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Optical Absorption of Impurities and Defects in Semiconducting Crystals

Hydrogen-like Centres

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Introduction

1.1 Basic Concepts

In this monograph, semiconductors and covalent or partially covalent insulators are considered. These materials differ from metals by the existence, at low temperature, of a fully occupied electronic band (the valence band or *VB*) separated by an energy gap or band gap (E_g) from an empty higher energy band (the conduction band or *CB*). When E_g reduces to zero, like in mercury telluride, the materials are called semimetals. In metals, the highest occupied band is only partially filled with electrons such that the electrons in this band can be accelerated by an electric field, however small it is.

From a chemical viewpoint, most of these semiconducting and insulating crystals are elements or compounds in which all the valence electrons are used to form covalent or partially covalent chemical bonds, leaving no extra electron for electrical conduction. This is the case for the diamond form of carbon, for silicon and germanium, for many crystals resulting from the combination of group-II*B* or -III*A* elements of the periodic table with group-V or -VI elements (the II–VI or III–V compounds), or for the partially ionic I*B*–VII (e.g., CuC*l*) compounds. In purely ionic insulators, like sodium chloride, electron capture from the electropositive element by the electronegative element produces ions with closed shells.

From an optical viewpoint, on the other hand, the difference between semiconductors and insulators lies in the value of E_g. The admitted boundary is usually set at 3 eV (see Appendix A for the energy units) and materials with E_g below this value are categorized as semiconductors, but crystals considered as semiconductors like the wurtzite forms of silicon carbide and gallium nitride have band gaps larger than 3 eV, and this value is somewhat arbitrary. The translation into the electrical resistivity domain depends on the value of E_g, and also on the effective mass of the electrons and holes, and on their mobilities. The solution is not unique; moreover, the boundary is not clearly defined. "Semi-insulating" silicon carbide 4*H* polytype samples with reported room temperature resistivities of the order of $10^{10}\,\Omega\,\mathrm{cm}$ could constitute the electrical limit between semiconductors and insulators, but the definition of such a limit is of moderate significance. In the following, for simplification, the term "semiconductors and insulators" are replaced by "semiconductors".

In a category of materials known as Mott insulators, like MnO, CoO or NiO, with band gaps of 4.8, 3.4, and 1.8 eV, respectively ([2], and references therein), the upper energy band made from $3d$ states is partially occupied resulting in metallic conduction. The insulating behaviour of these compounds is attributed to a strong intra-atomic Coulomb interaction, which results in the formation of a gap between the filled and empty $3d$ states [35].

In the covalent or partially covalent semiconductor crystals, a free electron is created in the *CB* once sufficient energy has been provided to a *VB* electron to overcome the energy gap E_g. This energy can be produced thermally under equilibrium at temperature T, by optical absorption of photons with energies $h\nu \geq E_\mathrm{g}$, or by irradiation with electrons in the keV energy range. These processes leave in the *VB* a positively charged free "hole", which has no equivalent in metals, and whose absolute electric charge is the elementary charge. When free carriers can only be produced by the above processes, the materials are said to be intrinsic. When molecules and solids are tightly bound, the value of E_g for covalent or partially covalent semiconductors with sp^3 bonding has been related to a covalent energy of the bonds, modulated by the so-called metallic energy involving atomic states [19].

A consequence of the existence of an electronic band gap is that at sufficiently low temperature, intrinsic semiconductors or insulators show no absorption of photon related to electronic processes for energies below E_g. Inversely, the photons with energies above E_g are strongly absorbed by optical transitions between the valence and conduction bands, and this absorption is called fundamental or intrinsic.

Compound semiconductor crystals show strong infrared absorptions in certain specific spectral region at photon energies below E_g, due to the vibrations of the atoms of the crystal lattice. In these regions, the lattice absorption can be so strong that the crystals are opaque for the usual thicknesses. At energies below the lattice absorption region, the crystals become transparent again. In elemental crystals like diamond ($\mathrm{C_{diam}}$) or silicon, this first-order vibration of the lattice atoms is not infrared-active and hence, the pure crystals of this kind do not become opaque, but they show, however, weaker absorption bands due to combinations of vibration modes of the crystal lattice.

Extrinsic semiconductors are materials containing foreign atoms (FAs) or atomic impurity centres that can release electrons in the *CB* or trap an electron from the *VB* with energies smaller than E_g (from neutrality conservation, trapping an electron from the *VB* is equivalent to the release of a positive hole in the otherwise filled band). These centres can be inadvertently present in the material or introduced deliberately by doping, and, as intrinsic, the term extrinsic refers to the electrical conductivity of such materials. The electron-releasing entities are called donors and the electron-accepting ones acceptors. When a majority of the impurities or dopants in a material is of the donor (acceptor) type, the material is termed n-type (p-type) and the electrical conduction comes from electrons (holes). In semiconductors with $E_\mathrm{g} \gtrsim 0.6\,\mathrm{eV}$, the intrinsic free-carrier concentration can usually be neglected at room temperature (RT) compared to the extrinsic one. In these semiconductors, when the energy required to release a free carrier from the dominant donor or acceptor (the ionization energy) is comparable to the RT thermal energy ($\sim$26 meV), a measurement of the RT resistivity $\rho = (ne\mu)^{-1}$, where μ is the mobility of the free carrier, gives a representative value of the concentration n of the dominant donor or acceptor. Above a temperature depending on the value of E_g, the concentration of the electron-hole pairs produced thermally in extrinsic materials can become comparable to the extrinsic carrier concentration, and the semiconductor is said to move into the intrinsic regime. The presence of free electrons produces at RT a Drude-type continuous optical absorption, increasing as λ^2, where λ is the wavelength of the radiation. The wavelength dependence of the free-hole absorption is not as simple. For some values of the donor or acceptor concentrations depending on E_g, the free-carrier absorption can be so large that the material becomes opaque in the whole spectral range. For still higher dopant concentrations, a transition to a quasi-metallic state occurs, which will be discussed later.

