlaps the E' resonance line, reported in fig.22a for comparison, and is characterized by at least three peaks with field splitting: (1.15 ± 0.03) mT and (1.36 ± 0.03) mT, respectively. Similar structures were reported by Shendrik and Yudin [71] and by Griscom [75, 95]. In particular, Griscom measured magnetic field splittings of 1.22 mT and 1.37 mT [95] and he used for the first time the name *weak satellite structure* of the E' resonance.

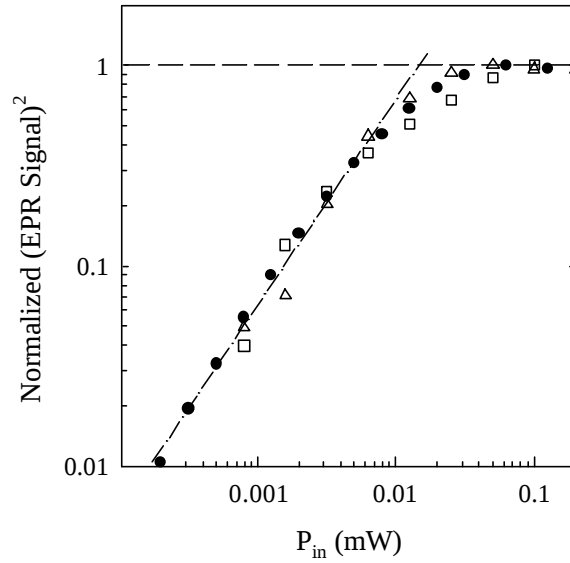


Figure 23. Dependence on P_{in} of the normalized double integral of E' centers signal (circles) and the normalized intensity of the peaks P_2 (triangles) and P_3 (squares) of the weak satellite structure in the sample I301/5000. The linear dependence is evidenced by the dash-dotted line.

In order to characterize the weak satellite structure, we studied its dependence on the input microwave power, P_{in} . In particular, in fig.23, we report the squared heights of the peaks P_2 and P_3 (fig.22) normalized to their maximum values as a function of P_{in} in the sample I301/5000. Both peaks have similar dependence on the microwave power. In fact, their linear dependencies on P_{in} are superimposed, and they reach saturation nearly at the same power. These features support the attribution of the two peaks to the same EPR signal. Another interesting and surprising aspect is that, as evidenced in fig.23, P_2 and P_3 intensities have dependence on P_{in} very similar to the signal of the E' centers. In particular, the regions of linear dependence on P_{in} are superimposed and the

three signals are saturated at the same input power. These features suggest that the related spin centers share the same values of T_1 and T_2 .

The study of the third peak, P_1 in fig.22, as a function of the microwave power is hampered by its very low intensity. However, this peak always appears together with P_2 and P_3 when good detection conditions are set, so, it can be reasonably considered as a part of the overall EPR signal of the weak satellite structure.

We note that, the signal-to-noise ratio of the weak satellite structure spectra was maximized by using $B_m = 0.07$ mT and $\omega_m = 100$ kHz and fixing P_{in} at the beginning of the microwave power saturation $P_{in} = 50$ μ W. We verified that these settings do not distort the line shape but enhance the signal. We also note that the intensity of the satellite structure signal is reported hereafter as the sum of the peak heights P_2 and P_3 in analogy with other literature data [75]. If we consider that these peaks are features of a given EPR signal, this sum should be proportional to the overall concentration of the related paramagnetic centers. This choice arises because the full resonance line was not determined in any case owing to the overlap with the E' resonance line.

7.2 The growth of the weak satellite structure induced by irradiation

The weak satellite structure of the E' center was revealed in all the investigated materials, both natural and synthetic, after γ -irradiation and with the main spectral characteristics reported in fig.22. We measured the growth of the weak satellite structure intensity as a function of the irradiation dose in all the samples reported in Table 1 (Chap.5) [168-169]. These data were obtained in the same samples used for the investigation of the E' centers. As shown in fig.24, the satellite structure in materials EQ906, H1, S300 and S1, exhibits a saturation-type growth by irradiation. In particular, we observe that the intensity starts to grow, on increasing the irradiation dose, and then reaches an asymptotic value. Similar growths are observed in other materials but with different asymptotic values and dose regions where the intensity of the weak satellite structure grows. Besides, we observe that the synthetic wet samples are more resistant to irradiation (see fig.24d). In

fact, in the latter samples, the satellite structure intensity reaches asymptotic value at doses higher than the other materials by approximately two orders of magnitude, as can be inferred comparing figs.24a÷d.

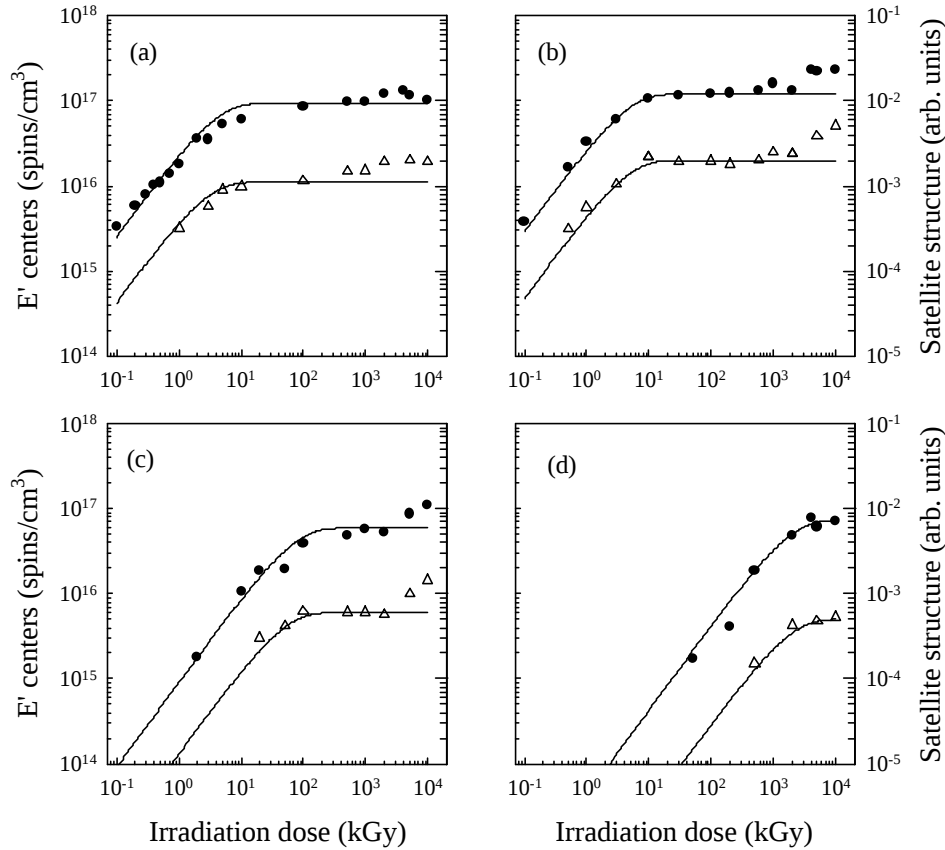


Figure 24. EPR intensity of the E' centers satellite structure as a function of the γ -irradiation dose (triangles, right vertical scale), in the materials: (a) EQ906; (b) H1; (c) S300; (d) S1. Each point refers to a different sample. For comparison the growth of the E' centers is reported (circles, left vertical scale). The continuous lines are guides to the eye obtained with the curves $N(D) = N_{\text{sat}}(1 - e^{-kD})$ where k is taken from Table 3 as obtained with the E' centers.

A remarkable feature is that the growth of the weak satellite structure reproduces that of the E' centers in all the investigated materials, as evidenced in fig.24 where the growth of the E' centers is reported for comparison. As shown, in all the materials the weak satellite structure intensity increases and reaches its asymptotic value for the same doses as the E' centers, moreover, the same dependence on the material occurs for both signals. In fig.24 we have superimposed to the data of the weak satellite structure the growth law (6.1): $N(D) = N_{\text{sat}}(1 - e^{-kD})$, with the same value of k

obtained for the E' centers (see Table 3 in Chap.6), and N_{sat} determined by a best-fit procedure. As shown, this growth law fits all the data both of the satellite structure and of the E' centers with the same accuracy so indicating that, in a given material, the same k can be used for the generation process of both centers. We can conclude that the center responsible for the satellite structure and the E' center have precursors characterized by the same conversion probability.

Further investigation of the weak satellite structure generation process was carried out by means of the electron (β -rays) irradiation in the materials EQ906, EQ912, QPA, P453, CNG5F and CSB. This irradiation induced the satellite structure in all the materials employed starting from the lowest irradiation dose, 1200 kGy, and with the same main spectral features reported in fig.22. Also in the β irradiated materials the growth of the satellite structure was similar to that of the E' centers, as evidenced in fig.25a, b. In particular, in the natural material EQ906, fig.25a, a constant intensity is maintained below 10^5 kGy and then a growth is observed. In the synthetic material CSB, fig.25b, the satellite structure intensity increases for doses less than 10^4 kGy then an asymptotic value is reached and maintained up to 10^6 kGy where the growth restarts. Such coincidence in the signal intensity dependence on β irradiation dose of E' centers and the weak satellite structure was confirmed in all the investigated samples.

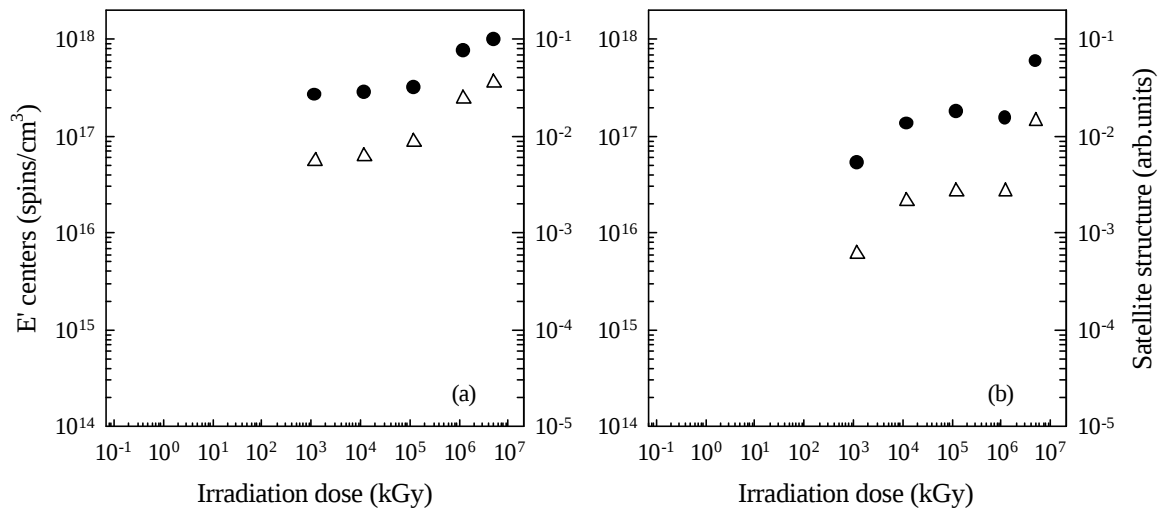


Figure 25. EPR signal dependence on β irradiation dose of E' centers (circles, left vertical scale) and their weak EPR satellite structure (triangles, right vertical scale) as detected in the natural EQ906 (a) and synthetic CSB (b) materials. Each point refers to a different sample.

7.3 Discussion

The above reported results evidence that a weak EPR satellite signal of the E' centers resonance line is induced by irradiation in all the materials investigated, both natural and synthetic. The growth of this signal as a function of the irradiation dose suggests that the center responsible for the weak satellite structure is generated from precursors.

The intensities of the weak satellite structure and of the E' centers EPR signals have similar dependence on γ irradiation dose no matter from the particular material, as shown in fig.24. In particular, both signals increase and reach an asymptotic value in the same dose range. This correlated dependence was confirmed by experiments on β -irradiated materials (fig.25).

These features suggest that, independently from the material and from the irradiation source, the E' center and the center responsible for the weak satellite structure have the same process of growth. In particular, as already observed here and in the previous chapter, this process is dominated by the mechanism of generation from precursors. As reported in par.6.2 and evidenced in figs.19 and 24, this process can be approximated for both centers by a simple exponential law, eq.(6.1). With this approximation it is possible to evidence that identical growth rate parameters k can be assumed for the weak satellite structure and the E' centers in any given material.

Since the parameter k depends strongly on the material, as shown in fig.20 (Chap.6) and discussed in the previous chapter, distinct precursors and mechanisms of generation of the E' centers should be postulated in the different materials. Our data suggest that the same precursor and mechanism of generation as the E' centers can be assumed also for the weak satellite structure. As a consequence, for any given process of generation, a part of the precursors is converted into the center responsible for the weak satellite structure.

More quantitative comparison between the two EPR signals is carried out in fig.26, by plotting the intensity of the satellite structure at irradiation dose $\sim 10^4$ kGy as a function of the E' center intensity at the same dose. We note that for this dose the two signals investigated reach asymptotic values in their growth in almost all the samples, as reported in figs.24 and 25.

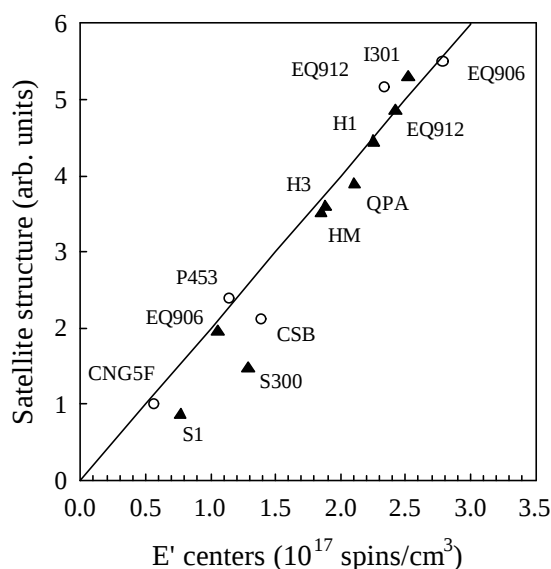


Figure 26. Comparison of the intensity of the E' centers and the weak satellite structure in the samples irradiated at doses: 10^4 kGy with γ -rays (triangles), 1.2×10^4 kGy with β -rays (circles). The continuous line is the best-fit curve.

It is interesting to note that in fig.26 the points relative to materials with different OH contents (see Table 1 in Chap.5) are mixed. This result suggests that there is no evident relation between the presence of the OH group in the material and the generation of the weak satellite structure. This aspect should be considered in the determination of the structural model for the center responsible for the weak satellite structure. The points in fig.26 representative of the various materials and irradiation sources are well aligned. A best fit of the data according to $I_{\text{satellite}} = \alpha N_{E'}$, where $I_{\text{satellite}}$ is the intensity of the weak satellite structure and $N_{E'}$ is the E' center concentration in spins/cm³, gives a good correlation coefficient (0.989) and a value $(2.0 \pm 0.1) \cdot 10^{-17}$ cm³/spins for the parameter α .

Another evidence of the correlation between E' centers and the weak satellite structure arises from the study of the signal dependence on the microwave power, reported in fig.23. The weak satellite signal and the E' centers signal reach intensity saturation at the same microwave power. This is an indication of similar coupling of these spin centers to the lattice vibrations.

On the basis of the reported results, we suggest that the satellite signal arises from an E' center with a nearby nuclear spin and that the signal is an hyperfine structure. The weakness of the

hyperfine interaction (~ 1.3 mT) evidences a poor overlap between the electron spin orbital and the nuclear spin and a large distance of the nucleus from the electron spin. Moreover, the observed similar microwave power dependence (fig.23) of the E' and the weak satellite signals leads to the hypothesis that the atomic structures of these centers and their neighborhood should be very similar. These data prove that the satellite structure can be attributed to the hyperfine interaction with a second neighboring atom of the E' center with nuclear spin non-zero [95, 99].

As outlined in fig.6 (Chap.2), two models were proposed having these characteristics. The former relates the hyperfine interaction to an H atom, having nuclear spin $I = 1/2$, terminating a "basal" O atom of an E' center (*model A*) [95]. The latter attributes the interaction to a ^{29}Si atom, nuclear spin $I = 1/2$, substituting a normal ^{28}Si atom bonded to a "basal" O atom but projected in the opposite direction with respect to the unpaired electron orbital (back-bond configuration, *model B*) [70, 99].

