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Optical Absorption of Impurities and Defects in Semiconducting Crystals

Hydrogen-like Centres

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Preface

Most of the technological applications of semiconducting or insulating crystals come from the adjunction in these materials of foreign atoms which modify their electrical, optical, or optoelectrical properties. These dopant atoms can have to compete with foreign atoms or atomic complexes already present in the initial materials or arising from pollution during growth or technological processing. The properties of natural crystals, and, especially, their colour, are also modified by the presence of foreign impurity centres. From a general point of view, much has been learnt of the properties of these centres and on their mutual interaction by the methods of optical spectroscopy.

Spectroscopic measurements have shown that these centres, when electrically active, could be generally characterized by their electronic absorption, luminescence, and Raman scattering spectra, while vibrational absorption and Raman scattering are independent from the electrical activity.

From the coupling of the spectroscopic results with electrical measurements has emerged a classification of the electrically-active foreign centres into hydrogen-like (H-like) centres on the one side, opposed to deep centres on the other side. This classification is somewhat abrupt as there exist centres, like those related to the transition metals, which can display properties related to one or to the other category.

A H-like centre in a crystal can be vizualized as a fixed ion (atom or complex) with a positive or negative elementary charge interacting through a screened Coulomb potential with a negative or positive elementary charge able to move in the crystal with the effective mass of a free electron or hole. The resulting entity resembles, mutatis mutandis, a H-like atom in atomic spectroscopy, hence its name. A consequence of the above structure is that the energies of its electronic excited states depend only on the effective mass of the charged particle and on the dielectric constant of the crystal, so that the H-like centres are also called effective-mass (EM) centres. This definition excludes from my presentation of the purely ionic insulators, in which no H-like centre of this kind can exist.

The fact that shallow p- and n-type dopants of germanium could be considered as H-like atoms emerged at the end of the 1940s to explain the electrical conductivity of this material, and this was clearly expressed by William Shockley in his monograph "Electrons and holes in semiconductors", first published in 1950.

The absorption of H-like centres in semiconductors has been one of my main fields of research. In this volume, I provide a status of their electronic absorption, as known in 2009, and show its evolution from the mid-twentieth century and what this spectroscopy has brought to the understanding of the properties of semiconductors. This evolution has been marked by the improvement of the spectrometer–detector combinations, which have allowed an increase of the spectral resolution by nearly three orders of magnitude, and the production of semiconductor materials like the quasi-monoisotopic crystals, which bring new information on the H-like centres and on the role of isotopic disorder.

In an applied perspective, the interest in the spectroscopy of shallow impurities in semiconductors has been linked for a long time with the production of detectors for the medium and far infrared, but the possibility to produce terahertz lasers based on the transitions between discrete shallow levels has aroused a renewed interest in this spectroscopy in silicon. Another new potential field of application is the domain of quantum computing. A large part of the results presented in this book concerns silicon and this reflects the relative volume of investigations devoted to this material.

This book is the first of two books devoted to the optical absorption of impurities and defects in semiconducting and insulating crystals. The second one deals with the electronic absorption of deep centres like the native and irradiation defects or some transition metals, and with the vibrational absorption of impurity centres and defects.

Chapter 1 of the present volume provides the basic concepts related to the properties and characterization of the centres known as shallow dopants, the paradigm of the H-like centres. This is followed by a short history of semiconductors, which is intimately connected with these centres, and by a section outlining their electrical and spectroscopic activities. Because of the diversity in the notations, I have included in this chapter a short section on the different notations used to denote the centres and their optical transitions. An overview of the origin of the presence of H-related centres in crystals and guidelines on their structural properties is given in Chap. 2. To define the conditions under which the spectroscopic properties of impurities can be studied, Chap. 3 presents a summary of the bulk optical properties of semiconductors crystals. Chapter 4 describes the spectroscopic techniques and methods used to study the optical absorption of impurity and defect centres and the methods used to produce controlled perturbations of this absorption, which provide information on the structure of the impurity centres, and eventually on some properties of the host crystal. Chapter 5 is a presentation of the effective-mass theory of impurity centres, which is the basis for a quantitative interpretation

of the impurity spectra. Extensive sets of calculated energy levels obtained by variational or nonvariational methods are given in this chapter for EM donors and acceptors in silicon and germanium. For donors, it is shown how numerical values of the energy levels can be obtained for other cubic semiconductors of known band structures and dielectric constants. The implication of the degeneracy of the conduction band on the symmetry and eventual splitting of the donor states is discussed with application to silicon and diamond. A brief discussion is also given of the results of the calculations for the wurtzite form of SiC. For acceptors, I stress the importance of the value of the spin–orbit splitting of the valence band on the occurrence of EM impurity levels associated with the split-off valence band. This chapter ends with the calculation of the oscillator strengths of the main transitions of the donor and acceptor spectra. Experimental results on the absorption and photoconductive EM donor spectra in semiconductors can be found in Chap. 6. The main part is devoted to group-IV semiconductors, starting with the relatively well-known isolated single and double donors and pursuing with the donor complexes, with a large part devoted to thermal donors in silicon and germanium. Some results on EM-like spectra associated with interstitial iron and on donor-like properties of group-I atoms in silicon are also presented. It is also shown that isoelectronic-bound excitons in silicon can give, under appropriate conditions, absorption spectra similar to those of the EM donors. In the absorption of donors in compound semiconductors, we distinguish between the quasi-hydrogenic EM donors in direct-gap semiconductors and the donors in indirect-gap semiconductors with camel's back structure. As the quasi-hydrogenic donors in III–V compounds are characterized by rather small ionization energies, the widths of the lines of their spectra are broad and spectroscopic results obtained under a magnetic field, giving sharper lines are also presented. When possible, information on calibration coefficients relating the intensities of the absorption lines and the concentrations of the centres is provided. This chapter ends with a section dealing with the low-frequency excitations associated with the equivalent in semiconductors of the negative hydrogen ion in atomic physics, and to impurity absorption features due to hopping processes in heavily doped semiconductors. Chapter 7 is the equivalent of Chap. 6 for acceptors, and the spectroscopic properties of shallow acceptors in different semiconductors are described, showing the importance of the valence band structure and more specially of the spin–orbit interaction for the acceptor spectra in silicon and diamond. In Chap. 8, the effects of external and internal perturbations, including mechanical stress, magnetic, and electric fields on the absorption spectra of impurities are discussed. This allows also to discuss more synthetically of the line widths of the EM transitions observed in semiconductors and insulators as a function of the actual properties of different samples. To facilitate reading, appendices on energy units, energy-gap values, Bravais lattices, and group theory have been included.

This book, intended for students and scientists interested in the optical properties of semiconductors, should also be useful to scientists and engineers

interested or involved in the characterization of semiconductors. For the understanding of the principles underlying the experimental data, an elementary knowledge of quantum mechanics applied to spectroscopy and of solid-state physics is required.

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