When the temperature is reduced, the free carriers in the extrinsic materials are normally re-trapped by the donor or acceptor centres that had released them and the resistivity of the materials increases.

A large number of semiconductors, used in various technologies and in pure and applied research, are known, and most of them are grown artificially. It is difficult to grow intrinsic semiconductors because FA contamination affects the crystal growth; moreover, except for very special uses[1], there are not many applications for truly intrinsic materials. The purest available crystals thus contain residual impurity atoms or more complex centres. Some of the residual impurities are not electrically active and they cannot be detected by electrical methods, and hence, the term intrinsic cannot be taken as a synonym for high purity.

1.2 A Short Historical Survey

The Italian term "*semicoibente*", found in the presentation by Alessandro Volta before the Royal Society of London in 1782, could be translated into "semi-badly-conducting", but eventually was translated to "semi-conducting" in English, and qualified nearly insulating substances [53]. The review by Busch [6] gives an interesting historical survey of the emergence of the semiconductor physics and chemistry, but a good account of the early work

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[1] The fabrication of ionization bolometers used at very low temperatures ($\sim$60 mK) for the detection of weakly interacting massive particles (WIMPs) from outside of the solar system requires intrinsic silicon or germanium material.

on semiconductors can also be found in the first chapter of the book by Smith [46]. Near 1908, on the ground of measurements performed on different solids, Johann Königsberger, from the Albert-Ludwig University, in Freiburg in Brisgau, proposed that the mobile charge carriers in solids resulted from the thermal dissociation of the atoms of a "metallic" conductor into electrons and remaining positive ions. As a function of the value of a parameter Q, proportional to a dissociation energy, Königsberger classified the solids into insulators, with Q tending to infinity, metals, with Q tending to zero at high temperature, and "variable conductors" (*Variable Leiter*), for which Q was found to have a finite value. The consequence for "variable conductors" was that their electrical conductivity increased exponentially with temperature. These so-called variable conductors were iron oxides, and iron and lead sulfide polycrystalline minerals. In 1911, Weiss, a student of Königsberger, used for the first time the word "semiconductor" (*Halbleiter*) in his thesis "Experimental Contribution to the Electronic Theory in the Field of Thermoelectricity" (*Experimentelle Beiträge zur Elektronentheorie aus dem Gebiet de Thermoelektrizität*). In this work, he studied the thermoelectric effect of different metals, graphite, silicon, and metallic oxides and sulfides and compared the results with the existing electron theories. In the above context, the terms "variable conductors" and "semiconductors" had the same meaning. The term "semiconductor" is found again in a common publication [29]. The electrical properties of these early semiconductors were often irreproducible, partly due to inhomogeneities, impurities, structural imperfections and poor electrical contacts (silicon was not explicitly recognized as a semiconductor then). Some physicists were wary of these problems encountered in the study of semiconductors, which lasted till the end of the 1930s, when potential uses were conceived beyond their use as materials for photodetectors for the infrared.

A basis to the understanding of the electronic properties of semiconductors was provided in two papers by Wilson [56], where the concepts of intrinsic and extrinsic semiconductors were introduced. The fundamental nature of extrinsic semiconduction in relation to the atomic dopants in silicon was demonstrated [44] and it was presented in a very pedagogical manner with germanium as an example in the textbook of Shockley [45]. Around the same time, silicon was prepared with an acceptable purity allowing transmission measurements to be performed (see for instance [15]). Subsequently, optical spectroscopy, which was used for the study of insulators like diamond [42] became and is still a widely used tool for the study and characterization of semiconductors. This is acknowledged in several books devoted to the optical properties of semiconductors including the spectroscopy of impurity centres [28, 34, 37], but other contributions have been written on specialized topics, like the ones by Ramdas and Rodriguez [41] on the electronic absorption of hydrogen-like donor and acceptor atoms in semiconductors, by Davies [9] on the optical properties of the luminescent centres in silicon, or the book by Newmann [36] on the vibrational absorption of impurity centres.

1.3 General Properties of the Hydrogen-Like Centres

The spectroscopic absorption of impurities and defects in semiconductors is in itself a vast subject as it includes electronic and vibrational absorption. Moreover, two kinds of electronic absorptions can be roughly distinguished: the one related to the p- and n-type dopants, which proved to be related to a more general category of centres called hydrogen-like or effective-mass centres, and the other due to the deep centres. The spectroscopic properties of transition metals (TMs) are an intermediate category as the spectra of these atoms and of their complexes display in some cases hydrogen-like properties. The content of this book is limited to the absorption of hydrogen-like centres, including complex centres, and to facilitate the understanding of the subject, a general presentation of the properties of these centres is given.