In the absence of quantitative estimation of the concentration of the centers giving the weak hyperfine interaction it is difficult to resolve the question on the correct model. However, as reported in fig.26, we note that our data show that there is no evident dependence of the hyperfine structure on the OH content of the material, as should be expected for the model A. In addition, the strong similarity of the generation process of the E' center and the center responsible for the weak hyperfine interaction suggests that they should have very similar precursors. In this respect the model B is favored as it could arise from the same generic precursor of the E' center "differing" only for the presence of a "basal" ^{29}Si . In fact, if model A is assumed, the environment of the precursor should be somewhat different, having a nearby H atom and this should affect the generation mechanisms. Besides, this structural difference should also affect the microwave dependence of the EPR signal in contrast to the observation reported in fig.23. So, our data strongly support the attribution of the model B to the center responsible for the weak hyperfine interaction.

Recently, a study of silica fibers treated in hydrogen atmosphere supported the attribution of the weak satellite structure to a generic hydrogen related E' center [98]. In that paper it was also

reported that a thermal treatment at ~ 400 K removed completely the weak satellite structure. In a preliminary trial, we found that a prolonged thermal treatment at ~ 500 K of one of our materials, the S300, did not remove the satellite structure but only reduced ($\sim 20\%$) both its intensity and that of the E' centers. Basing on these observations we can conclude that our data support the attribution of the hyperfine interaction to the model B; however, the model A cannot be completely ruled out. In this respect, it could be possible that besides the weak satellite EPR signal another signal due to the model A center is present in the same resonance region.

In conclusion, our data have evidenced that the weak satellite structure has the same generation mechanisms as the E' centers both under γ and β irradiation, independently from the silica type. This proof establishes a similarity between the center generating the weak satellite structure and the E' center. On the basis of the analogy in the growth of these signals with irradiation and their dependence on the microwave power it is concluded that the weak satellite structure arises from an E' center interacting with a second neighboring nuclear spin. So, our data strongly support the model reported as B (fig.6 in Chap.2).

Chapter 8

Experimental results: Conversion of point defects induced by gamma ray

As reported in par.2.3, the optical activity type B is characterized by the absorption band $B_{2\beta}$ (at 5.15 eV) and by two emission bands, the α_E (at 4.2 eV) and the β (at 3.1 eV) [110-112]. This activity is peculiar of high-purity natural and Ge-doped silica. Here we report experimental results on the bleaching of the B-type activity induced by gamma rays and the simultaneous growth of the 11.8 mT EPR doublet. We interpret these results in terms of γ -induced conversion of point defects and we show that this conversion is reversible. Our results allow to assign well-defined structural models to both defects and make clear the role played by Ge impurities.

8.1 The native optical B-type activity

The main features of the optical B-type activity are reported below, as observed in our natural materials type I and II (Table 1, Chap.5). This activity is not revealed in synthetic materials.

By measuring the optical absorption (OA) of as grown silica samples, in the spectral range 4.0-6.0 eV, a band can be isolated in many natural materials. A typical absorption profile is reported

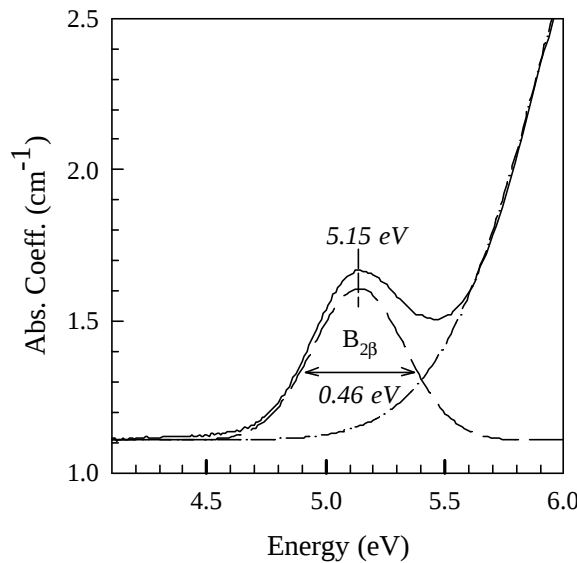


Figure 27. Typical absorption profile in natural samples in the spectral region from 4.0 eV to 6.0 eV as detected in I301/0. The dashed curve evidences the $B_{2\beta}$ band with its spectral parameters.

in fig.27 where the band is clearly distinguishable, even if partially superimposed to the tail of another OA structure at higher energies. This band is usually named $B_{2\beta}$ [110-111, 115] and it is well fitted by a gaussian profile with peak energy value of 5.15 ± 0.01 eV and Full-Width-at Half-Maximum (FWHM) of 0.46 ± 0.02 eV.

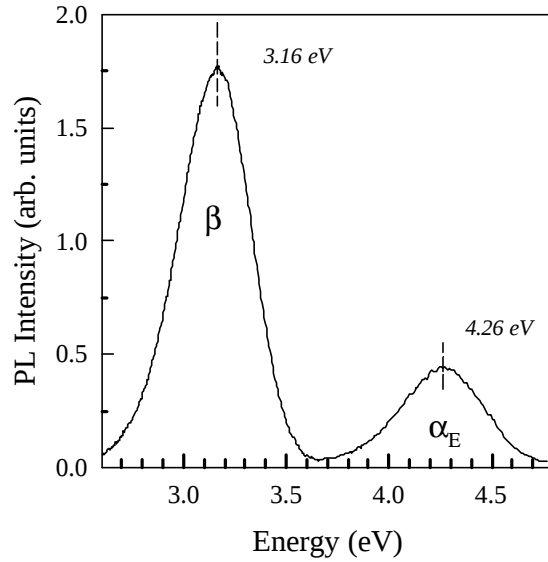


Figure 28. Room temperature emission spectrum in the range 2.6-4.8 eV as detected in the sample I301/0 under excitation at 5.0 eV. Two emission bands peaked at 3.16 eV (β band) and 4.26 eV (α_E band) are well distinguishable.

The excitation within the $B_{2\beta}$ band gives rise to two well-defined emission bands in the range 2.5-5.0 eV that can be revealed by stationary photoluminescence (PL) measurements. A typical PL spectrum at $T = 300$ K, excited at 5.0 eV, is reported in fig.28 for the same natural sample as in fig.27. The band at lower energy is peaked at 3.16 ± 0.01 eV, and has a FWHM = 0.43 ± 0.01 eV; the other band, at higher energy is peaked at 4.26 ± 0.01 eV and has a FWHM = 0.48 ± 0.01 eV. These two bands are indicated in literature as β and α_E , respectively [112-113].

The correlation between the β and α_E bands and the OA $B_{2\beta}$ band has been reported in literature [115, 170-174]. Evidence for this correlation, in our samples, is shown in fig.29. We report the linear correlation between the β and α_E PL bands, fig.29a, and the linear correlation

between the sum of the area of β and α_E PL bands and the area of the $B_{2\beta}$ OA band, fig.29b [174, 175].

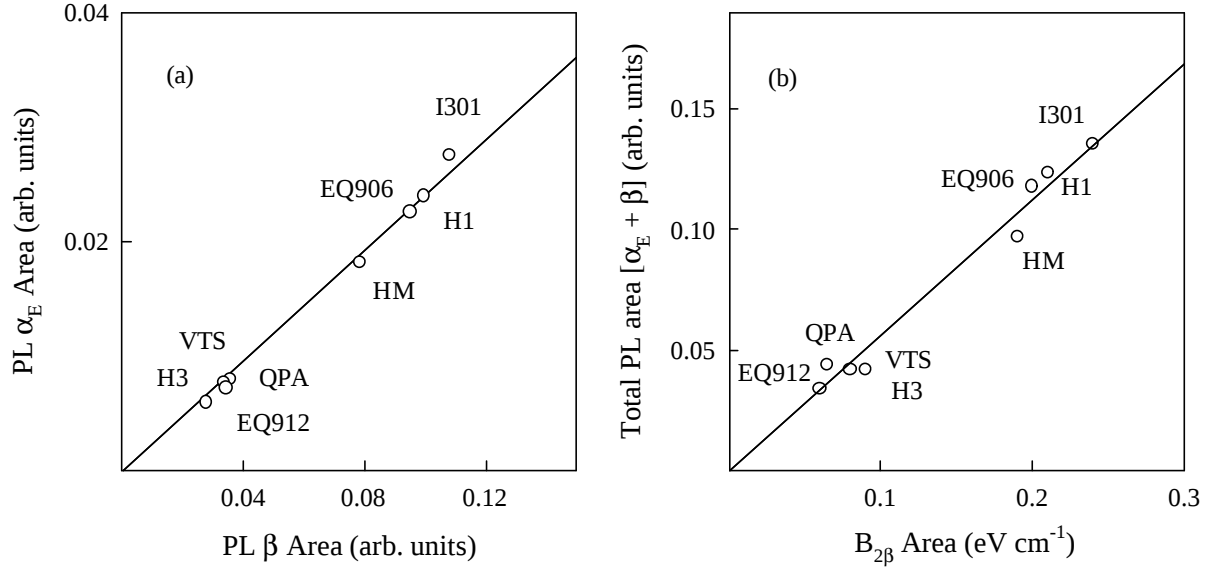


Figure 29. Optical activity B-type as detected at $T = 300$ K in the natural samples of Table 1 (Chap.5). (a) Correlation between the emission bands β and α_E excited at 5.0 eV. (b) Relationship between the area of the OA band $B_{2\beta}$ and the total area of the emission bands β and α_E excited at 5.0 eV.

The B-type activity was detected in all the natural "as grown" materials with exception of the P453. In this material the dominant absorption band, $B_{2\alpha}$ (~ 5.02 eV) and the correlated emission band, α_i , at ~ 4.4 eV, attributed to the A-type activity (par.2.4) [115], prevents the observation of the B-type activity. Different concentrations of the B-type defects are present in various materials as evidenced from the values of the $B_{2\beta}$ band area reported in Table 5. Note that this area has been calculated from the experimental spectra after subtracting a baseline equal to the tangent to the minima of each band, following a well-established procedure [147, 175].

We observe that, in all the materials here reported, the maximum intensity of the $B_{2\beta}$ is less than 0.5 cm^{-1} . As noted in par.3.2.2, this value, for sample thickness of 0.1 cm, ensures that the PL emission spectra are simply related to the absorption coefficient. As a consequence, not only the $B_{2\beta}$ area but also the β and α_E areas are proportional to the number of B-type defects. This aspect is

particularly useful for measuring the concentration of active centers from the luminescence spectra, if the absorption band is masked by other bands.

TABLE 5. Spectral parameters at room temperature of the absorption and emission bands related to the optical B-type activity (peak energy E_0 , full width at half maximum FWHM and integrated intensity M_0).

Sample	OA band $B_{2\beta}$			PL band β			PL band α_F		
	E_0 (eV) ^(a)	FWHM (eV) ^(b)	M_0 (cm ⁻¹ ·eV) ^(c)	E_0 (eV) ^(a)	FWHM (eV) ^(b)	M_0 (a.u.) ^(d)	E_0 (eV) ^(a)	FWHM (eV) ^(b)	M_0 (a.u.) ^(d)
I301	5.15	0.46	0.24	3.16	0.42	108	4.26	0.46	28
QPA	5.13	0.41	0.07	3.16	0.41	36	4.27	0.44	8.0
EQ906	5.14	0.42	0.20	3.16	0.41	95	4.27	0.44	23
EQ912	5.13	0.40	0.06	3.17	0.41	28	4.26	0.45	5.9
VTS	5.15	0.44	0.09	3.16	0.41	34	4.26	0.43	7.7
H1	5.16	0.46	0.21	3.16	0.42	100	4.27	0.44	24
H3	5.12	0.43	0.08	3.16	0.41	35	4.26	0.44	7.2
HM	5.15	0.47	0.19	3.16	0.41	79	4.27	0.44	18

^(a) ± 0.01 eV; ^(b) ± 0.02 eV; ^(c) ± 0.01 cm⁻¹·eV; ^(d) $\pm 10\%$.

8.2 Bleaching effect

8.2.1 Effects of g-irradiation on the optical B-type activity

We observed that γ irradiation induced variation of the B-type activity in all the samples. As reported in fig.30a for the sample H1, the $B_{2\beta}$ OA band was progressively reduced on increasing the γ dose up to a 0.4 kGy, where the minimum intensity is reached and maintained for higher doses. This bleaching effect is evidenced in fig.30b where we report the difference between the OA spectra after each irradiation and the spectrum of the un-irradiated sample. In this sample the absorption coefficient is reduced by ~ 0.2 cm⁻¹ after a dose of 0.4 kGy. The decrease of the $B_{2\beta}$ band was detected in all the other natural materials with essentially the same main features but for the rate of reduction as a function of the dose, which was found to depend on the silica type. This dependence will be further investigated and commented in the following sections.

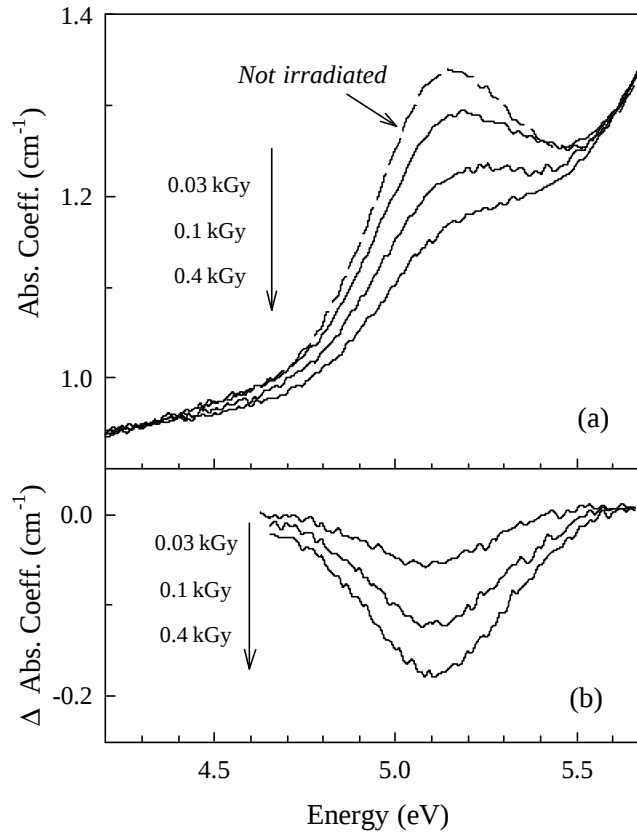


Figure 30. (a) Absorption spectra in the region 4.2-5.7 eV in the natural wet sample H1, before γ irradiation (dashed curve) and after irradiation at doses of 0.03, 0.1, 0.4 kGy (solid curves). (b) Differences between the absorption spectra of the sample irradiated at the doses reported in (a) and the as grown sample.

As expected, γ -irradiation caused as well the reduction of both β and α_E PL emission bands, whose intensities showed the same dose dependence as the corresponding $B_{2\beta}$ OA band. This is the reason why the bleaching of the B-type activity could be better monitored by detecting the PL emissions than the OA signal, as the PL bands are more isolated from other spectral structures. In particular, after irradiation, measurements on the $B_{2\beta}$ are no longer reliable because of the superposition of a γ -induced OA band at ~ 5.8 eV ascribed to the E' centers [26, 81].

The detailed study of the irradiation induced variations of the β and α_E bands is reported in fig.31 for the sample I301 [176]. The data for the β band are the maxima of its intensity (at 3.15 eV), while the α_E data represent the intensities of the gaussian curves that best fit this PL bands in a fitting procedure accounting for the superposition with another γ -induced PL band centered at

~4.4 eV [171]. It is evident, in fig.31, that the intensities of both PL bands decrease on increasing the γ dose in the range $D \leq 2 \times 10^3$ Gy and tend to saturate down to ~50% of their initial intensity. A well-correlated dependence on the dose was observed for both bands and in fact both sets of data reported in fig.31 can be fitted by the law: $I_{PL} = k' I_0 [1 + \exp(-kD)]$, where I_0 represents the intensity of either β or α_E at $D = 0$ kGy, $k' = 0.51 \pm 0.03$ and $k = (2.0 \pm 0.6) \text{ kGy}^{-1}$ for both curves. Similar dependencies were observed in all the other irradiated materials, with k' varying in the range $0.3 \div 0.5$.