1.3.1 What are the Hydrogen-Like Centres

Either from natural or artificial origin, the semiconducting and insulating crystals contain impurity centres, doping atoms or defects. These centres can be either electrically active or not electrically active, and we consider here the electrically active ones. A centre is electrically active if it can display more than one electronic charge state; this is the case for donor and acceptor centres. In the neutral charge state, the electrically active centres can contain one or two electrons (holes) bound to an inner core, and these electrons (holes) can be ionized in the conduction (valence) band with well-defined ionization energies. When the contribution of the inner core can be considered as that of a global ion or pseudo-ion, the interaction between the lowest energy electron (hole) and the inner positive (negative) core, including eventually the second particles, is mainly Coulombic. This has led to compare these centres to hydrogen-like (H-like) pseudo-atoms with excited states comparable to those of the H atom. A main difference originates from the embedding of these centres in a crystal matrix with static dielectric constant ε_s, which reduces the Coulomb energy by a factor ${\varepsilon_\mathrm{s}}^{-2}$ when the particle is not too close from the charged core. The second difference comes from the mass of the particle (the outer electron or hole), which is different from the mass m_e of the free electron *in vacuo*. In a first step of the modelling of the properties of H-like centres, the relevant masses are replaced by scalar "effective" masses ${m^*}_\mathrm{e}$ or ${m^*}_\mathrm{h}$, for electrons and holes, respectively. As will be seen later, this is an oversimplification, but scalar values of the effective masses can be obtained from a modelling of the RT electrical measurements. The scaling factor of the energy of these centres with the energy spectrum $E_{0\mathrm{n}} = R_\infty/\mathrm{n}^2$ of H in vacuum is $\mathrm{s} = (m^*/m_\mathrm{e})/{\varepsilon_\mathrm{s}}^2$, where m^* is the appropriate effective mass. The energy E_n of the effective-mass particle in the nth excited state is thus $1.36 \times 10^4\,\mathrm{s}/\mathrm{n}^2$ (meV), where n is the principal quantum number. This is the basis of the effective mass theory (EMT), which is discussed in more detail in Chap. 5. Within this approximation, the ground state energy or level for a H-like acceptor in silicon ($m^*{}_\mathrm{h} \cong 0.6m_\mathrm{e}$, $\varepsilon_\mathrm{s} = 11.7$) is separated from the *VB* continuum by 60 meV compared with E_g =1170 meV, and for the donors in GaAs ($m^*{}_\mathrm{e} \cong 0.07m_\mathrm{e}$, $\varepsilon_\mathrm{s} = 12.9$) by 5.7 meV from the *CB* continuum, compared with E_g =1519 meV. These values are orders of magnitude of the ionization energies of the shallowest of these centres, known as shallow centres, and the crude assumptions made cannot account for the effect of the *VB* and *CB* structures on the effective masses, as well as for the effect of the chemical nature of the impurity on the ionization energies, which can be important for semiconductors like silicon.

The technological importance of the shallow donors or acceptors is that they bind the electrons or holes with energies comparable to the RT thermal energy and that the carriers released at RT by these shallow centres act as a reservoir to control the electrical conductivity of the crystals. Under equilibrium, this release is a thermal process and as the electrons and holes are particles with non-integer spins, their energy distributions follow Fermi-Dirac statistics. At a given temperature T, the concentration of electrons and holes in the continua can be expressed as a function of the chemical potential μ of the semiconductor and of the density of states (DoS) in the *CB* and the *VB* (see [3]). In metal physics, the Fermi level E_F is the energy of the electron level whose occupancy probability is ½ and it has the same meaning as the more general chemical potential. The term "Fermi level" has been extrapolated from metal to semiconductor physics, despite the fact that in semiconductors, E_F lies in the band gap, with a limited number of discrete allowed states. To comply with the common use, we keep the "Fermi level" which is at best a quasi-Fermi level.

At very low temperature, the concentration of free carriers in the continuum is negligible as they are trapped by the ionized impurity centres of opposite charges and E_F is close to the energy level E_i of the dominant impurity. This level separates the band gap into two regions: one, between E_i and the relevant band continuum, taken as the energy origin and a second one for energies between E_i and the opposite band continuum. In energy diagrams for single donors (D) or acceptors (A), the zone contiguous to the opposite continuum is denoted "+" for donors and "−" for acceptors as, when E_F lies in this zone, the centre is ionized (D^+ or A^-). Similarly, the second zone is denoted "0" because when E_F lies in this zone, the centre is neutral at low temperature (D^0 or A^0).

1.3.2 Electrical Activity

From a chemical aspect, the electrical activity of substitutional impurities and dopants is determined by the presence or absence of electrons after bonding with the nearest neighbour crystal atoms. Thus, it usually depends on the chemical nature of the impurity or, more simply, on the column of the periodic table it belongs to, compared to the atom(s) of the crystal. For a monoatomic semiconductor crystal, a FA from the column next to the column of the atom it replaces acts usually as a single donor[2], and when from the preceding column, as a single acceptor. Similarly, substitutional FAs from the second next column or before the column of the atom(s) of the crystal are double donors or acceptors, respectively. When the crystal is made up of two kinds of atoms belonging to different columns of the periodic table, the electrical activity of a substitutional FA depends on the site occupied, and when behaving as an acceptor on one site, it can behave as a donor or be electrically inactive on the other site. Centres other than the isolated FAs can also be electrically active and give H-like levels in the band gap, like the substitutional chalcogen pairs, which are double donors in silicon, but there are more complicated centres like the complexes made from a shallow impurity and from an electrically inactive impurity, or the family of O-related thermal donors in silicon and germanium, which are relatively shallow donors, and where the origin of the weakly bound electrons is not as obvious as for substitutional donors. Besides substitutional impurities, interstitial FAs with ns or ns^2 external atomic configuration like Li in silicon and germanium and Mg in silicon can display H-like donor behaviour, and there are also evidences that this is the case for sodium and potassium in silicon ([30] and references therein).

In a semiconductor, substitutional FAs from the same column of the periodic table as the one of the crystal atom they replace are usually electrically inactive and they are called isoelectronic with respect to the semiconductor. It can occur, however, that for some isoelectronic impurities or electrically-inactive complexes, the combination of the atomic potential at the impurity centre with the potential produced by the local lattice distortion produces an overall electron- or hole-attractive potential in a given semiconductor. This potential can bind an electron or a hole to the centre with energies much larger than those for shallow electrically-active acceptors or donors. The interaction of these isoelectronic impurities traps the free excitons producing isoelectronic bound excitons which display pseudo-donor or pseudo-acceptor properties. This is discussed later in this chapter in connection with the bound excitons, and examples of these centres are given in Chaps. 6 and 7.

At low temperature, the free carriers of a semiconducting crystal are trapped by donor or acceptor ions of the opposite sign. With increasing concentration of these neutralized impurities, the separation between the electronic clouds around each impurity centre decreases. To simplify, when these electronic clouds overlap in the ground state, an impurity band is formed at low temperature, in which electrons or holes have an appreciable electrical mobility. This is the limit of the concept of a semiconductor at low temperature and it goes through a transition to the metal-insulator transition or MIT [35], corresponding to a critical doping level N_c which depends on the ionization energy of the impurity considered: for P-doped silicon, N_c is $3.5 \times 10^{18}\,\mathrm{cm}^{-3}$

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[2] Nitrogen is a notable exception in silicon and in germanium [26].

and it is lowered to $1.9 \times 10^{17}\,\mathrm{cm}^{-3}$ in Ga-doped germanium, but it rises to $\sim 4 \times 10^{20}\,\mathrm{cm}^{-3}$ in B-doped diamond. The doping level for which the impurity band merges with the semiconductor continuum and for which the material becomes truly metallic occurs for doping levels significantly larger than N_c. Thus, for P-doped silicon, it is estimated to be $3N_\mathrm{c}$ [18].