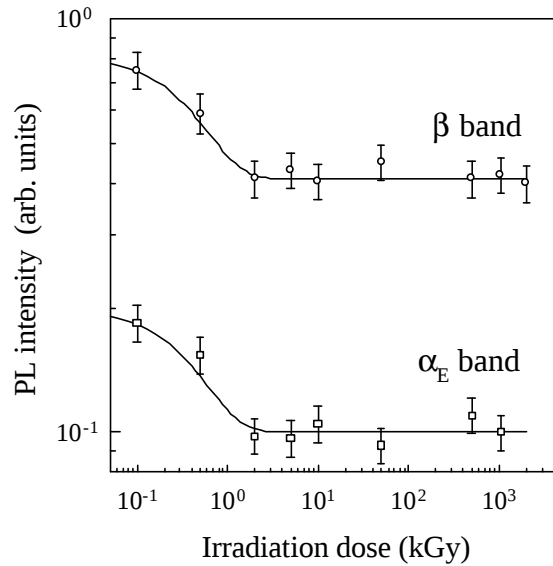


Figure 31. Dependence of the intensity of β and α_E PL bands on the γ irradiation dose as detected in the sample I301. Full lines represent the function $I_{PL} = k' I_0 [1 + \exp(-kD)]$ that best fits the data for both β and α_E .

According to the above reported results, the concentration of B-type defect decreases on increasing D . Moreover, the bleaching process shows saturation at high doses ($\sim 10^3$ kGy), independently on the material, suggesting an equilibrium between the preexisting defects and those generated by the irradiation [176]. We have also verified that the optical intensity reductions occur without any remarkable variation of the line shapes of both the β and α_E PL bands. This feature indicates that the same main optical properties pertain to the removed and residual B-type defects.

8.2.2 Irradiation induced 11.8 mT EPR doublet: spectral properties

The irradiated samples were investigated also by EPR measurements at room temperature. Only two resonance lines were revealed in all the natural materials in the dose range 0÷10 kGy where the bleaching effect occurs. The former is due to the E'-Si [53] centers already discussed in Chap.6. The latter consists of a pair of lines and is reported in fig.32, as detected in the sample H1/1, using $P_{in} = 3.2$ mW, $B_m = 0.4$ mT, $\omega_m = 100$ kHz. Note that the central line in fig.32, due to the E'-Si centers, is strongly distorted in these experimental conditions.

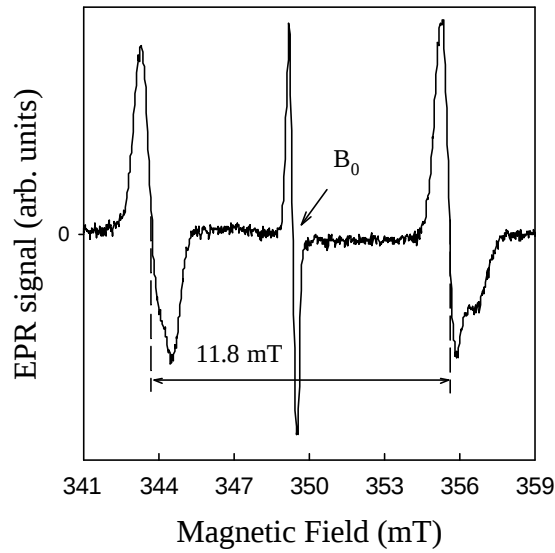


Figure 32. Isolated EPR doublet of the H(II) center as detected in the sample H1/1. The central feature is due to the strongly distorted E' resonance line.

The pair of lines, observed only in the natural silica samples, can be attributed to the hyperfine interaction with a nuclear spin $I=1/2$. This doublet has magnetic field splitting $B_H - B_L$ of 11.83 ± 0.02 mT. In addition, taking as a reference the magnetic field B_0 at which the E'-Si resonance line changes sign (see fig.32), we find that the doublet has a slightly asymmetric separation. In particular, we measure $B_0 - B_L = 5.64 \pm 0.02$ mT and $B_H - B_0 = 6.19 \pm 0.02$ mT.

This asymmetry has been further investigated by means of the second order perturbation theory calculation of the hyperfine interaction, reported in par.3.1.5. We assume for simplicity isotropic A tensor: $A_{\perp} = A_{//}$, and calculate the field splitting of the hyperfine doublet with respect to

the E' centers resonance field using the eqs.(3.22), (3.23). By substituting

$$\frac{\hbar\omega}{gb} = B_0 = 349.35 \text{ mT} \text{ and } \frac{K}{gb} = B_H - B_L = 11.83 \text{ mT}, \text{ we find: } B_0 - B_L = 6.02 \text{ mT and } B_H -$$

$B_0 = 5.81 \text{ mT}$. The predicted asymmetry is in the opposite direction with respect to the experimental one as $B_0 - B_L > B_H - B_0$ excluding any relation between the doublet and the E'-Si center.

On the other hand, we can calculate the theoretical value of $B = \frac{\hbar\omega}{gb}$, the resonance field of the

electron spin without hyperfine interaction (see par.3.1.5). Substituting B_H and $B_H - B_L$ in eq.(3.22),

we find $B = 349.8 \text{ mT}$ and the spectroscopic value $g = 1.9996$. This value is compatible with the g-

values reported in literature for the E'-Ge centers [102, 106, 108], and supports the attribution of the

doublet to a Ge related paramagnetic defect. In addition to these observations, we recognize that the

EPR doublet has spectral characteristics similar to those reported in ref.101, and discussed in

par.2.3. As a consequence, we identify this signal with that reported in literature and assume,

hereafter, the name H(II) center for the related paramagnetic defect in accordance to [103].

Further characterization of the EPR doublet has been made determining the dependence of

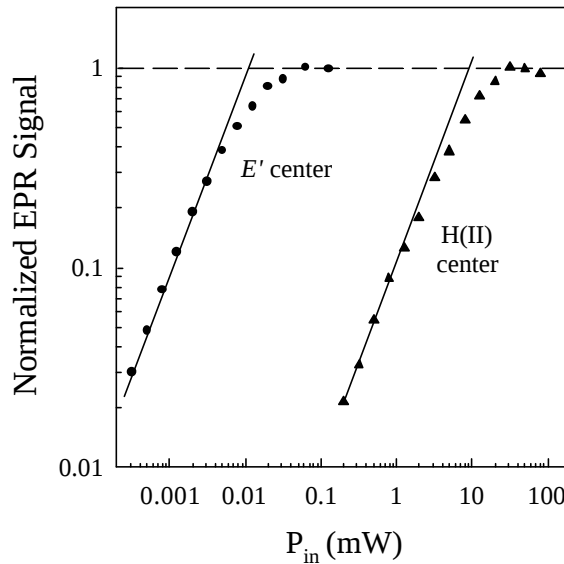


Figure 33. Dependencies of the squared EPR signals of the E' centers (circles) and of the H(II) centers (triangles) on the microwave power, in the sample I301/5000. Straight lines evidence the power regions of non-saturation.

its signal intensity on the microwave power. As reported in fig.33 for the sample I301/5000, the doublet intensity has a linear dependence on the microwave power up to ~ 2 mW. Comparing this dependence with that of the E' centers signal, fig.33, we observe that the latter has linear microwave power dependence up to ~ 3 μ W, namely three orders of magnitude below that of the doublet. So, the centers responsible for the two signals have strongly different couplings with the lattice vibrations. Besides, it further proves the distinction of the structural models to be attributed to the H(II) and the E' centers.

The EPR measurements has not evidenced the presence in the low range of doses where the doublet and the E' centers signals were already observable of other resonance signals common to all the samples in which the bleaching effect was observed.

8.2.3 Growth of the 11.8 mT doublet under g-irradiation

By measuring the intensity of the 11.8 mT doublet signal as a function of the accumulated γ dose in the natural materials, we determined the corresponding variation of H(II) centers concentration. As reported in fig.34a for the sample I301, the typical concentration shows a growth for low doses and reaches an asymptotic value at high doses. This kind of dependence on the dose is indicative of the generation of the H(II) centers from precursors. The comparison with the growth of the E' centers (fig.34b) unequivocally indicates a different dependence of the E' and H(II) centers on the accumulated dose: in particular the E' signal increases in a dose range where the H(II) centers signal has already reached its constant value. This result proves definitively that the two EPR signals originate from different centers.

We used a simple exponential law $N(D) = N_{\text{sat}}(1 - e^{-kD})$ (see eq.(6.1)), to fit the data on H(II) centers. We recall that a similar procedure was applied to the E' centers growth in par.6.2. The results of the fitting procedure are summarized in Table 6. In all the materials, the conversion rate, k , for the precursors of the H(II) centers differs at least by an order of magnitude from that of the E'

centers. Moreover, the maximum concentration of the H(II) centers is always much less than that of the E' centers.

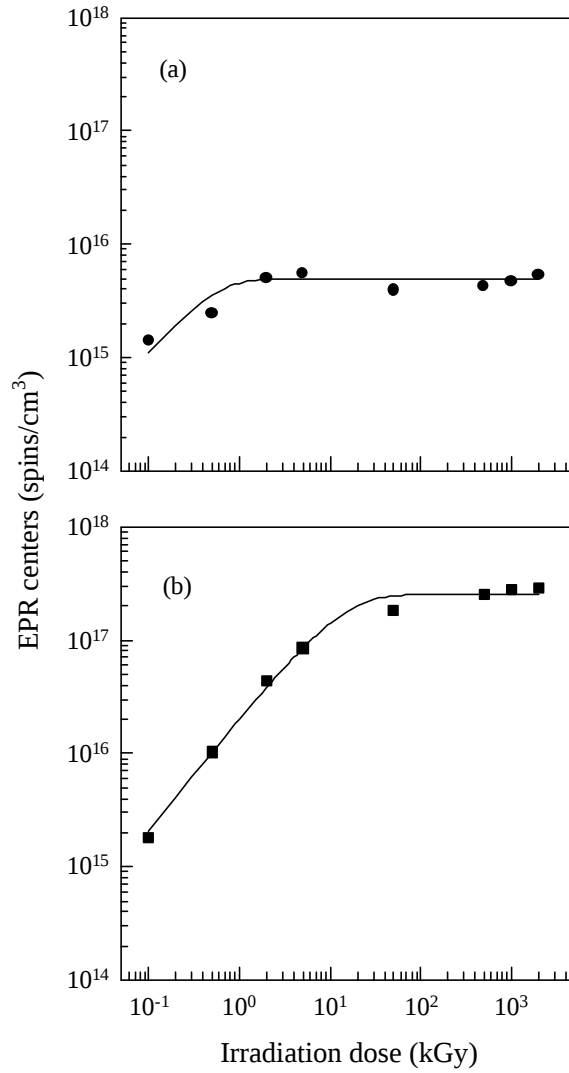


Figure 34. Dependence of the EPR centers concentration on the γ -irradiation dose in the sample I301. (a) H(II) centers, (b) E'-Si centers. The full lines represent the functions $N(D) = N_{\text{sat}}(1 - e^{-kD})$ that best-fit the data.

TABLE 6. Best fit parameters of the growth kinetics of E' (from. par.6.2) and H(II) centers analyzed in term of the law $N(D) = N_{\text{sat}}(1 - e^{-kD})$ in γ -irradiated samples.

Sample	N_{sat} (E' centers) (10^{17} spins/cm ³)	k (E' centers) (10^{-2} /kGy)	N_{sat} (H(II) centers) (10^{15} spins/cm ³)	k (H(II) centers) (10^{-2} /kGy)
I301	2.8	8	5.3	240
EQ906	0.94	26	4.1	300
EQ912	1.7	10	1.6	> 100
QPA	2.2	5	1.6	> 100
H1	1.2	24	3.8	2800
H3	2.1	0.2	2.0	>100
HM	2.0	≤ 0.05	4.3	2200

8.2.4 Correlation between the bleaching of the B-type activity and the generation of the H(II) centers

The comparison between the concentration of the H(II) centers induced by γ -irradiation, fig.34a, and the intensities of the β and α_E emission bands, fig.31, as a function of γ dose, evidenced an anticorrelated behavior. In particular, the number of B-type defects decreases in the same γ dose range in which the H(II) centers are progressively generated. We compared quantitatively the B-type activity in the not-irradiated samples, represented by the β emission, with the maximum concentration of the H(II) centers as detected after a dose of 500 kGy (largely above the threshold of saturated intensity). As shown in fig.35, where the experimental points are representative of various silica materials, a direct proportionality (linear correlation coefficient 0.976) exists between the number of native B-type defects and the final number of induced EPR centers, independently on the material.

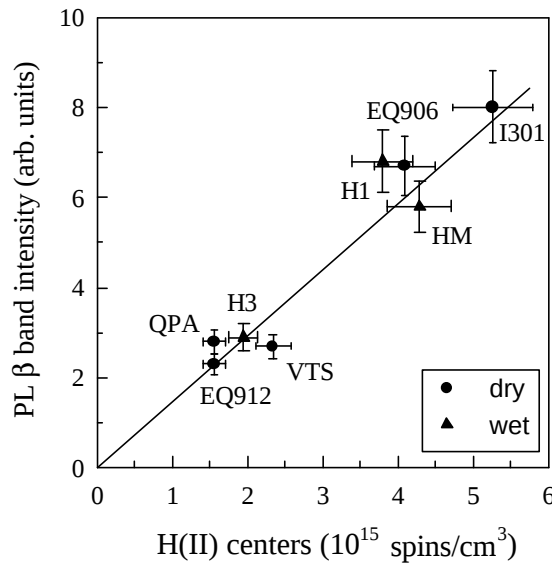
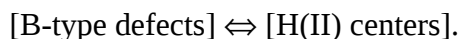


Figure 35. Intensity of the PL β band, as detected before irradiation, as a function of the H(II) centers, concentration measured at the γ -irradiation dose 500 kGy. The full line is the best-fit curve.

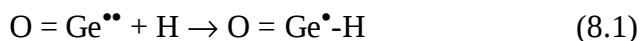
The above reported results evidence that two main effects are induced by γ irradiation in natural silica. The first one is the partial bleaching of the optical B-type activity reduced to about

50% of its initial value in each sample. The second effect is the appearance of a doublet of lines with a split of 11.8 mT in the EPR spectra ascribed to the H(II) center. The paramagnetic and optical defects increase and decrease, respectively, in the same dose range and the number of the H(II) defects generated is proportional to the native B-type defects one. This correlation suggests the occurrence of a conversion process, activated by γ rays, from the B-type defects to the paramagnetic H(II) centers. In addition, to explain the partial bleaching we hypothesize a counteracting back-conversion process from the H(II) centers to the B-type defects so that a dynamical equilibrium is reached on increasing the irradiation dose [176-177]:



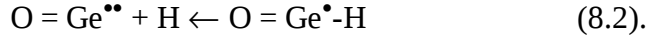
To clarify the possible conversion mechanism, we considered the structural models proposed in literature for the optically active defect and for the paramagnetic one. In this respect, one possible candidate for the B-type defect is the twofold coordinated Ge atom having an electron lone pair localized on Ge ($O = \text{Ge}^{\bullet\bullet}$) [107, 116-118]. On the other hand, the model proposed for the H(II) center consists in an unpaired electron in a Ge atom bonded to two oxygen and to one hydrogen ($O = \text{Ge}^{\bullet} - H$) [103, 107]: in this model, the 11.8 mT doublet arises from the hyperfine interaction between the electron and the H ($I = 1/2$) nuclear spin. This attribution of the H(II) center to a Ge related defect is supported by the experimentally observed asymmetric splitting of the 11.8 mT doublet lines, reported in par.8.2.2. In fact, the g value 1.9996 deduced for the related paramagnetic center is consistent with the g-values reported in literature for the Ge related defects [102, 106, 108].

Starting from these models, the conversion process from the B-type defect to the H(II) schematized by reaction R1 (see par.2.3) can be outlined by hypothesizing that γ rays remove H bonded in the glassy matrix, letting them free to move and to be trapped by a B-type defect [120]:



resulting in a H-bonded Ge center (H(II)).

This mechanism accounts very well not only for the reduction of the B-type defects and the simultaneous growth of the H(II) centers, but also for the partial bleaching of the B-type activity. In fact, the γ rays are expected to break as well Ge-H bonds reconvertng some H(II) into B-type centers [176, 177]:



In this scheme, the γ rays initially reduce the B-type defects population and increase the H(II) one until the back-conversion process is as probable as the conversion, then the conversion and back-conversion become competitive and an equilibrium between B and H(II) centers populations is reached.

8.3 Effect of the silica OH content on the bleaching process

The mechanisms of conversion proposed above in eq.(8.1) requires the availability of H atoms under γ -irradiation, with concentration comparable to that of irradiation induced H(II) centers, $\sim 10^{15}$ spins/cm³ (see Table 6 and fig.35). As known, H atoms are present in silica as hydroxyl groups (OH), so we can suppose that this is the "reservoir" of H atoms for the bleaching since the γ rays easily break OH bonds [18, 24]. In order to check this hypothesis we have experimentally compared the bleaching effect in materials with different OH content [177]. Four representative samples were considered, two natural dry (type I) with low OH concentration: I301 and EQ906, with nominal content of OH groups of 10-20 part per million (ppm) by weight ($\sim 10^{18}$ centers/cm³); and two natural wet (type II): H1 and HM with nominal OH content of 150 ppm ($\sim 10^{19}$ centers/cm³).

Fig.36 shows the PL spectra, excited at 5.0 eV, for the samples I301 (a) and HM (b), before irradiation and after exposure to various γ doses. Note that the same sample has been used in each irradiation experiment. As evidenced by the figure labels, the bleaching is effective in dose ranges depending on the silica type. In the HM sample the PL emission is reduced up to an accumulated

dose of ~ 0.5 kGy whereas in the I301 sample up to a dose of ~ 5 kGy. In particular, in the HM sample at 0.5 kGy both the β and α_E PL bands have intensity 33 % of the value before any irradiation. At variance, in the I301 sample at 0.5 kGy the intensity of the PL bands is 76 % of the initial value and reaches the 40 % only increasing the dose up to 5 kGy. The same differences between dry and wet silica were confirmed by the samples EQ906 and H1, where the PL intensity dose dependence was analogous to the I301 and HM, respectively.

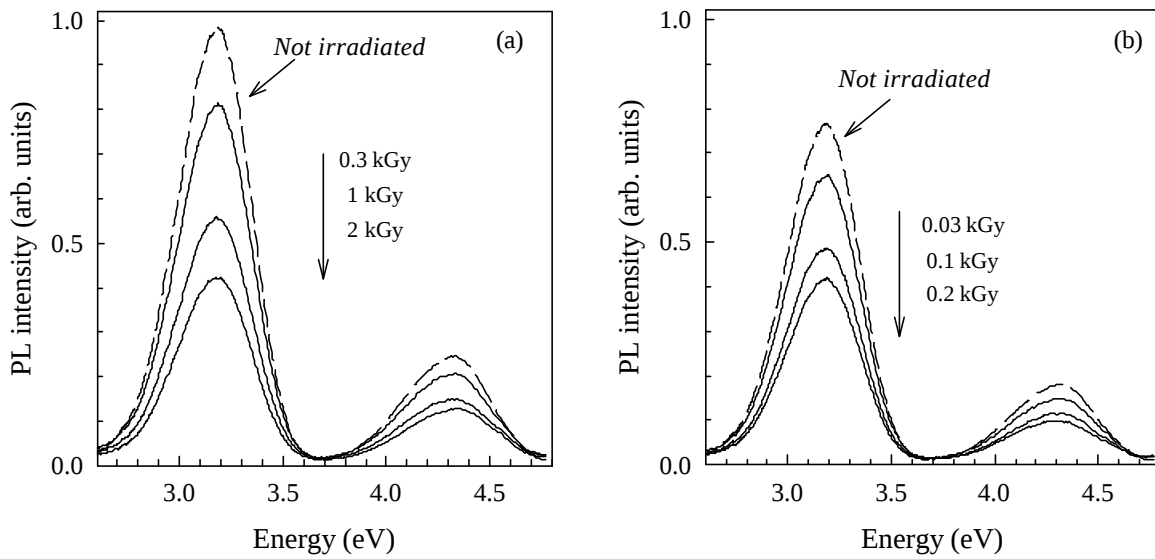


Figure 36. Photoluminescence spectra in the region 2.6-4.8 eV for the samples I301 (a) and HM (b), excited at 5.0 eV. In both panels the dashed line refers to the not-irradiated sample, the solid lines are the spectra of the same sample γ -irradiated at doses increasing up to 2 kGy, as evidenced by the labels.

The different photobleaching sensitivity of dry and wet silica under γ irradiation is confirmed by the EPR measurements. In particular, as shown in fig.37 for the samples I301 and HM, in both wet samples the 11.8 mT doublet reaches constant intensity for a saturation dose of ~ 0.3 kGy; at variance, in the dry samples the doublet intensity saturates at ~ 3 kGy. We note that, in spite of these differences of about one order of magnitude in the saturation dose, the concentration of induced centers in the samples I301, EQ906, H1 and HM has the same order of magnitude, as evidenced in fig.35.

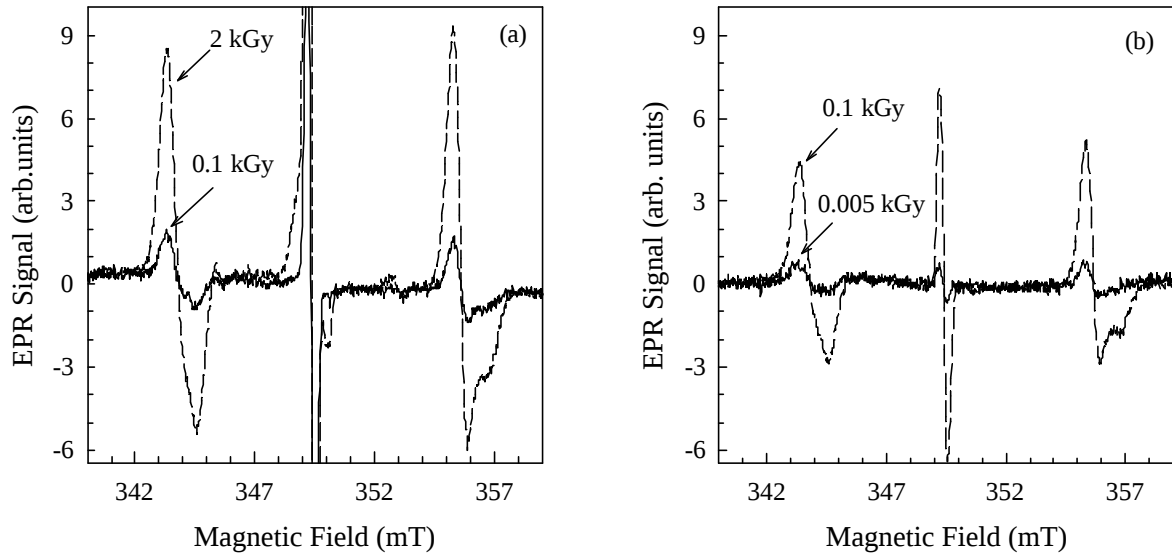


Figure 37. EPR spectra of the samples I301 (a) and HM (b) γ -irradiated at various doses up to 2 kGy, as evidenced by the labels.

All these features are summarized in fig.38, where the bleaching of the B-type activity, represented by the β band intensity normalized to the intensity before irradiation (in the insets), and the growth of the H(II) centers concentration as a function of irradiation dose are reported for the dry sample I301 and for the wet sample HM.

Comparing panel (a) and (b), we note that the ratio between the growth rates of the H(II) centers (and analogously the bleaching rates of the β band) measured in the two samples, is proportional to the ratio of their respective OH concentration. In particular, as already noted by comparing the saturation doses, the conversion rate is larger by a factor ~ 10 in sample HM, whose OH content is about 10 times larger than in sample I301. At variance, as reported in the insets, the β PL band intensity is $\sim 30\%$ of its initial value in the HM sample, and $\sim 40\%$ in the I301, irrespective of the different OH content of the two materials.

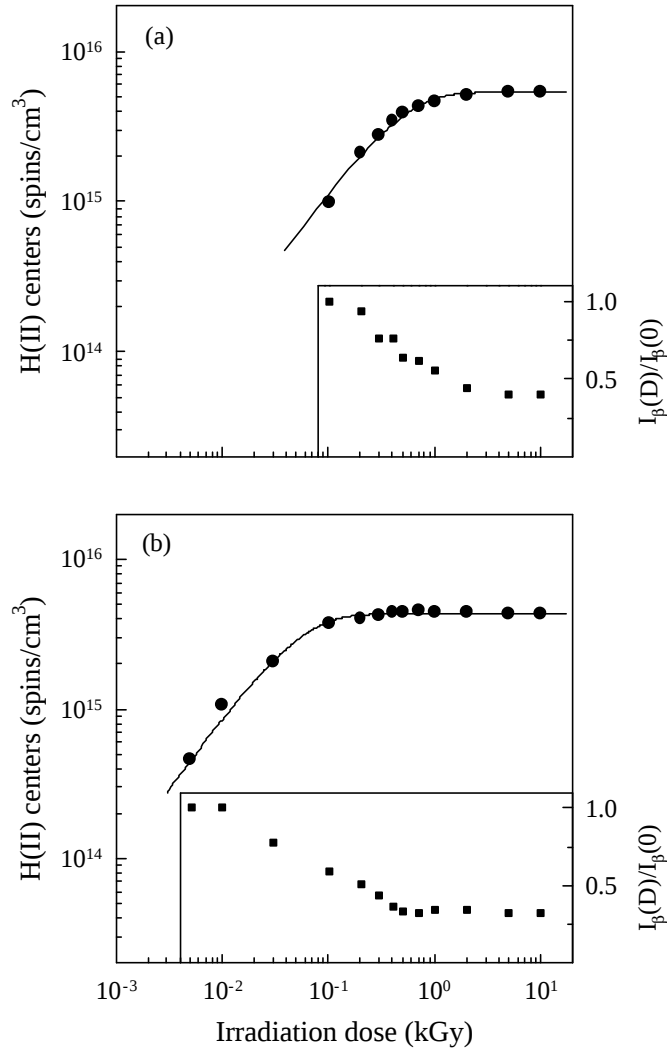


Figure 38. Dependence on γ -irradiation dose of the H(II) centers concentration in the I301 (a) and HM (b) samples. Solid lines represent the best fit with the function $N_{\text{EPR}}(D) = a(1 - e^{-bD})$. In the insets, the intensity of the photoluminescence β band (3.15 eV) is reported, normalized to its intensity before irradiation.

8.4 Conversion from B-type defects to H(II) centers: Conversion law and rate equations

In the previous sections we have evidenced that a conversion between optically B-type defects to H(II) paramagnetic centers is effective under γ irradiation. The main features of this conversion process can be summarized as follows:

- (a) the bleaching of the optical defects is partial in all the investigated samples and their number is reduced by a factor from 2 to 3 of its native value;

(b) the conversion rate from optical to paramagnetic defects depends on the OH content of the material.

(c) the maximum concentration of H(II) centers is estimated to be $\sim 10^{15}$ spins/cm³ (Table 6) much less than the concentration of OH groups: $> 10^{17}$ /cm³ (Table 1, par.5.1)

These features can be utilized to clarify some theoretical and structural aspects of the bleaching process.

The feature (a) speaks for the occurrence of a γ activated back-conversion process from the paramagnetic centers to the B-type defects counteracting the conversion (par.8.2.4). Just on the basis of such a competition the complete process of conversion and back-conversion may be formally represented with the following reaction scheme:



where N^{OPT} and N^{EPR} are the B-type defects and the H(II) centers concentrations, respectively, and k_c and k_{bc} indicate the conversion and back-conversion rates. Under this assumption, a dynamical equilibrium is reached when $N^{OPT} k_c$ equals $N^{EPR} k_{bc}$.

The feature (b) can be related to the involvement of H atoms in the reaction process from the optical to the paramagnetic centers, as already illustrated in par.8.2.4 and by the eq.(8.1). More specifically, it is possible to assume that the γ -rays break O-H bonds in the glassy matrix and, as a consequence, H atoms are free to migrate and to be involved in the reaction of eq.(8.1). In this respect, a simple law relating the incremental number of γ -activated H atoms to the incremental γ dose dD is the following:

$$dN^H = (N^{OH} - N^H) P_g dD \quad (8.4)$$

where N^{OH} is the residual concentration of OH groups, N^H is the concentrations of H atoms and P_g is the H generation probability per unitary dose.

If the assumption is made that all the H atoms generated in this way are involved in the reaction (8.3), their maximum number should be equal to that of generated H(II) centers. The feature (c) evidences that the necessary amount of H atoms is less than the disposable OH groups one by at least one order of magnitude. This estimation implies that $N^H \ll N^{OH}$ and eq.(8.4) can be approximated by

$$dN^H \approx N^{OH} P_g dD \quad (8.5)$$

and in addition it can be assumed that N^{OH} coincides with the initial concentration of OH groups in the not-irradiated material.

It is possible to write down the rate equations for the process (8.3) observing that, on the basis of the hypothesized conversion, the sum of N^{OPT} optically active and N^{EPR} paramagnetic defects at each irradiation dose D must be constant and equal to the number of native B-type defects

$$N^{OPT}(D) + N^{EPR}(D) = const = N^{OPT}(0) \quad (8.6).$$

Then, under the conditions (8.5) and (8.6), the following rate equation can be written

$$\frac{dN^{OPT}}{dD} = -\frac{dN^{EPR}}{dD} \approx N^{OH} P_g (-k_1 N^{OPT} + k_2 N^{EPR}) \quad (8.7)$$

where the probabilities of conversion k_1 and k_2 of an optical center and of a paramagnetic one, respectively, have been introduced. The solutions of eq.(8.7) are

$$N^{OPT}(D) = N^{OPT}(0) \frac{1}{k_1 + k_2} (k_2 + k_1 e^{-P_g (k_1 + k_2) N^{OH} D}) \quad (8.8a)$$

$$N^{EPR}(D) = N^{OPT}(0) \frac{k_1}{k_1 + k_2} (1 - e^{-P_g (k_1 + k_2) N^{OH} D}) \quad (8.8b)$$

that can be easily connected to the process (8.3), provided the conditions $k_c = P_g k_1 N^{OH}$ and $k_{bc} = P_g k_2 N^{OH}$.

These solutions agree with the experimental observations of the bleaching process. In particular, the concentration variations of the optical and paramagnetic defects as a function of the accumulated dose are predicted to occur with a dose rate proportional to the OH content, in

agreement with the experimental results in fig.38. Moreover, the final number of optical and paramagnetic centers is independent on the OH content, as experimentally observed, and is proportional to $N^{OPT}(0)$, i.e. the initial concentration of B-type defects. Besides, the saturated value of optical centers, $N^{OPT}(\infty)$, is reduced by a factor $k_2/(k_1 + k_2)$ with respect to the initial value $N^{OPT}(0)$. So, on the basis of the experimental values (from 0.3 to 0.5) of this ratio, we can infer that the conversion and back-conversion probabilities have the same orders of magnitude, $k_1 \approx (1 \div 2)k_2$. Finally, the saturated value of EPR centers, $N^{EPR}(\infty)$, is proportional to the initial concentration of optically B-type defects, in agreement with the data reported in fig.35.

According to eq.(8.8b), the number of native B-type defects can be determined from the maximum number of induced H(II) centers at room temperature. In addition, it can be shown that:

$$N_{OPT}(0) = N_{EPR}(\infty)/P(\infty) \quad (8.9)$$

where $P(\infty)$ is the percentage of bleaching calculated at saturation ($D = \infty$):

$$P(\infty) = \{[N_{OPT}(0) - N_{OPT}(\infty)]/N_{OPT}(0)\} \quad (8.10)$$

that can be estimated from the experimental relative variation of the emission bands intensities:

$$[I(0) - I(\infty)]/I(0) \quad (8.11).$$

By using eq.(8.9), we can estimate the concentration of native B-type defects, $N^{OPT}(0)$, from the experimental value of the H(II) centers concentration and the percentage of bleaching.

If we consider the sample I301, and employ the concentration of H(II) centers determined from EPR measurements (see Table 6), we find $N^{OPT}(0) \sim 9 \times 10^{15} \text{ cm}^{-3}$. This value can be compared with that determined by using eq.(3.31) (see par.3.2.1) and the literature values for the oscillator strength, $f = 0.1 \div 0.12$ [114, 121, 124], and for the refractive index, $n = 1.46$ [121]. In particular, for the I301, where $\alpha(5.15 \text{ eV}) = 0.46 \text{ cm}^{-1}$ (see Table 7), FWHM = 0.46 eV (see Table 5), we find $N^{OPT}(0) = 1.6 \times 10^{16} \text{ cm}^{-3}$, in good agreement with our calculated value.

A more quantitative comparison between the eqs.(8.8) and the experimental results has been done by fitting eq.(8.8b) to the experimental data for the H(II) centers concentration in I301,

EQ906, H1 and HM samples. In particular, we employed the best-fit function $N_{\text{EPR}}(D) = a(1-e^{-bD})$, formally equal to eq.(8.8b), where $N_{\text{EPR}}(D)$ is the H(II) center concentration as a function of the dose D , and a , b are the maximum concentration and the conversion rate to be determined, respectively.