1.3.2.1 Compensation

In a real semiconductor, more than one kind of donor and acceptor impurities are usually present at the same time, but to simplify, a material containing only one kind of FAs of each type is considered. The one with the highest concentration N_maj is the majority impurity, which determines the electrical type of the semiconductor and the other one is the minority impurity with concentration N_min. The net concentration of active centres able to contribute each a free carrier is $N_\mathrm{maj} - N_\mathrm{min}$ and this evolves from the annihilation of a concentration N_min of electron-hole pairs. This situation is called compensation, and it can also arise from the presence of centres in concentration N_trap which can trap carriers from the majority impurity. The compensation ratio K is usually defined as the ratio $N_\mathrm{min}/N_\mathrm{maj}$. When one neglects the intrinsic concentration of electrons and holes, the net concentration is close to the free-carrier concentration measured when these active centres are thermally ionized, or to the number of neutral centres which can be spectroscopically detected at low temperature under thermal equilibrium. Between the low-temperature region where the electron concentration n in a n-type semiconductor is practically zero and the exhaustion region where it is $N_\mathrm{maj} - N_\mathrm{min}$, the temperature dependence of the electron concentration n released in the *CB* by the donor with ionization energy E_i is:

$$n = \frac{N_\mathrm{maj} - N_\mathrm{min}}{N_\mathrm{min}} \mathrm{N_c} \mathrm{e}^{\frac{E_\mathrm{i}}{k_\mathrm{B} T}} \tag{1.1}$$

where $\mathrm{N_c}$ is the effective density of states (DoS) in the *CB*. A similar equation holds for the hole concentration p in the *VB* in a p-type semiconductor, by replacing $\mathrm{N_c}$ by the effective DoS $\mathrm{N_v}$ in the *VB*. Expression (1.1) shows that for shallow impurities, E_i can be derived from $n(T)$ and it can be obtained, for instance, from the temperature dependence of the Hall coefficient $R_\mathrm{H} = -\mathrm{r}/ne$ (the Hall factor $\mathrm{r} =< \tau^2 >/< \tau >^2$ depends on the electron or hole scattering process through their lifetime τ, and in most semiconductors, it is close to $3\pi/8$). An example of the temperature dependence of the free-carrier concentration deduced from Hall measurements is shown in Fig. 1.1. An alternative is a measurement of the energy absorption spectrum of the hydrogen-like impurities at low temperature, from which ionization energies can be extrapolated and this method is fully explained later in the book.

Compensation reduces the concentration of active majority impurities, but it also produces additional impurity ions of both charges. These ions are the

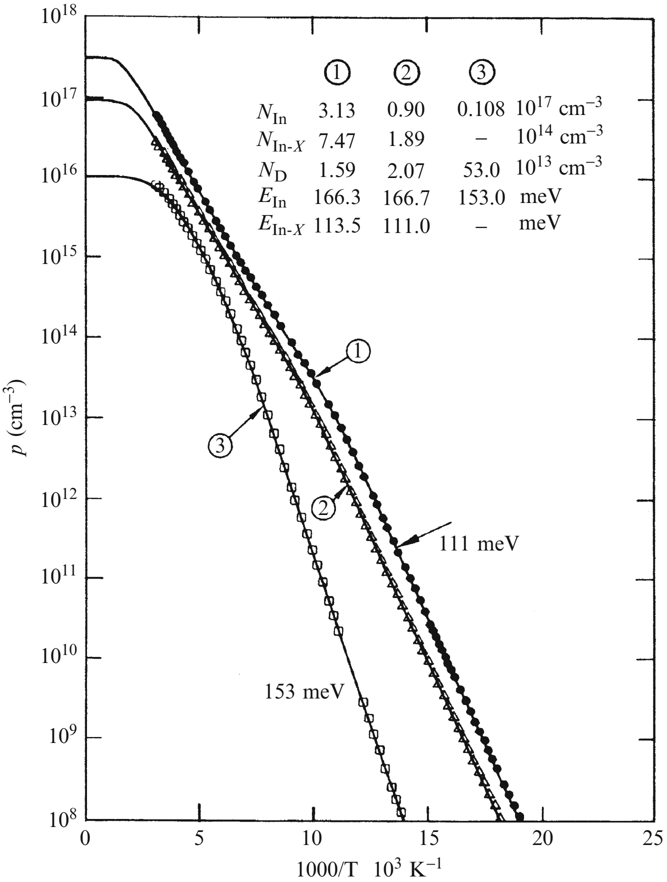

Fig. 1.1. Temperature-dependence of the free-hole concentrations p in three In-doped silicon samples measured by Hall effect. The fit of the curves shows that the dominant acceptor in sample 3 is isolated In ($E_\mathrm{i} = 153\,\mathrm{meV}$) and the In-$X$ centre ($E_\mathrm{i} = 111\,\mathrm{meV}$) in samples 1 and 2. The compensating donor compensation N_D resulting from the fit is indicated (after [4]). Copyright 1977, American Institute of Physics

source of the so-called impurity scattering for the majority free carriers and it reduces their lifetime. The electrical conductivity of a crystal is proportional to the number of free carriers and to their electrical mobility, which in turn is proportional to their lifetime. As a consequence, in the extrinsic regime, a high resistivity (or a low value of the carrier concentration measured directly from Hall effect) does not necessarily mean a high purity of the material.