TABLE 7. Absorption coefficient α at 5.15 eV ($B_{2\beta}$ band), OH content and best fit parameters of the H(II) centers growth data with the function $N_{\text{EPR}}(D) = a(1-e^{-bD})$, where D is the accumulated γ rays dose, in different natural samples

Sample	α at 5.15 eV (cm^{-1})	[OH] (ppm by weight)	a (10^{15} spins/ cm^3)	b (kGy^{-1})
I301	0.46 ± 0.02	≤ 8	5.3 ± 0.5	2.4 ± 0.1
EQ906	0.39 ± 0.02	20	4.1 ± 0.4	3.0 ± 0.1
H1	0.41 ± 0.02	150	3.8 ± 0.4	28 ± 1
HM	0.36 ± 0.02	150	4.3 ± 0.4	22 ± 1

The best-fit parameters are reported in Table 7, and the theoretical curves are superimposed to the experimental data in fig.38. As can be seen, good agreement between the theoretical curves and the experimental data is obtained. Also, we note that the conversion rate b depends on the OH content; in fact, it increases by an order of magnitude passing from [OH]~10 ppm to 100 ppm. This quantitative agreement supports the hypothesis that the H involved in the reaction originates from the OH groups and that the conversion rates k_c and k_{bc} depend on the native OH content of the material. In this respect, it should be noted that in the absence of OH groups the conversion from the B-type defects to the H(II) centers does not happen as noted in ref.121, however, in this limit conditions our solutions do not apply since N^{OH} becomes less than the number of convertible centers. The agreement of the eqs.(8.8) with the experimental results is evidence also of the supposed coexistence of a conversion and of a back conversion, as the equilibrium value of the optical centers is shifted from zero. Another important aspect, predicted by the conversion model, is the independence on the OH content of the number of converted centers, a , as long as $N^{\text{OH}} \gg$ (B-type defects). The parameter a , rather, can be related to the concentration of B-type defects in the pristine glasses through the absorption coefficient, α , at 5.15 eV. In this respect, the OH groups are relevant to activate the conversion process but they do not influence the equilibrium.

8.5 Other experimental evidences for the B-type activity conversion

8.5.1 Bleaching at $T = 77$ K

The conversion between B-type defects and H(II) centers has been investigated also by γ irradiating the samples at low temperature. These experiments were carried out to evidence the effect of the thermal phonons activation of the matrix and of the diffusion activity of radiolysis products on the conversion. In addition, the study of the dependence of the conversion rate k_c and k_{bc} , eq.(8.3), on the temperature may clarify other aspects of the postulated mechanism.

We refer to Chap.5 for the details of the γ irradiation procedure at $T = 77$ K; here we limit to report that after the low temperature irradiation the samples were warmed at room temperature for measurements. Experiments were carried out on two samples, a natural dry (I301) and a natural wet (H1) in order to explore the effects of the OH content. In addition, two samples for each silica type were used, one irradiated at low temperature and the other irradiated in the same conditions at room temperature to take into account the effects of the employed apparatus. The samples were irradiated up to a dose of 10 kGy, at which, at room temperature, the conversion process was completed in both silica types (fig.38).

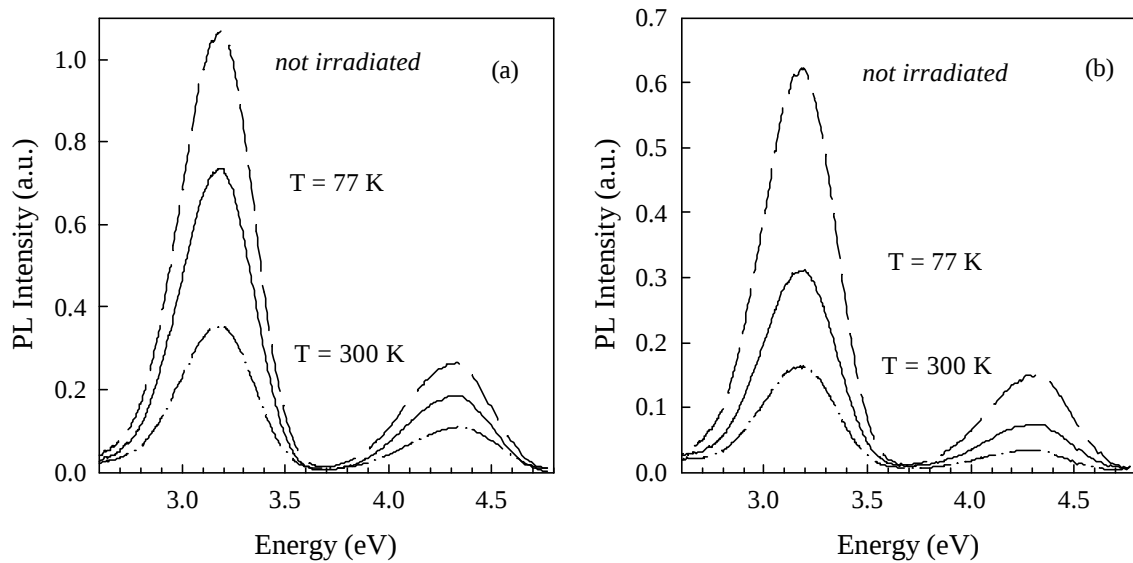


Figure 39. Room temperature emission spectrum in the range 2.6-4.8 eV with excitation at 5.0 eV of the samples I301(a) and H1 (b) γ -irradiated to 10 kGy at $T = 77$ K (continuous line), at $T = 300$ K (dash-dotted line) and not irradiated (dashed line).

In fig.39 we report the luminescence spectra of the samples I301 and H1 after γ -irradiation at 77 K and at 300 K, excited at 5.0 eV. It is observed that the irradiation at 77 K reduces the β and α_E bands in both materials. In particular, in the sample I301, after 77 K irradiation the B-type activity is $\sim 70\%$ of its initial value, whereas after 300 K irradiation it is $\sim 40\%$. In the H1 sample, we find $\sim 50\%$ and $\sim 30\%$ after 77 K and 300 K irradiation, respectively.

Also for the EPR 11.8 mT doublet we found a less efficient conversion in the irradiation at low temperature with respect to room temperature. In fact, in both materials fewer centers are induced with respect to the same dose at room temperature. However, a comparison with the room temperature irradiated samples evidenced that the induced centers in the H1 samples are nearer to the room temperature concentration with respect to the I301 sample. This effect, as well as the higher percentage of bleaching in the H1 sample, evidenced that the irradiation efficiency is higher in the natural wet sample with respect to the natural dry also at low temperature, at least as regards this conversion process.

The results on the bleaching effect both at $T = 77$ K and at $T = 300$ K are summarized in fig.40, where the concentration of γ -induced H(II) centers (determined by EPR measurements) is plotted versus the percentage of bleached B-type defects determined as (compare with eqs.(8.9-11))

$$P(D) = \{[N_{OPT}(0) - N_{OPT}(D)]/N_{OPT}(0)\} = \{[I(0) - I(D)]/I(0)\} \quad (8.12)$$

where D is the irradiation dose, $N_{OPT}(D)$ the concentration of B-type defects and $I(D)$ is the intensity of the PL β band, representative of the B-type defects content.

In fig.40 it is evident that the point representative of the irradiation at 77 K (triangles) and that representative of the irradiation at 300 K (circles) are on a straight line passing through the origin. This feature confirms that independently from the irradiation procedure the concentration of γ -induced H(II) centers is proportional to the concentration of converted optical centers. These results confirm the validity of the conversion from B-type defects to H(II) centers, independently from the irradiation temperature, and confirm also a dependence of the reaction process on the OH

content of the material. In this respect, the reaction scheme proposed by eq.(8.3) and the solutions eqs.(8.8) are supported.

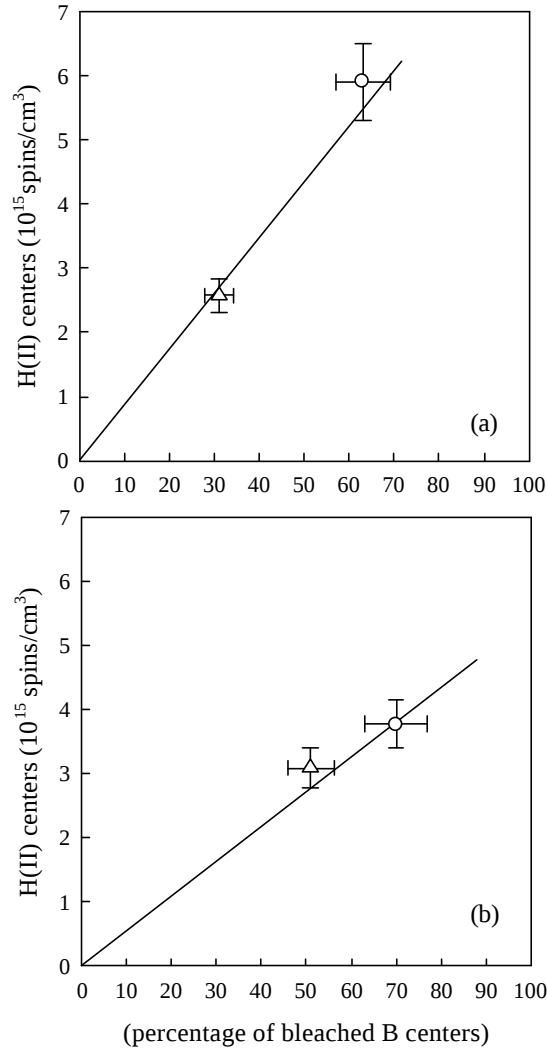


Figure 40. Comparison between the induced H(II) centers and the percentage of bleached B-type defects in the I301 (a) and H1 (b) samples γ -irradiated to 10 kGy at: $T = 300$ K (circles), $T = 77$ K (triangles).

The dynamics of the reaction at low temperature is still an open problem. It is possible that it occurs already at low temperature supposing, for example, that the H atoms have been activated with sufficient kinetic energy to reach the optical centers and react with them. Another possibility is that, as suggested in ref.120, the conversion occurs after irradiation in the post irradiation relaxation at room temperature when the H atoms can diffuse. In this case it is necessary to assume that the H remains activated as long as possible in the post irradiation time so that it can reach the target of the

B-type defect without relaxing on the center from which it originated. In each case other experiments are needed to evidence the details of the mechanisms acting at low temperature as the conversion rate dependence on temperature, and the efficiency of the process as evidenced from the minor number of bleached centers with respect to room temperature.

8.5.2 Bleaching effect by neutron and electron irradiation

We have also investigated the bleaching effect as caused by other irradiation sources: neutron and electron bombardment. Also in these cases we have examined a natural dry sample, I301, and a natural wet, H1, in order to evidence any dependence on the OH content of the material.

Neutron irradiation

The details of this irradiation are described in par.5.2.3. The trial with *thermal neutrons* at the fluxes $[N]_3 = 3.6 \times 10^{13} \text{ n/cm}^2$ and $[N]_4 = 8.6 \times 10^{14} \text{ n/cm}^2$ showed that both in I301 and H1, the B-type activity was reduced and the H(II) centers were induced. A comparison of the bleached and generated centers is made in fig.41 (diamonds), in which the H(II) centers concentration is reported versus the percentage of bleaching determined by eq.(8.12) (to be compared with fig.40). It is observed that again we find a good agreement with the conversion process already hypothesized. We further observe that the before evidenced greater efficiency in the conversion process when the sample is a natural wet is confirmed also with neutron irradiation. In particular, by comparing panel a and b of fig.41, we find that in the H1 sample the bleached centers are at the maximum attainable value whereas in the I301 sample less centers than maximum are bleached, even if the same neutron fluxes are accumulated. These features request further investigation to explain the details of the bleaching kinetics under neutron irradiation, anyway they agree with the correlation between B-type defects and H(II) center and the reaction scheme reported in eq.(8.3).

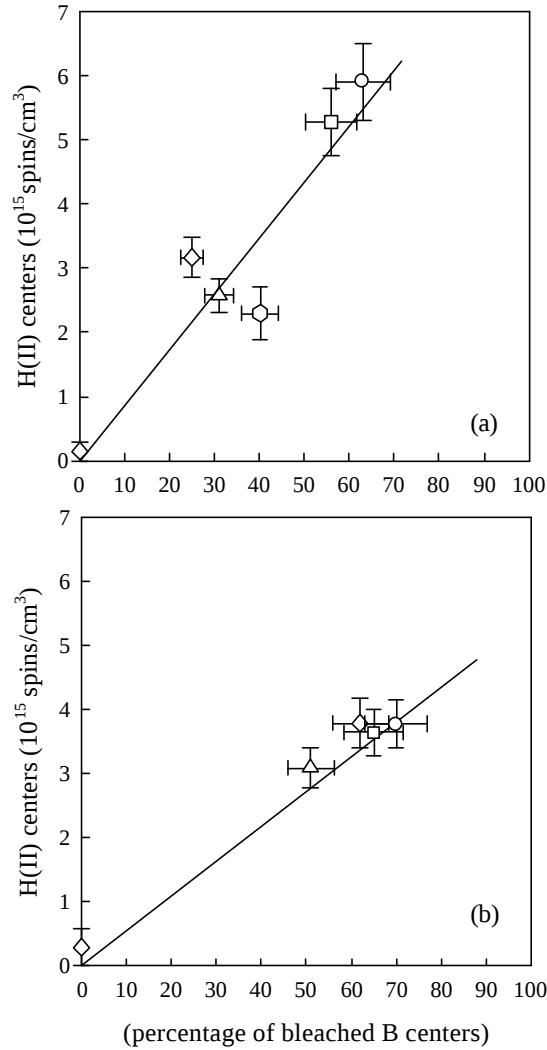


Figure 41. Comparison between the induced H(II) centers and the percentage of bleached B-type defects with different irradiation sources in the I301 (a) and H1 (b) samples: thermal neutrons (diamonds), in-reactor neutrons (hexagon), electrons irradiation to 20 kGy (square). Triangles and circles refer to γ -irradiation to 10 kGy at T= 77 K and T= 300 K, respectively.

In the other trial with the *in-reactor irradiation* at flux $[N]_1 = 1.6 \times 10^{17} \text{ n/cm}^2$ we observed that in all the samples the B-type activity was almost completely removed and also no H(II) centers were detected. At variance, by irradiation of the I301 sample at a minor flux $[N]_2 = 8 \times 10^{13} \text{ n/cm}^2$, we found results in quantitative agreement with those obtained by γ irradiation, as shown in fig.41 (hexagon). This feature leads us to conclude that for $[N]_1$ some great effect on the matrix occurs [3, 53] that avoids quantitative comparison of the in-reactor irradiation with the previous reported results.

Electron irradiation

A final test of the bleaching process hypothesized was done by electron irradiation using again a natural dry I301 and a natural wet H1 materials. These irradiations were carried out with the LINAC accelerator at two doses 20 kGy and 200 kGy, the details being reported in par.5.2.2.

The electron caused the reduction of the B-type activity and the generation of the H(II) centers. In the sample I301, both doses gave the same reduction of the B-type activity and the same concentration of the H(II) centers. Analogously, in the H1 sample we observed equal results for 20 kGy and 200 kGy. These features are in agreement with the kinetics of bleaching found in the experiments with γ irradiation where the effect of bleaching was completed for doses below ~ 10 kGy. The quantitative comparison of the bleached and the H(II) centers is reported in fig.41 (squares) for the lower dose, 20 kGy. We find good agreement with the other irradiation procedures both for the H1 and the I301 samples.

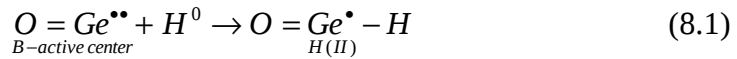
All the reported features on the different attempts to induce bleaching effects evidence that the conversion of the B-type defects into the H(II) centers is quite general. In fact, independently from the employed irradiation source and from the irradiation temperature we found that such conversion happens with the same main features depending on the OH content of the pristine material.

8.6 Mechanism of conversion from B-type defects to H(II) centers: structural aspects of the conversion process

The experimental results and the theoretical model reported above constitute a good basis for discussing about the structures of the diamagnetic and the paramagnetic defects involved in the conversion mechanism and for refining the considerations of par.8.2.4. Firstly, our experimental results show that the H(II) center is compatible with a structural model involving a Ge atom; secondly, we have unambiguously proved that the B-type defects are precursor defects of the H(II) centers; finally, our data also prove that the B-type defect does not contain OH. In fact, the

concentration of H(II) centers at the saturation does not depend on the OH content and, on the contrary, it is proportional to the content of native B-type defects.

If one assumes for the H(II) center the model ($O = Ge^{\bullet} - H$) [103, 107], among the structural models proposed for the B-type defect the one that best fits to the role of precursor of the H(II) center in the conversion process outlined in par.8.2.4 is the twofold coordinated Ge ($O = Ge^{\bullet\bullet}$) [107, 116-118]. Also, on the basis of the dependence of the conversion rate on the OH content, we can reasonably state that the H atoms involved in the conversion process originate from the OH groups by γ irradiation. Then, the reaction scheme (8.1) for the conversion mechanism is reasonably proven



where H^0 is the atomic hydrogen activated by γ -rays.

As regards the back-conversion process in which the H(II) centers are converted into the B-type defects, a reaction scheme can be outlined in which γ activated H atoms break the $Ge - H$ bond of the H(II) center, restoring the B-type defect and, maybe, forming H_2 molecules. That is the following



The reactions (8.1) and (8.13) describe the conversion and back-conversion mechanisms, respectively, of the reaction (8.3) and they can explain both why k_c and k_{bc} depend on the OH content and why an equilibrium can be reached between the populations of B-type defects and of H(II) centers. It must be also noted that recent results from *ab initio* calculations [107] on the structural models for the defects responsible for the 11.8 mT EPR doublet and the B-type activity are in agreement with the structural defects involved in the reactions (8.1) and (8.13).

The reliability of the attribution of B-type and H(II) centers to Ge related defects is based also on the fact that the measured Ge concentrations, ≤ 1 ppm by weight ($\sim 10^{16} \text{ cm}^{-3}$) as verified by neutron activation measurements, see Table 2 (par.5.1), are consistent with the defect

concentrations estimated by EPR measurements, $10^{15} \div 10^{16}$ spins/cm³. In addition, this result also suggests that Ge is present as a substitutional impurity, being involved in structural defects like the ($O = Ge^{\cdot\cdot}$), in accordance to other reported observations [33, 114, 178].

As a final remark, a bleaching effect has been observed also in UV irradiated Ge-doped silica [105, 121-122, 124, 126] where different conversion processes have been hypothesized. However, other paramagnetic structures have been supposed to be involved in those conversion processes, as the Ge-E' center: ($O \equiv Ge^{\bullet}$) [126], the positively charged Ge lone-pair center: ($O = Ge^{\bullet+}$) [121, 124], and the negatively charged four-fold coordinated Ge: (GeO_4)⁻ [122]. These centers have not been observed in any of our investigated samples.

These differences may be explained by noting that the materials employed in this Ph.D. thesis have a Ge content $\leq$ 1ppm, very less than in the doped materials where Ge concentrations $\geq$ 1% are used. In the latter case there should be a large number of substitutional four-fold coordinated Ge atoms together with the two-fold coordinated ones and other reaction channels could be activated. It could be concluded that the conversion from two-fold coordinated Ge to H(II) centers is the most effective process in natural silica and that a conversion process is more effective than another one depending on the Ge and/or OH contents of the material.

8.7 Thermal reversibility of the bleaching process

The conversion processes from B-type defects to H(II) centers induced by γ -irradiation is a fully reversible process. This result was achieved by studying the effects of thermal treatments of irradiated silica samples. We report below the data obtained in two representative natural samples, thermally treated after γ irradiation to 10 kGy, well above the value required to complete the bleaching of the B-type activity. The chosen samples are a type I (I301) and a type II (H1) in order to consider the effects of the OH content. Isochronal thermal treatments were performed at

temperatures from $T = 330$ K to $T = 430$ K by steps of 10 K, and following the procedure described in par.5.2.4 [179].

8.7.1 B-type activity recovery

The effects of the isochronal thermal treatments on the optical B-type activity are showed in fig.42, in which the α_E and β PL emissions, excited at 5.0 eV, are reported for the H1 sample. In details, for treatments at temperatures less than 330 K both bands maintained their post-irradiation intensity. At variance, treatments at higher temperatures caused the emission signals to increase progressively until that at $T = 410$ K exactly the same PL intensity as that detected in the not-irradiated sample was recorded.

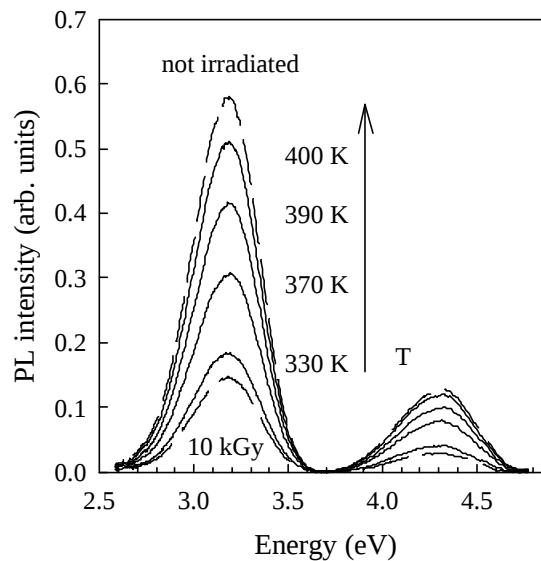


Figure 42. Room temperature emission spectra in the range 2.5-4.8 eV in the sample H1 excited at 5.0 eV. Full lines represent the spectra of the sample after isochronal thermal treatments at the temperatures in the labels. Dashed lines are the spectra in the same sample before (top) and after (bottom) γ -irradiation to 10 kGy.

In the same temperature range in which the B-type activity is completely recovered, also the EPR doublet due to H(II) centers varies its intensity. This effect is reported in fig.43, where we plot the high field structure of the 11.8 mT EPR doublet after various thermal treatments, as detected in the sample H1. The doublet was unaffected by thermal treatments below $T = 330$ K; then a

progressive decrease occurred which was completed at $T = 410$ K where the doublet intensity falls below the instrumental sensibility.

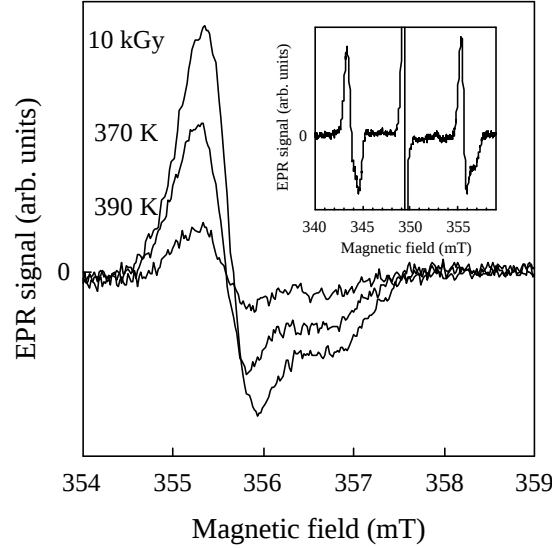


Figure 43. Room temperature EPR signal of the high field structure of the 11.8 mT doublet as detected in the H1 sample γ -irradiated to 10 kGy (top line) and after isochronal thermal treatments at 370 and 390 K. The inset shows the full spectrum of the sample after γ -irradiation to 10 kGy.

The same evolution of both PL and EPR signals was observed in the I301 sample and a summary of the effects of the thermal treatments performed is reported in fig.44a and fig.44b for our two samples. In the top of the figures, the normalized doublet variation $P_{\text{EPR}} = I_{\text{hpf}}(T)/I_{\text{hpf}}$ is reported, as a function of the treatment temperature T , where $I_{\text{hpf}}(T)$ is the doublet intensity after a given treatment and I_{hpf} is the intensity after the irradiation to 10 kGy.

Analogously, in the bottom of the figures, the normalized PL variation $P_{\text{PL}} = (I_{\text{PL}}(T) - I_{\text{PL}})/(I_{\text{PL}/0} - I_{\text{PL}})$ is reported, where $I_{\text{PL}}(T)$ is the intensity of the β PL band after a given treatment, $I_{\text{PL}/0}$ is the intensity of the not irradiated sample and I_{PL} is the intensity after the irradiation to 10 kGy. As both EPR and PL signals are proportional to the number of the respective active centers, the values $(1 - P_{\text{EPR}})$ and P_{PL} represent the percentage of destroyed and of regenerated centers, respectively.

The data reported in fig.44 show that a strict correlation exists between the temperature range where P_{EPR} changes and the corresponding range of variation of P_{PL} , both in the H1 and in the I301 sample. In addition, the comparison of the thermal dependencies detected in the two samples shows a slight difference in the temperature range where the signal variations are effective, namely this range is larger in sample H1 than in sample I301 by about 20 K.

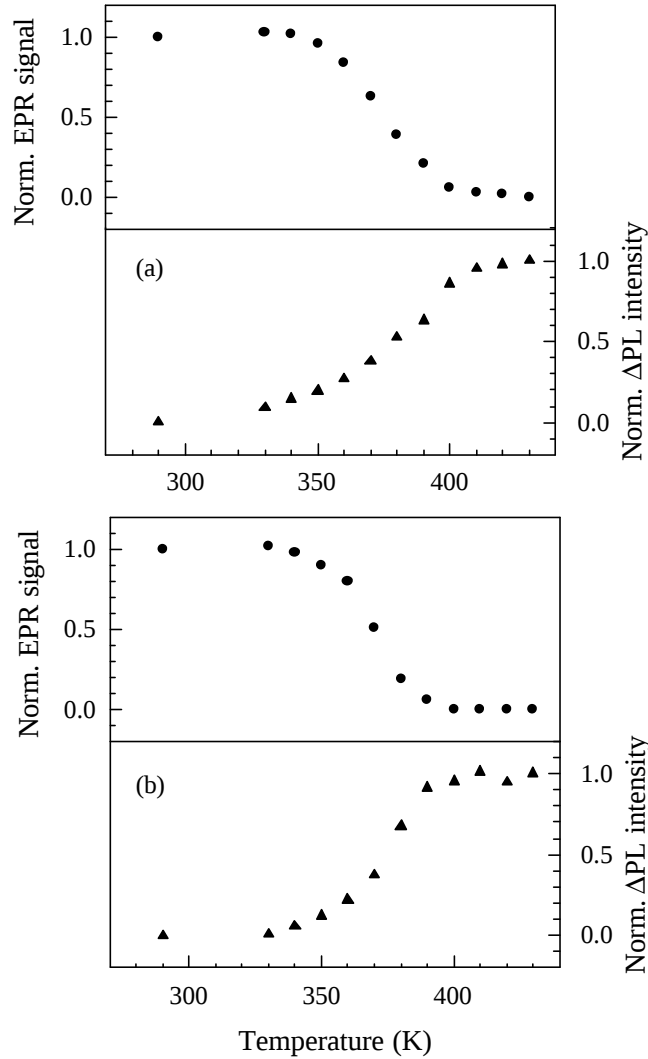


Figure 44. Room temperature PL and EPR signals detected in H1 (a) and I301 (b) samples after isochronal thermal treatments in the range of T 330–430 K. Top panels: 11.8 mT doublet intensity after treatment at T normalized to the value after γ -irradiation to 10 kGy; bottom panels: variation of PL β band after treatment at T with respect to the value after γ -irradiation to 10 kGy, normalized to the variation between not irradiated sample and irradiated sample.

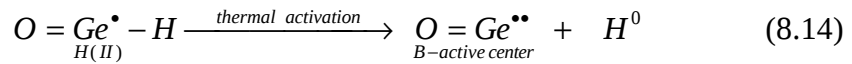
By repeating thermal treatments and irradiation cycles in the same sample we observed that both the bleaching and the thermal recovery of the B-type activity are fully reversible processes. In

fact, in the same samples thermally treated up to $T = 430$ K, a second irradiation by a 10 kGy γ dose bleached the B-type activity to the same extent as the first one, as determined by measuring the intensity of the PL bands and of the 11.8 mT EPR doublet. Successively, a second series of thermal treatments, step by step from $T = 330$ K to $T = 430$ K, completely restored the B-type activity of the not irradiated sample.

8.7.2 Thermal back-conversion process

The above reported data show that by heating the samples up to $T \sim 430$ K the paramagnetic H(II) centers induced by γ irradiation are destroyed and the pre-existing optically B-type defects are restored, recovering their pre-irradiation concentration. These features indicate that a back-conversion from H(II) centers to B-type defects can be thermally activated and it can reconvert the totality of the defects induced by irradiation. We also observed that a further irradiation, after a thermal treatment, was found to produce the same effects as the first irradiation on the "as grown" material. This result suggests that the thermal treatments do not affect significantly the matrix.

In the frame of the structural model described in sections 8.2.4-8.6, the thermal activated back-conversion process can be explained by a mechanism in which the H atom of the H(II) center acquires enough thermal energy to move away from the defect, restoring the two-fold coordinated Ge center. This process can be visualized by the following reaction scheme [179]:



where H^0 is the released atomic hydrogen.

As shown in fig.44, the largest variations both of the PL and EPR signals occur at nearly $T = 380$ K. This effect indicates a maximum efficiency of the thermally activated process around this temperature. This feature has been further investigated by new thermal treatments, the so called isothermal treatments (see par.5.2.4) [77, 180]. Such treatments have been carried out in a H1 sample γ -irradiated to 10 kGy. In fig.45 we report a summary of the results by plotting the

concentration of B-type defects, as derived from the intensity of the β PL band, and that of H(II) centers as a function of the treatment time at a given temperature. The first treatment was carried out at $T = 350$ K where, according to fig.44, the recover of the B-type activity starts. It is evident that the optical centers increase and the paramagnetic centers decrease with steep variations for $t \leq 60$ min and thereafter it is observed a slope change tending to very low variations at $t \sim 150$ min.

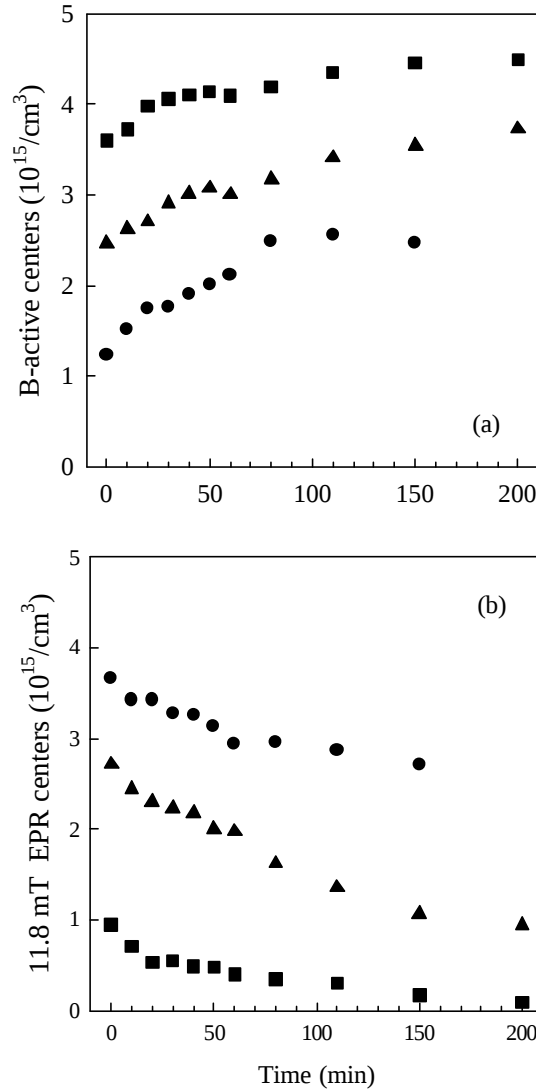


Figure 45. Recover of the optical B-type activity (a), and annealing of the 11.8 mT doublet (b) by thermal treatments at $T = 350$ K (circles), 370 K (triangles) and 390 K (squares) in the sample H1 γ irradiated to 10 kGy.

After 150 min at this temperature, the treatment was restarted at the higher temperature $T = 370$ K. In the first minutes of the treatment both the optical and the paramagnetic defects

restarted to change. Once more, a slope change is evident when the overall treatment time exceeds 80 min and very small variations are detected for $t \sim 200$ min. By changing again the treatment temperature to $T = 390$ K, a new steep variation of the concentrations of both centers is observed, followed by a variation with a lower slope until the paramagnetic centers intensity was below the instrumental sensibility and the optical B-type defect restored its pre-irradiation intensity. In all the treatments the sum of the two kinds of center concentration was found to be constant, within the accuracy of our measurements, evidencing that a one-to-one conversion occurs.