We have mentioned the situation of a dopant atom (Si in GaAs, for instance) that can be located on two different sites, where it behaves either like a donor or an acceptor. For some growth condition, this possibility can produce what is known as self-compensation, and this can occur indeed for GaAs:Si. Another example of self-compensation is the doping of ZnO with Li: this results in a material with a relatively high resistivity and the reason for this is attributed to the occupancy with comparable probabilities by a Li atom of interstitial sites, where it acts as a donor, and of Zn sites, where it acts as an acceptor. In some cases, compensation is necessary to measure the properties associated with impurities: for instance, in an uncompensated crystal containing only a double donor DD, which can release in the *CB* two electrons with different energies, this donor is neutral at low temperature and its optical ionization is that of the neutral charge state (the electronic level corresponding to $\mathrm{DD}^0/\mathrm{DD}^+$). To observe the optical ionization from the $\mathrm{DD}^+/\mathrm{DD}^{++}$ electronic level and the optical spectrum of the DD^+ charge state, it is necessary to ionize permanently the first electron to produce DD^+. This can be obtained by increasing the temperature to produce thermal ionization of DD^0, but the higher the temperature, the broader the spectral line widths. Another method is the counter-doping of the material with acceptor minority impurities or deep traps, which partially compensate the double donor and produce DD^+.

The compensation of impurities is an equilibrium process resulting from the minimization of the electronic energy in the crystals. Thus, under equilibrium conditions at low temperature, donors or acceptors can be either neutral (D^0 or A^0) or ionized (D^+ or A^-). In weakly-compensated materials, the out-of-equilibrium partial photoionization of donors in n-type materials or of acceptors in p-type materials produces photoelectrons or photoholes. At very low temperature, these photocarriers can then be trapped by neutral donors or acceptors to produce D^- or A^+ ions. These centres are equivalents of the H^- ion and they are introduced in Sect. 1.3.3.

The actual compensation in a material is more complex than a simple balance between a majority impurity and a minority impurity as the material usually contains a combination of residual impurities, dopant and deep centres, whose concentrations must be estimated to determine the actual degree of compensation in the material. As mentioned before, compensation of the majority impurities by adding opposite type dopant leaves in the material charged ions, which reduce the lifetime of the free carriers. When the lifetime of the carriers in a given pure material is known, a lifetime measurement of an unknown sample of this material can determine the degree of compensation of the sample.

Correlations between the free-carrier concentration and the RT resistivity have been made for n- and p-type silicon by Irvin [22] as a function of the dopant concentration (cm^{-3}) assuming no compensation. From these measurements, in n-type silicon with $\rho \geq 1.4\ \Omega\,\mathrm{cm}$, N_P or n is about $5.0 \times 10^{15}\,\rho^{-1}$ and in p-type silicon with $\rho \geq 0.9\ \Omega\,\mathrm{cm}$, N_B or p is about $1.3 \times 10^{16}\,\rho^{-1}$. For a more extended range in P-doped silicon, see [52].

A very close compensation between donors and acceptors is sometimes required to obtain, for instance for epitaxial growth, substrates with a resistivity close to the intrinsic one. In the case of GaAs, this can be realized nearly "naturally" as the GaAs crystals grown by the LEC method contain a native deep defect labelled EL2, whose main ingredient, if not the only one, is an As antisite ($\mathrm{As_{Ga}}$). This defect is a deep double donor with a level 0.75 eV below the *CB* and it traps the residual acceptors present in the crystal. By limiting the C acceptor doping of the crystal in the $10^{15} - 10^{16}$ at/cm^3 region, it is possible to obtain semi-insulating GaAs LEC crystals with electrical resistivities of the order of the intrinsic resistivity of the material ($\sim 10^8\,\Omega$ cm). In GaAs containing residual donors, this result is obtained by doping with chromium.

1.3.2.2 Passivation

In the compensation process, there is only a change in the charge state of the impurity or dopant atom and it is temporarily reversible, for instance by illumination of the crystal with band-gap or above-band-gap radiation, which produces electrons and holes that are trapped by the ionized centres. This is a non-equilibrium condition, which exists only during illumination.

When studying the interaction of hydrogen plasmas with crystalline silicon surfaces, it was discovered that hydrogen could penetrate in the bulk of the material and decrease its electrical conductivity [38, 43]. What could have been due to a compensation effect revealed itself as a passivation effect where hydrogen interacted chemically with the shallow acceptors in silicon to form a complex. This was reminiscent of older studies which showed that hydrogen played a role in the passivation of deep centres at the $\mathrm{Si/SiO_2}$ interfaces and later on the bulk and interface defects in crystalline silicon, not to mention the role of hydrogen in amorphous silicon. An evidence of this interaction with shallow acceptors in silicon was the observation of IR vibrational modes related to hydrogen-acceptor complexes. These complexes were electrically inactive and hence, they did not contribute to the ionized impurity scattering. This process has been naturally called passivation and it has been observed for many donors and acceptors in semiconductors (for a review, see for instance [8]). The stability of hydrogen passivation is limited by the thermal dissociation of the electrically-inactive complexes, which produces the reactivation of the dopant atoms, and for an annealing time of about 30 min, this usually takes place in the $350 - 500°$C range. However, the interaction of hydrogen with impurities in semiconductor crystals is complex and in some cases, it can turn electrically inactive impurities into electrically active complexes. Moreover, for double donors or acceptors, it can passivate partially the centre and turn a deep impurity into a shallow donor or acceptor complex.