The appearance of steep concentration variations at short times in all the thermal treatments and the tendency to an asymptotic value of concentration after prolonged heating suggest the presence of a complex thermal conversion mechanisms [180]. Our data evidence this effect but more experimental proofs are needed in order to clarify the peculiarities of this process.

Chapter 9

Experimental results: Simultaneous generation of the A-type activity and of the 7.4 mT EPR doublet

Our investigation of the γ -induced effects in silica ends in this chapter, where we are concerned with the “A-type” optical activity and with the EPR doublet split by 7.4 mT. The A-type activity is present in as grown natural materials, but it can be induced as well by gamma irradiation, both in natural and synthetic materials. The EPR doublet is a gamma-induced effect. The reason for a common consideration is that they share the same growth by irradiation in all the materials types.

The questions regarding both the EPR doublet and the A-type activity have been already introduced in par.2.4. We report here the study by optical and EPR measurements, of the γ irradiation effects on various silica materials that could be related to these questions.

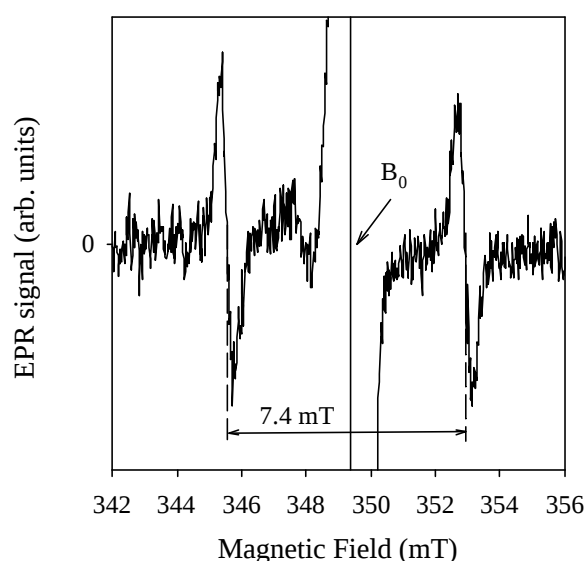


Figure 46. Isolated EPR doublet of the H(I) centers as detected in the sample S1/10⁴. The central signal is due to the strongly distorted E' centers resonance line.

9.1 The 7.4 mT EPR doublet: EPR properties

We detected the 7.4 mT EPR doublet in all the natural and synthetic materials after γ -irradiation. A typical signal is reported in fig.46 as observed in the sample S1/10⁴ where it is well

isolated from other resonance signals. The spectrum was carried out using $P_{in} = 50 \mu W$, $B_m = 0.4 \text{ mT}$, $\omega_m = 100 \text{ kHz}$. The pair of lines suggests that this structure could arise from an hyperfine interaction involving a nuclear spin $I = 1/2$.

As evidenced in fig.46, the doublet splitting is $B_H - B_L = 7.36 \pm 0.02 \text{ mT}$. Taking as reference the magnetic field B_0 where the E' resonance line changes sign (see fig.46), we found that the doublet is asymmetrically centered on B_0 with distances $B_0 - B_L = 3.84 \pm 0.02 \text{ mT}$ and $B_H - B_0 = 3.52 \pm 0.02 \text{ mT}$. It is observed that, independently from the manufacturing, the 7.4 mT EPR doublet is generated with the same spectral features reported in fig.46 in all the investigated materials.

The observed asymmetry can be interpreted as a second order effect of the hyperfine interaction, employing the eqs.(3.22-3.23) introduced in par.3.1.5, and assuming for simplicity isotropic A tensor. Substitution with $\frac{\hbar \omega}{g\beta} = B_0 = 349.35 \text{ mT}$ and $\frac{K}{g\beta} = B_H - B_L = 7.36 \text{ mT}$, yields: $B_0 - B_L = 3.72 \text{ mT}$ and $B_H - B_0 = 3.64 \text{ mT}$. This calculation shows that the predicted asymmetry is in the same direction as the experimental one, in fact $B_0 - B_L > B_H - B_0$, and we find also a fairly good quantitative agreement. This feature is compatible with the attribution of the doublet to a Si related center. The comparison with the data reported in refs.95, 101 suggests that the 7.4 mT EPR doublet is the same EPR structure investigated by those authors. According to the literature, we will adopt the name H(I) center for the defect responsible for this EPR signal [103].

We have investigated the dependence of the EPR doublet intensity on the microwave power. In fig.47 we report the results obtained in the sample I301/5000. We observe that the region of not-saturated signal extends up to $\sim 0.3 \text{ mW}$. This result can be compared to the microwave power dependence of the other relevant EPR signals observed in the irradiated silica samples, those related to the E' centers, the weak satellite structure and the H(II) centers (see previous chapters). For comparison, in fig.47, we have reported the E' centers and the H(II) centers signals dependencies on the microwave power, the weak satellite structure is not shown since it has the same dependence as

the E' centers (fig.23, par.7.1). We observe that the microwave power dependencies of these EPR signals strongly differ from that of the H(I) centers signal, suggesting a different structural model.

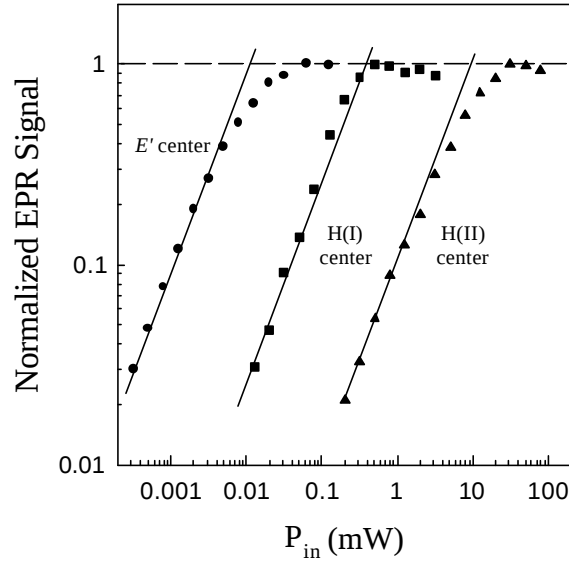


Figure 47. Dependence of the squared EPR signals of E' (circles), H(I) (squares) and H(II) centers (triangles) on the microwave power, in the sample I301/5000. Straight lines evidence the power regions of non-saturation.

9.2 Irradiation effects

The growth under γ irradiation at room temperature of the 7.4 mT doublet was investigated in all the materials of Table 1 (see Chap.5) [181]. As shown in fig.48 for the sample H1, the doublet signal, reported as the concentration of the related H(I) centers, is above the instrumental sensibility only after the dose 100 kGy. This dose is higher than the doses required to observe the other EPR signals. On increasing the dose no saturation in the doublet intensity was observed up to 10^4 kGy, which is the maximum attained dose, and a maximum concentration of H(I) centers 6.2×10^{15} spins/cm³ was measured.

The existence of relationship among the generation processes of γ -ray induced EPR signals was investigated. A comparison is made between the growth under irradiation of the E' centers, reported in the inset of the fig.48, and that of the H(I). As already noted (see Chap.6), the E' centers

intensity grows for low doses and then reaches an asymptotic value. At variance, the 7.4 mT doublet intensity grows also in the region of doses where no variation is observed for the E' centers.

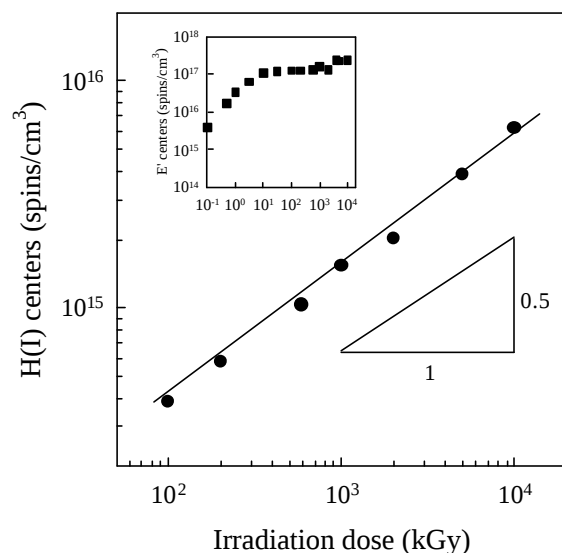


Figure 48. Dose dependence of the H(I) centers concentration in the natural wet sample H1. In the inset the dose dependence of the E' centers is reported. The full line is the power law $D^{0.5}$ that best-fits the data.

Analogous observations apply to the comparison with the other irradiation induced paramagnetic centers, as shown in fig.24b (par.7.2) and in Table 6 (par.8.2.3). So we can rule out any relationship between the generation processes of the H(I) centers and the E', the weak satellite structure or the H(II) centers.

Further examination of the growth under irradiation of the H(I) centers, for the H1 sample, shows that the concentration has a square root dependence on dose. We observed this square root dependence also in other materials but this law is not general. In fact, a detailed study of the growth of the doublet evidenced that a sublinear dependence on the irradiation dose, D^v ($v < 1$), without concentration saturation, is generally characteristic in all the materials, with the exception of the S300. In particular, the doublet has a linear growth in the latter material, which is a synthetic dry. Nevertheless also in this material no concentration saturation is observed up to the highest doses investigated, where a maximum concentration 1.9×10^{15} spins/cm³ is reached.

γ -irradiation generated in all the investigated samples an optical absorption band, centered around 5 eV and partially overlapping the absorption band at 5.8 eV, due to the E' centers [26, 81]. Excitation within the 5 eV band gives rise to a photoluminescence band. The latter band is reported in fig.49 as observed in our sample S300/10⁴, where it is well separated from other emission spectral features, under excitation at 5.0 eV.

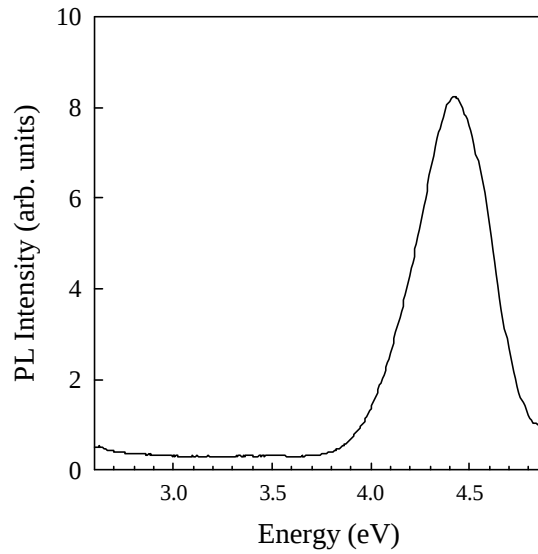


Figure 49. Room temperature emission spectrum in the range 2.6-4.9 eV as detected in the sample S300/10⁴ under excitation at 5.0 eV. The band peaked at 4.4 eV is the α_R band, the steep rise at higher energy is the shoulder of the excitation band.

This luminescence band is centered at 4.4 eV, has FWHM 0.45 eV and is identified with the α_R band [115, 136]. It has been already reported in literature that the absorption band at 5 eV and the α_R luminescence band increase with the irradiation dose, R-type activity [136].

We have determined the variation of the α_R band with γ irradiation in our samples. In particular, in those samples where this band overlapped the α_E band (see par.8.1) a fitting procedure has been employed to separate the α_R and the α_E bands, taking into account the observed proportionality between α_E and β band (see fig.29a par.8.1). As reported in fig.50 for the H1 sample, the α_R PL band grows with irradiation and no saturation is found. In addition, it is observed

a sublinear growth of the α_R band that resembles the one observed for the 7.4 mT doublet. For the particular case of the H1 sample, a square root growth is found in agreement to the EPR signal growth of the 7.4 mT doublet.

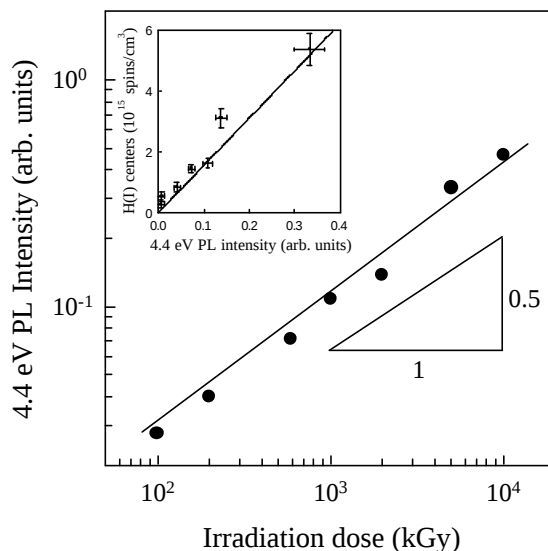


Figure 50. Dose dependence of the 4.4 PL emission (α_R) band, excited at 5.0 eV in the natural wet sample H1. The full line is the power law $D^{0.5}$ that best fits the data. In the inset the H(I) centers concentration is reported as a function of the α_R band intensity. The full line is a best-fit curve.

Further analysis of the growth of the α_R PL band evidenced that in all the materials it has a sublinear growth in strong similarity to the observed growth of the H(I) centers. This power law growth is observed also in the sample S300, at variance to the growth law measured for the H(I) centers in this material.

In order to elucidate the connection between the EPR H(I) and the PL α_R active centers, we have compared the intensities of their signals in each silica materials as a function of the irradiation dose. As shown in the inset of fig.50, a pretty good correlation is found between the two signals in all the materials; we found a correlation coefficient of 0.968, in the case of the H1 sample. In addition, the intensity ratio of the 7.4 mT EPR doublet and the 4.4 eV PL band, $I_{\text{EPR}}(7.4 \text{ mT})/I_{\text{PL}}(4.4 \text{ eV})$, is found to depend on the silica type. In particular, it is related to the OH content. This fact is well evidenced in fig.51, where $I_{\text{EPR}}(7.4 \text{ mT})/I_{\text{PL}}(4.4 \text{ eV})$ is plotted against the

concentration of OH groups in the samples irradiated at a dose 10^4 kGy. We observe that this ratio increases on increasing the OH content of the material from 1 (synthetic dry S300) to 1000 ppm (synthetic wet S1), suggesting that, at a given dose, the relative amount of H(I) centers with respect to the PL α_R active centers, is larger in silica having a higher OH content.

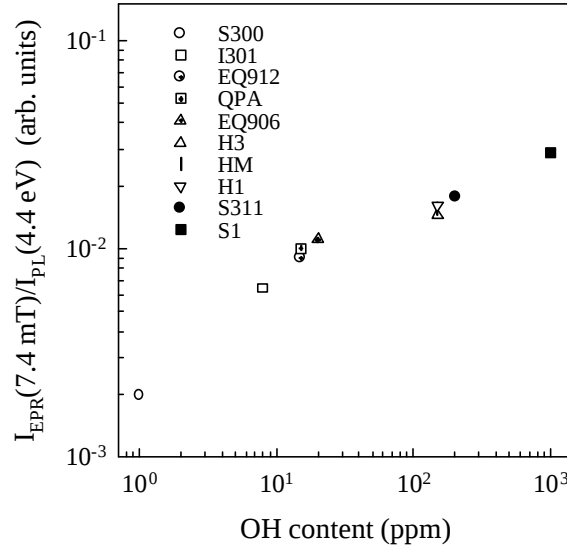


Figure 51. Dependence of the intensity ratio between the 7.4 mT EPR doublet and the 4.4 eV PL band on the OH content of the investigated materials.

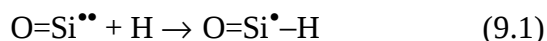
9.3 Generation mechanism of the 7.4 mT EPR doublet

Our results show that γ irradiation of silica induces an EPR doublet split by 7.4 mT, identified as the H(I) center [103]. By analyzing the intensity dependence on the accumulated irradiation dose it has been evidenced that a square root law, with the only exception of the S300 material, is predominant in all the materials, independently from their OH content. Similar dose dependence was found for the intensity of the γ induced optical emission band at 4.4 eV, identified as the α_R band and associated to the A-type activity [115, 136]. Moreover, a linear correlation between the induced EPR and the optical centers is evidenced, their ratio being related to the material OH content of the material [181].