1.3.3 Optical Transitions

Atomic hydrogen excited in a discharge tube gives an emission spectrum originating from transitions between excited states and the $1S$ ground state [32]. This discrete spectrum extends, in the UV, from 121.57 nm to the ionization limit of 91.13 nm corresponding to the Rydberg energy R_∞. When the above-described H-like donor or acceptor centres are neutral, i.e., when they are not electrically compensated and when temperature is low enough for the ground state to be populated, a discrete electronic absorption spectrum from the ground state to the excited states is observed. By analogy with the case for hydrogen, such a spectrum is often referred to as a Lyman spectrum. The exact spectral region of observation depends on the ground state energy, which is the ionization energy of the centre, but it is located in the IR region of the electromagnetic spectrum. This absorption, determined by the electric-dipole selection rules, is best observed at LHeT; it is relatively intense and allows the detection of shallow impurities down to concentrations in the $10^{11} - 10^{12}\,\mathrm{cm}^{-3}$ range when the absorption lines are sharp and when high resolution is used. This limit of detection can even be lowered to the $10^{7} - 10^{9}\,\mathrm{cm}^{-3}$ range using the photoconductivity-based techniques described in Sect. 4.4.2.2. In compensated crystals containing donors and acceptors, one observes under equilibrium the absorption spectrum of the active uncompensated majority impurities. The randomly distributed positive and negative ions due to compensation produce statistical electric fields which interact with the weakly bound electrons or holes whose transitions are observed. The resultant inhomogeneous Stark effect broadens the spectral lines of the EM spectra of the majority centres with respect to their standard values and this broadening is generally the signature of compensated samples. When the compensated samples are illuminated during the absorption measurement with band-gap or above-band-gap radiation, photoelectrons and photoholes trapped by the compensated ions of both types convert them into neutral atoms that participate in the optical absorption. It thus reveals the absorption spectra of both the majority and minority centres. When the absorption spectra have been previously calibrated, this even allows a determination of the compensation ratio K. Examples of this method are given in Chaps. 6 and 7. At energies above the ionization energy, the electronic absorption of the neutral centres is continuous and is called the photoionization spectrum. The spectral dependence of this continuous spectrum has been actively investigated in silicon and germanium in relation with the production of extrinsic photodetectors.

Population inversion between discrete hydrogenic states of impurities can in principle be produced by optical pumping in the photoionization spectrum of the impurities. When the population of the state with the lowest energy (E_{low}), i.e., the one nearest from the continuum, is higher than the one of the state with higher energy (E_{high}), emission at energy $E_{\mathrm{high}} - E_{\mathrm{low}}$, can take place, and ultimately, for sufficiently high pumping power, stimulated emission or laser effect occurs. At the end of the 1990s, stimulated emission between excited levels of phosphorus donors in silicon has indeed been reported [39].

Some of the possible transitions are forbidden by the electric-dipole selection rules, but they can be allowed by the polarizability selection rules and can subsequently be observed in Raman scattering experiments [24, 57].

Electronic absorption of impurities can couple with phonon modes of the host crystal and a photon is absorbed at an energy corresponding to the sum of the electronic excitation and the phonon mode, and such features, resonant with the photoionization absorption spectrum of the impurities are often observed. For indirect-band-gap semiconductors, the phonon energy can correspond to that of a phonon promoting the scattering of a bond electron from a CB minimum to another minimum, and its momentum is well-defined. For acceptor impurity transitions, corresponding to degenerate electronic states at the maximum of the VB at $k = 0$ (the usual situation), the phonon coupling takes place with zone-centre optical phonons. In covalent semiconductors, the resonance of these coupled excitations with the photoionization spectrum of the impurity can be strong and it results in what is known as a Fano resonance, after the theoretical explanation by Fano [16] of similar resonances of atomic auto-ionizing states. For smaller couplings, generally encountered in crystals with significant ionicity, one observes phonon replicas which can involve several optical phonons.

In an indirect-gap semiconductor containing neutral H-like donors or acceptors, illumination with RT thermal radiation of a sample held at LHeT is sufficient to partially ionize the neutral impurities. Coulomb interaction implies that the recombination mainly takes place on the photoionized impurities, but as has been mentioned in Sect. 1.3.2.1, these photocarriers can also be trapped by the neutral impurities giving A^+ acceptor ions and D^- donor ions. These ions are the equivalents of the H^- ion, studied first by Chandrasekhar in relation with astrophysics (for an early review, see [7]). The ionization energy of H^- calculated by Pekeris [40] is 6083.1 cm^{-1} or 0.7542 eV (0.0554 Rydberg), close to the experimental value of 0.75 eV. The existence of such ions in semiconductors was predicted by [31]. Their absorption spectra have been observed at very low temperature for several donor impurities in silicon, germanium and compound semiconductors, and also for acceptors in silicon and germanium. The binding energies of these equivalents of the H^- ion are small, but evidence for their absorption (and photoconductivity) in the very far IR has been given; it is presented and discussed in Sects. 7.5 and 6.9.

Under strong band-gap excitation, the photo-neutralized ions can de-excite thermally, but in direct-band-gap semiconductors, they can also de-excite efficiently by radiative recombination of the bound electrons with the bound holes. Such photoluminescence (PL) lines are known as donor-acceptor pair (DAP) spectra. In a semiconductor with dielectric constant ε, the energy of the photon emitted by a pair whose constituents, with ionization energies E_D and E_A, are both in the ground state and at a distance R is:

$$h\nu(R) = E_\mathrm{g} - (E_\mathrm{D} + E_\mathrm{A})\frac{e^2}{4\pi\varepsilon_0\varepsilon R} + J(R) \tag{1.2}$$

The term $J(R)$, which depends on the donor-acceptor interaction, becomes important when the distance R becomes comparable with the largest effective

Bohr radius of the two constituents. The DAP spectrum consists of many lines whose energies differ by the Coulomb term, resulting in a continuum for large values of R (see for instance [13]). It is also possible to create a pair separated by R with the acceptor in an excited state A^*. The energy required, which is larger than $h\nu(R)$, is:

$$h\upsilon_\mathrm{x} = h\nu^*(R) = E_\mathrm{g} - (E_\mathrm{D} + E_\mathrm{A}{}^*) + \frac{e^2}{4\pi\varepsilon_0\varepsilon R} + J^*(R) \tag{1.3}$$

As the lifetime of the hole in the excited state is much shorter than that of the DAP, the radiative recombination occurs at $h\nu(R)$. Thus, by scanning energies $h\nu_\mathrm{x} > h\nu(R)$ and detecting at $h\nu(R)$, one obtains an excitation spectrum of the acceptor excited states from which the energies of these states can be derived. One chooses for $h\nu(R)$ a plausible energy value, provided it is large enough for neglecting $J(R)$ and $J^*(R)$. This method has been proposed by Street and Senske [48], who applied it to the study of the shallow acceptors in GaP and it is known as selected pair luminescence (SPL). Nevertheless, sharp PL lines due to DAPs have also been reported in indirect-gap semiconductors [58].