On the basis of the reported results and according to the structural model proposed for the H(I) center, we can speculate on its generation mechanism. In particular, it has been proposed and well verified that a model for the H(I) center should be the structure $\text{O}=\text{Si}^\bullet\text{-H}$ [107]. This is an E' like center, $\text{O}=\text{Si}^\bullet$, where a H atom substitutes an O atom. But, from the comparison of the growth kinetics of the H(I) and the E' centers we have found no analogy, so it is unlikely that these centers have similar precursors (for example oxygen vacancies). On this basis, it can be said that the H(I) centers are not a fraction of the total number of γ induced E' centers. At variance, it can be suggested a relation between the irradiation induced optical A-type activity and the H(I) center, basing on the similarities of their growth by irradiation.

On the other hand, it has been shown [136] that the γ -induced optical activity type R and the native "type A", quite similar to each other, originate from essentially similar defects. It has been hypothesized that the two-fold coordinated silicon atom ($\text{O}=\text{Si}^{\bullet\bullet}$) may be responsible for both activities [135].

According to the reaction R2 (see par.2.4)



the optical center can be converted into the H(I) center by trapping an hydrogen. By examining our results, it can be hypothesized that the irradiation firstly generates the optical center; successively, some H atoms, that are made free in the matrix by irradiation, can react with the optical center transforming it into the H(I). In this context, the optical centers could be generated by the rupture of Si-O bonds, whereas the H atoms may originate from preexisting O-H groups. In this way, at a given dose a fraction of the optical centers generated by irradiation should be converted into the H(I) center, the number depending on the availability of OH and on a dynamical equilibrium like that hypothesized in the previous chapter for the bleaching effect (see par.8.2.4 and par.8.6).

These features could explain why similar kinetics are found for the optical and paramagnetic centers in the majority of materials. In fact, it is reasonable that when a lot of activated H atoms are

present the conversion of the optical center is very likely and the bottleneck is constituted by the effective generation of the optical centers. So, the growth by irradiation is controlled by the mechanism of generation of the optical centers also for the paramagnetic centers.

In this framework, the anomaly observed in the case of the S300 sample deserves some comments. In this sample the OH content is the lowest one (<1 ppm); so, a higher number of optical centers may be produced before that they are converted by the attachment of H. In this case the linear regime in the generation of H(I) centers could be due to the linear dependence of the generation of H atoms on the dose.

Finally, it is worth to note that several explanations of the sublinear growth kinetics have been already proposed in literature, e.g. by postulating ad hoc generation mechanisms involving different precursors of a given defect with a distribution of the activation energies [88] or by assuming complex generation mechanisms involving more steps and the competition between generation and conversion of a defect [89]. These ad hoc solutions are to be considered as preliminary and not based on strong experimental evidences. Admittedly, we too cannot explain the sublinear growth of the optical activity.

In conclusion, our data are consistent with a relation between the irradiation induced H(I) centers and the irradiation induced optical A-type defects. This relation supports the reaction (9.1) and the structural models attributing the H(I) center to the structure $\text{O}=\text{Si}^{\bullet}-\text{H}$ and the optical center to $\text{O}=\text{Si}^{\bullet\bullet}$. We observe that the reaction (9.1) is analogous to that reported for the two-fold coordinated germanium, eq.(8.1) (see par.8.2.4); so, it is reasonable that the conversion occurs in the case of pure silica for the two-fold coordinated silicon as well. The complexity observed in the present case, with respect to the Ge-related centers, can be attributed to the fact that in the case of Si an increasing number of convertible optical defects is generated by irradiation, in concurrence with their conversion into paramagnetic defects.

Chapter 10

Conclusion and suggestions for future work

10.1 Conclusion and suggestions

The experimental results reported in this Ph.D. thesis are mainly concerned with the study of the processes of generation of point defects by γ irradiation in commercial silica materials. We have done a detailed study of some paramagnetic defects induced by the irradiation by means of the EPR technique. In particular, we have investigated four EPR signals (fig.52) that have been identified as the E'-Si center (fig.52a), the weak satellite structure of the E' center (fig.52b), the H(I) (fig.52c) and the H(II) (fig.52d) centers. In the case of the latter centers the EPR study was combined with the study of the optical properties of the material to evidence the relation with precursor defects. All these spectroscopic features are related to current questions regarding the generation mechanisms of point defects and the structural models to be attributed to them.

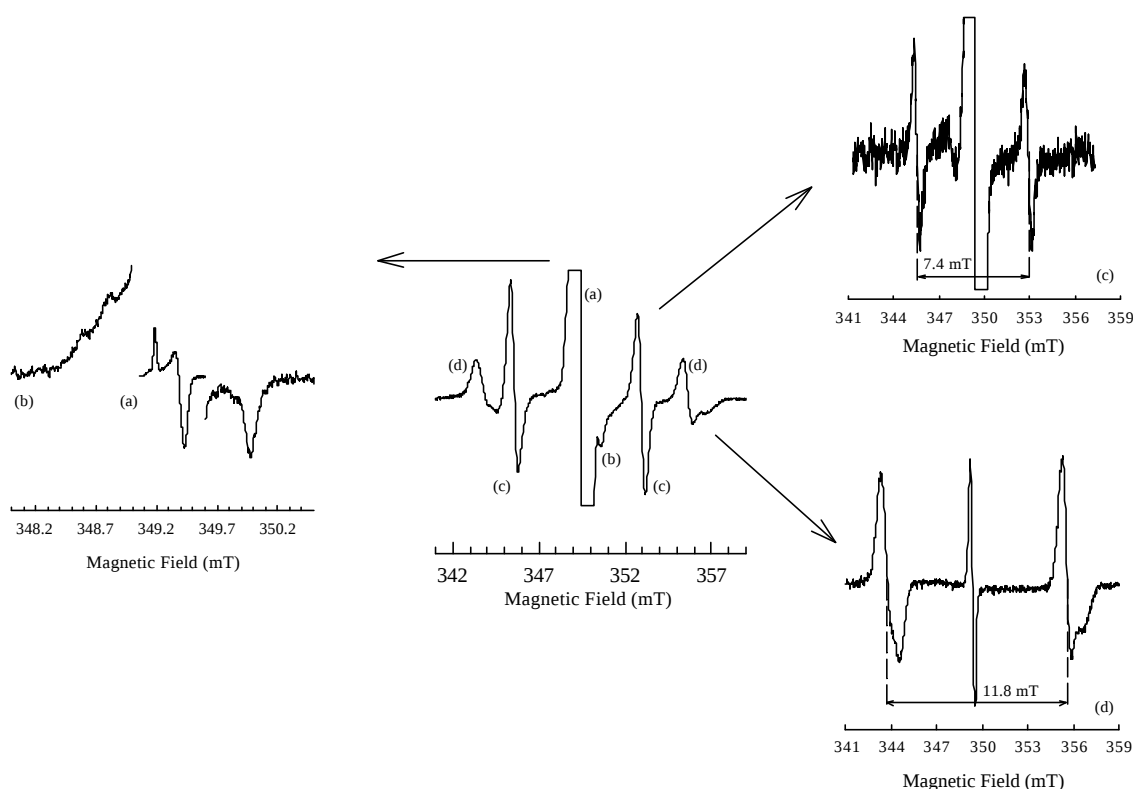


Figure 52. EPR signatures of the paramagnetic defects investigated in this Ph.D. thesis. (a) E'-Si center; (b) weak satellite structure of the E' center; (c) H(I) center; (d) H(II) center.

The experimental results relative to the E' centers have evidenced the novel feature that in all the investigated materials, both natural and synthetic, the dominant process of defect generation under irradiation is the conversion of precursor defects in the dose range from 100 Gy up to 10^7 Gy (see Chap.6). In fact, independently from the material, typical growth by irradiation is observed in which the concentration of E' centers reaches an asymptotic value on increasing the irradiation dose (see fig.19). This observation was confirmed both by γ and by β irradiation. In particular, the latter irradiation enabled us to extend the study, in some samples, to doses of two orders of magnitude higher than by γ irradiation. The examination of different types of silica (natural and synthetic, type I, II, III, IV) enabled us to show that strongly different precursors of the E' centers are activated in the various materials by comparing the generation rate constant k (see fig.20). These results support the observation that the same E' center can be induced from different precursors [23, 25]. The analysis of the experimental line shapes of the E' centers has shown that two different line shapes pertain to the low and to the high irradiation regime. This finding is nearly independent on the material, so suggesting the existence of a structural relaxation of the environment of the site where the center is induced, irrespective of the precursor.

In Chap.7 we have compared the growth by irradiation of the E' centers with that of the weak satellite structure (fig.24-25), and we have evidenced that their processes of generation under irradiation are similar. In particular, the weak satellite structure has the same growth kinetics as the E' centers in all the investigated samples. This effect was evidenced both by γ and by β -irradiation and, to our knowledge, this is the first time that such growth kinetics in a wide range of doses is reported. The correlation between the asymptotic concentrations of the weak satellite structure and of the E' centers supports the attribution of the former as an hyperfine structure of the E' center [99]. In particular, our data are consistent with the model ascribing this interaction to a second neighboring ^{29}Si [99].

Further investigation of the E' centers and also of the weak satellite structure can be carried out by thermal treatments. These procedures usually give information on the thermal

stability of the defects and in our opinion might clarify the correlation between the two structures. It would also be useful to extend the β irradiation to other silica types to complete the characterization of the growth kinetics of the E' centers, and in particular to the materials prepared by the sol-gel method. This other materials can be employed also to accomplish ad-hoc enrichments of ^{29}Si to study the correlation between the E' centers and the weak satellite structure. This is relevant since it has been suggested that the weak satellite structure could give information on the medium-range order in silica [99]. This aspect might be useful in the study of the structure of the amorphous as well as of the structural relaxation processes related to the defect generation.

Our experimental results reported in Chap.8 show that γ irradiation of natural silica samples induces the bleaching of the native optical B-type activity ($B_{2\beta}$ OA band and α_E and β PL bands), and the simultaneous growth of an EPR doublet with magnetic field split 11.8 mT. The detailed variations of both optical and EPR signals, as a function of the accumulated γ dose, strongly suggests the occurrence of a conversion process from the B-type defects to the paramagnetic ones counteracted by an irradiation induced back-conversion that gives rise to a dynamical equilibrium under irradiation. In addition, we evidenced a dependence of the overall process on the OH content of any given material. Both the conversion and back-conversion mechanisms have been described on the basis of a model involving in the reactions H atoms produced by γ -induced breaks of O-H bonds. This model is suitable to account for all our experimental results, provided the roles of the B-type defect and of the paramagnetic one are played by the two-fold coordinated Ge center ($O = \text{Ge}^{\cdot\cdot}$) and by the H(II) center ($O = \text{Ge}^{\cdot} - \text{H}$), respectively.

A back-conversion process from H(II) to B-type defects was also found to occur, after-irradiation, via thermal activation at relatively low temperatures ($330 \text{ K} < T < 430 \text{ K}$), proving the strict correlation between the two defects. In addition, the data reported on the thermal treatments

indicate that there is a complex thermal process, probably related to the different environments of the centers in the amorphous structure of the silica.

These results shed a new light in the controversial field of the structural models proposed for the B-type defect. They unequivocally indicate that the two-fold coordinated Ge is the most reliable structure for this defect. Also, the reported data are strong evidence for a clear conversion mechanism induced by irradiation from preexisting optical defects to paramagnetic defects. Our study evidenced the reliability of this process under various irradiation sources and irradiation conditions, and also evidenced the involvement of H atoms in the reaction. It is possible to conclude that the identified conversion process is peculiar of natural silica containing Ge and H impurities.

Further investigation of the conversion mechanisms evidenced by our data, can be carried out by studying the effects of irradiation with sub-gap photons, for example, by UV laser irradiation. This aspect is relevant to compare the effects of two deeply different irradiation sources. It should also be interesting to extend the study of γ -irradiation to materials with controlled content of Ge or of OH, prepared for example by the sol-gel technique. Also, the detailed study of the isothermal treatment after-irradiation should be interesting in evidencing features of the thermal back-conversion process.

The last effect of γ -irradiation that we have investigated regards the generation of the H(I) EPR centers and of the optically active A-type defects (see Chap.9). In particular, it was observed that both these centers are induced by irradiation with similar sublinear growth kinetics. Their intensities are correlated and their ratio depends on the OH content of the material. These observations can be explained assuming a conversion mechanism from the optical to the paramagnetic centers, in which H atoms are involved. In particular, this conversion is reliable assuming that the center responsible for the A-type activity is the two-fold coordinated silicon. In this respect, our data give new support to the two-fold coordinated silicon for the debated model of the A-type defect.

Further study of the A-type activity is intriguing as the observed sublinear growth by irradiation constitutes a relevant unsolved question of the generation mechanisms of point defect [23, 88-89]. In this respect, since we observed that the A-type activity has the same generation process in a large variety of materials, this radiation-induced activity could be a prototype to study the anomalous sublinear mechanisms of point defect generation in silica.

In many respects the results reported in this Ph.D. thesis have stressed the influence of the amorphous network both in the generation processes of the defects and in their structural configuration. The thermal stability of the defects has also evidenced complex aspects that could be related to the amorphous structure of the material and the structural variability of a defect environment. These features stimulate further investigation and stress the intriguing relationship between the vitreous state and the point defects. In this respect some radiation-induced defects seem to be best interpreted as variation at pre-existing “faults” in the glass network and their study should contribute to the understanding of the atomic-scale structure of the precursor and to stress features of the same glass system. The EPR technique is particularly powerful in studying this effects as it reveals peculiarities of the glass through the information that are gained from line-shape variations and hyperfine structures. Also, some of the reported data evidenced that the medium-range structural changes are related to the peculiarities of the paramagnetic center properties and accompany the defect formation processes. In this context, a skilful approach considering the vitreous silica structure could clarify better the processes of point defects generation.

The results for the commercial silica obtained in this Ph.D. thesis represent a background to extend the investigation to other silica types. It is possible to go further into the knowledge of defect generation mechanisms by investigating the dependence on aspects as the structural peculiarity of the material. In this respect the use of sol-gel methods for preparing bulk vitreous silica is a new way to obtain reproducible materials with a vitreous structure and a controlled distribution of impurity. This is a new approach to study the mechanisms of defect generation as a function of the material glass structure and composition.

Appendix

List of related publications

1. Agnello S., Boscaino R., Cannas M. and Gelardi F.M.; Journal of Non-crystalline solids (1998) Vol. 232-234, pag.323-328. "Gamma ray induced 11.8 mT ESR doublet in natural silica"
2. Leone M., Agnello S., Boscaino R. Cannas M. and Gelardi F.M.; Physical Review B (1999) Vol. 60, pag.11475-11481. "Conformational disorder in vitreous systems probed by photoluminescence activity in SiO₂".
3. Agnello S., Boscaino R., Cannas M., Gelardi F.M. and Leone M.; Nuclear Instruments and Methods in Physics Research B (2000) Vol. 166-167, pag. 495-499. "Bleaching and thermal recovery of PL emissions in natural silica".
4. Agnello S., Boscaino R., Cannas M., Gelardi F.M. and Leone M.; Nuclear Instruments and Methods in Physics Research B (2000) Vol. 166-167 pag.465-469. "Generation of a 7.4 mT ESR doublet induced by γ rays in amorphous-SiO₂."
5. Agnello S., Boscaino R., Cannas M., Gelardi F.M. and Leone M.; Physical Review B (2000) Vol. 61, pag.1946-1951. " γ ray induced bleaching in silica: conversion from optical to paramagnetic defects".
6. Cannas M., Agnello S., Boscaino R., Gelardi F.M. and Leone M.; in *Nuclear and Condensed Matter Physics*, Ed. A. Messina, AIP 2000, pag.63-66. "Contributions to the Photoluminescence activity in the UV range in Amorphous SiO₂".
7. Agnello S., Boscaino R., Cannas M. and Gelardi F.M.; in *Nuclear and Condensed Matter Physics*, Ed. A. Messina, AIP 2000, pag.7-10. "Defects induced by gamma irradiation in silica".
8. Leone M., Agnello S., Boscaino R., Cannas M. and Gelardi F.M.; in *Silicon-based Materials and Devices* Ed H.S Nalwa, Academic Press San Diego (in press). "Optical absorption, luminescence and ESR spectral properties of point defects in silica".
9. Gelardi F.M. and Agnello S.; in Proc. of the NATO advanced study institute *defects in SiO₂ and related dielectrics: Science and technology* Ed. G. Pacchioni, L. Skuja and D. Griscom (in press). " Gamma rays induced conversion of native defects in natural silica".
10. Agnello S., Boscaino R., Cannas M. and Gelardi F.M.; Applied Magnetic Resonance (in press). "Paramagnetic defects creation by gamma irradiation in amorphous silica".

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