Free electrons and holes produced by photoexcitation with energies above E_g can form free exciton (see Sect. 3.3.2), but a free electron (hole) can also recombine with a hole (electron) of a neutral acceptor (donor). The energy of the photon produced by this e-A^0 or h-D^0 recombination is $E_\mathrm{g} - E_\mathrm{i} + k_\mathrm{B}T/2$ where E_i is the ionization energy of the acceptor or of the donor and T the electron or hole temperature, which is close to the lattice temperature for moderate excitations close to E_g. In high-purity samples and at very low temperature, these lines can be sharp and when identified, they allow a good estimation of the impurity ionization energies when the value of E_g is known accurately.

When band-gap excitation is obtained by irradiation of the sample with electrons with energies in the keV range, the resulting PL is known as electroluminescence or cathodoluminescence.

1.3.4 Bound Excitons

Excitons are electron-hole pairs weakly coupled through the band gap by Coulomb interaction. When they are free to propagate in the crystal, they are logically called free excitons (FEs) and are characterized by a binding energy E_ex. Their properties are described in Sect. 3.3.2.

The FEs can bind to neutral shallow impurities and become bound excitons (BEs), with a value of E_ex slightly larger than the one of the FE. The difference is called the localization energy E_loc of the BE. For the P donor, it is ∼4 meV in silicon, but 75 meV in diamond. E_loc is given approximately by Haynes' empirical rule [20] as $0.1\,E_\mathrm{i}$, where E_i is the ionization energy of the impurity. BEs are created by laser illumination of a semiconductor sample at an energy larger than E_g and the study of their radiative recombination by PL has been and is still an active field of the optical spectroscopy of semiconductors [9,12,33,50]. The excitons can recombine radiatively by emitting a photon at energy $E_{\mathrm{gx}} = E_{\mathrm{g}} - E_{\mathrm{ex}}$, but in indirect-gap semiconductors, the conservation of the momentum of the weakly-bound electron, comparable to the one of a free electron, implies the creation of a lattice phonon of opposite momentum so that a part of the recombination energy is used to produce a phonon. The energy of the photon emitted is then $E_{\mathrm{gx}} - E_{\mathrm{phon}}$ where E_{phon} is the energy of the momentum-conserving phonon, and such transitions are called phonon-assisted transitions, or phonon replicas. For BEs in the indirect-gap semiconductors, however, zero-phonon-lines (ZPLs) at energies E_{gx} are also observed, but their intensities are smaller than those of the phonon-assisted recombination lines. Besides the phonon-assisted replicas, the recombination of excitons bound to complexes with internal vibration modes can take place with the excitation of some of these modes, producing what is known as vibronic sidebands. To obtain the emission of a momentum-conserving phonon, in the absorption measurements of BE, the absorption takes place at energy $E_{\mathrm{gx}} + E_{\mathrm{phon}}$, but for PL measurements, ZPLs can also be observed.

Radiative recombination of an exciton bound to a shallow impurity generally leaves this impurity in the electronic ground state, resulting in the principal BE (PBE) line, but weaker PL lines can also be observed at lower energies, where the impurity is left in an electronic excited state. These so-called two-electron or two-hole PL spectra are usually observed in their phonon-assisted form, and they mainly involve s-like excited states whose detection escapes the absorption experiments. These PL experiments are, therefore, valuable complements to absorption spectroscopy, which involves mainly the p-like excited states, and examples will be given when appropriate.

PL evidence for the binding of more than one exciton to a shallow impurity exists, starting with the excitonic molecule was first reported in silicon [20]. A model for the bound multi-exciton complexes in silicon (the shell model) has been elaborated by Kirczenow [27] to explain the experimental results of these centres. For a review on these centres, see [49].

In doped uncompensated semiconductors, very weak absorption lines due to the direct creation of excitons bound to neutral donors or acceptors can be observed at low temperature (typically 2 K) at energies close to E_{g} [11,14,21].

The optical properties of an exciton bound to a neutral donor or acceptor depend on the interaction of the exciton constituents with the neutral entity. When, for instance, the hole part interacts more strongly than the electron part with the neutral atom, the binding between the two exciton components decreases and the electron part can be considered as an electron bound to a pseudo-negative ion, forming some kind of pseudo-acceptor.

In semiconductors containing isoelectronic centres with an attracting potential for electrons or holes mentioned in Sect. 1.3.2, free excitons can be trapped because of the preferential interaction of these centres with the electron (or hole) part of the exciton. The hole (resp. electron) part of the exciton is then comparable to a hole (resp. electron) bound to a negatively (resp. positively) charged acceptor (resp. donor) ion, and a pseudo-acceptor (pseudo-donor) results. This process is somewhat similar to the one presented above for excitons bound to neutral donors and acceptors. The spectroscopy of excitons bound to isoelectronic centres in silicon and compound semiconductors (isoelectronic bound excitons or IBE) has been actively investigated in the 1980s. In compound semiconductors, one of the best-studied electron-attracting centre (pseudo-acceptor) is probably N_P in GaP [51]. Isoelectronic oxygen can also play this role in some II–VI compounds ([1] and references therein). Bi at a P site in GaP and InP seems to be the best documented hole-attracting centre [10,55]. In silicon, the potential near a C or Ge atom cannot bind an electron or a hole, but isoelectronic centres with pseudo-donor properties like the Be pair at a Si site or some (C,O) complexes in irradiated or annealed CZ silicon have been identified, and they are discussed in Sect. 6.7.

1.3.5 Spin Effects

Electron spin effects are observed for electrically active centres with an odd number of electrons. In charge states with an even number of electrons, the spins are generally paired. There are, however, a few cases where a 2-electron centre gives a resultant spin $\mathbf{S} = 1$ [23]. A centre in a charge state with non-zero spin is said to be paramagnetic. Such a centre interacts with an external magnetic field $\mathbf{B}$ through the magnetic dipole moment of the electron arising from the electron spin and the angular momentum. For many centres, the angular momentum of the electron is quenched in the ground state so that one can only consider the spin. In a solid, the Zeeman term can then be expressed as [54]:

$$H_{Zee} = \mu_B \, g \, \mathrm{SB}$$

where μ_B is the Bohr magneton and $\boldsymbol{g}$ a symmetric tensor whose values g_1, g_2, and g_3 with respect to the principal axes of the $\boldsymbol{g}$ tensor are close to 2. The ground state of a centre with spin $\mathrm{S} = 1/2$ is split by the magnetic field into a doublet with $M_\mathrm{S} = +1/2$ and $-1/2$ separated by $\mu_\mathrm{B} \, g \, \mathbf{B}$ (for a magnetic field of 1 T and $g \sim 2$, this separation is $\sim$30 GHz($\sim$ 0.12 meV)) and a magnetic dipole transition can take place between the two components. Non-cubic centres with different equivalent orientations in a cubic crystal present an orientational degeneracy. When these centres are paramagnetic, the doublet separation depends on the angle between the magnetic field and the main axis of the centres. In classical electron spin resonance (ESR) experiments, the transition between the two levels is induced by the magnetic field of a fixed microwave frequency for a critical value of $\mathbf{B}$. Practically, $\mathbf{B}$ oriented along a high-symmetry axis of the crystal (<100>, <111> or <110>) is tuned in order to make the splitting of the centres with different orientations to coincide with the microwave frequency and this is repeated for different orientations. The variation of the number of resonances for different orientations of $\mathbf{B}$ allows then to determine the orientational degeneracy of the centre.

A paramagnetic atom with T_d symmetry should give only one resonance line, but when this atom has a nuclear spin, the electron and nuclear spins can couple by hyperfine interaction, and for a nuclear spin $\boldsymbol{I}$, each electronic spin component splits into $2I + 1$ components giving the same number of $\Delta m_I = 0$ resonances. For instance, the ESR spectrum of tetrahedral interstitial A*l* ($\boldsymbol{I} = 5/2$) produced by electron irradiation of A*l*-doped silicon is an isotropic sextuplet due to transitions between the six nuclear sublevels of each electronic-spin component ([54], and references therein). The electron spin of a centre can also interact with the nuclear spins of neighbouring atoms to give additional structures and this is clearly shown for ^{29}Si atoms ($\boldsymbol{I} = 1/2$) in Fig. 4 of [54]. The ESR spectrum can thus also determine the atomic structure of the centre. This can also occur for non-cubic centres and the hyperfine structure is superimposed on the orientational structure.

For a given value of $\mathbf{B}$, the energies of $\Delta m_I = 1$ transitions between the nuclear sublevels of a given electronic spin state are much lower than those between the electronic spin components. Information on the amplitude of the wave function of the electron whose spin is responsible for the ESR spectrum at different lattice sites in the vicinity of the centre was obtained by Feher [17] by monitoring the ESR spectrum as a function of the frequencies in the nuclear frequency range, and this technique was called electron nuclear double resonance (ENDOR). Improvements in the sensitivity of ESR can be obtained using optical or electrical detection methods [47].

All the neutral single donors without d or f electrons have spin 1/2 while the double donors and acceptors have spin 0 in the ground state, but in some excited states, they have spin 1 and optically forbidden transitions between the singlet and triplet states have been observed. The spins of the neutral acceptors in the ground state depend on the electronic degeneracy of the *VB* at its maximum. For silicon, the threefold degeneracy of the valence band results in a quasi spin 3/2 of the acceptor ground state.

1.4 Notations for Centres and Optical Transitions

We are faced with two interconnected problems related to the intelligibility of the presentation. The first one concerns the nomenclature of the centres other than isolated atoms and the second the labelling of the optical transitions. These problems are not trivial, [5], but not as severe for H-like centres as for deep centres. The different notations for the shallow thermal donor complexes in silicon, discussed in Sect. 6.4.2, are however, a counter-example of this statement. In this book, on the basis of the present knowledge, names of centres, in direct relation with their atomic structure, have been privileged, but the usual label has however been indicated. When the exact structure is not simple and when there exist an acronym, like TDD for “thermal double donor”, it has been used. The labelling by their excited states of the transitions of the shallow donor centres and of similar species, whose spectra are experimentally and theoretically well identified, is a generally accepted rule. There are a few exceptions, as for some lines of transition metals and isoelectronic bound exciton spectra in silicon discussed in Chap. 6. From the beginning, the transitions of the shallow acceptors in silicon, whose direct attribution was much more difficult than for donors, were denoted by integers in order of increasing energies and there have been several labelling changes with the improvement in the resolution of the spectra. These labellings have to be related to "physical" ones by correlation between the experimental data and the calculated acceptor energy levels discussed in Sect. 5.3, assuming that the comparison is significant. There is an exception for the Au and Pt transitions in silicon, denoted I_N, where N is the number of corresponding acceptor lines in silicon. The label of the acceptor lines in other semiconductors (except for diamond) is based on the notation used for germanium in [25]: the lowest-energy transition is denoted G and the other ones denoted in inverse alphabetical order, with the resurgence, for the more recent spectra, of indexed I lines near from the photoionization continuum, to cope with the observation of additional transitions. The different notations in the case of the acceptors and the spectroscopic attributions are discussed in detail in Chap. 7.

In the labelling of defects, the ESR family is a world of its own and when an unidentified ESR spectrum was first observed in a given material, it has been the rule to label it by the initials of the laboratory, city or country and by an integer corresponding to the order of discovery (an indication of the nature of the centre is sometimes added). There are, however, exceptions to this labelling, where the atomic nature of the centre is indicated.

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