

Preface

Spectroscopy is a branch of physics that studies the interaction of an electromagnetic (EM) radiation with matter. The essence of spectroscopy is in the observation of the way in which atoms and molecules exchange energy with the outside world. The EM radiation is composed of two oscillating fields: electric field **E** and magnetic field **B**. The electric field **E** and the magnetic field **B** interact with the electric dipole moment and magnetic moment, respectively, and thereby cause transitions between different energy levels. Since the wavelengths of the electromagnetic radiation used in spectroscopy commonly exceed the size of atoms or molecules under study, one can ignore the fact that the magnitudes of the electric or the magnetic fields are not constant. The main task of spectroscopy is to determine the structure and to clarify the physical nature of the energy levels by spectral analysis of the response of matter to the impacts of electromagnetic radiation. Modern atomic physics and quantum mechanical approaches, including description of spin effects, have emerged from discoveries in the field of spectroscopy.

Magnetic resonance spectroscopy or radio spectroscopy examines the interaction of the magnetic component of electromagnetic radiation with magnetic moments existing in a material. The interaction with nuclear magnetic moments is the subject of nuclear magnetic resonance (NMR) spectroscopy, while that with magnetic moments of electrons is the subject of electron paramagnetic resonance (EPR) spectroscopy. Radio spectroscopy covers the EM radiation frequency range from zero to hundreds of gigahertz, i.e., from infinitely long to millimeter electromagnetic waves. The EM wave is characterized by a photon energy, oscillation frequency, or wavelength. The relation between the energy and frequency is named the Planck relation (German physicist Max Planck, 1900):

$$E = h\nu,$$

where h is Planck's constant, and ν is the frequency of electromagnetic oscillations. The Planck's constant is a physical constant that has the meaning of a quantum of action in quantum mechanics and is the proportionality constant between the energy (E) of a photon and the frequency (ν) of the associated electromagnetic wave. Since

the frequency ν , wavelength λ , and speed of light c are related by $\lambda\nu = c$, each of these variables can be used as a characteristic of the electromagnetic radiation.

The electron paramagnetic resonance (EPR) was discovered in 1944 by the Russian physicist E. Zavoisky [1] in Kazan and has developed since into a major scientific technique. The first observation of an electron paramagnetic resonance was made in radiofrequency range, and Zavoisky's results were interpreted by Frenkel [2] as showing paramagnetic resonance absorption. Later experiments at higher frequencies showed the advantage of the use of high frequencies and high magnetic fields.

Excellent general review books on the EPR are available [3–33]. The electron paramagnetic resonance is observed in various systems with unpaired electrons carrying magnetic moments when an oscillating magnetic field causes transitions between electron levels. Systems of this kind are named paramagnetic, hence the name “electron paramagnetic resonance”. As a rule, the level splitting is caused by an external magnetic field that interacts with the electron magnetic moments; however, levels may be split in some systems due to interactions within the system in a zero magnetic field.

The aim of the development of modern EPR spectroscopy is to increase the sensitivity and information content, i.e., resolving capabilities. These problems are solved simultaneously in several directions.

In the last decade, there has been a great interest in EPR at high frequencies and high-frequency EPR spectroscopy has seen a remarkable development (see e.g., [29]). Whereas 9 GHz (X-band) has remained the main frequency of operation for more than 50 years, it is now possible to perform EPR studies at frequencies as high as 95 GHz (W-band) and even higher. The main reason to go to high frequencies is the high absolute sensitivity and the high spectral resolution that can be obtained. The first aspect is important when small amounts of material are available such as in the case of thin layers, nanostructures, or biophysical and biochemical problems, and the second is of special significance to disentangle spectra that normally overlap at the conventional EPR frequency of 9 GHz.

EPR is a tool to manipulate electron spins in solids. Because of the limited sensitivity of conventional EPR, typically optically detected and electrically detected EPR is favored to detect small numbers of spins [32]. In both approaches, the spin state is transferred to a photon or charge state, respectively.

In spin-dependent optical emission or photoconductivity, the spin-to-photon or spin-to-charge transfer, respectively, is typically achieved via a spin-dependent process of recombination involving paramagnetic states of recombining partners. In optically detected magnetic resonance (ODMR), a microwave-induced repopulation of Zeeman sublevels is detected optically, i.e., there is a giant gain in sensitivity since an energy of optical quantum is by several orders of magnitude higher compared with microwave one, it becomes possible to detect a very small number of spins down to single spin! [34, 35] ODMR is a “trigger detection” in that the absorption of a resonance microwave photon triggers a change in emission (absorption) of an optical photon due to the selective feeding of the magnetic sublevels.

Until recently, the practical applications of semiconductors involved the use of charge- and spin-carrier ensembles. The capability to efficiently control spin states is the key question of semiconductor spintronics. The unique quantum properties of nitrogen-vacancy (NV) color centers in diamond [36] have opened a new era in spintronics: It has become possible to manipulate the spin states of a single atomic-sized center at room temperature using optically detected magnetic resonance. The optical detection of magnetic resonance in a single spin has become possible because of the existence of a unique cycle of optical alignment and, as a result, the creation of an inverse population of spin sublevels in the NV center ground state. Until recently, an NV center was the only known solid-state system in which such spin manipulations were possible.

The search for structures that exhibit unique quantum properties similar to those of NV centers in diamond and at the same time have broader functional capabilities is a highly hopeful task. The most promising material that may compete with diamond from the standpoint of spectroscopy of quantum systems is silicon carbide (SiC), which can be regarded as an artificial superlattice. A special feature of SiC is the existence of its different polytypes, and for each of the polytypes, the properties of spin color centers are unique; furthermore, even in one polytype, the center may be located in different nonequivalent positions in the lattice. This allows choosing the center with parameters (for instance, optical and microwave ranges) suited to a specific problem.

The great potential of the EPR spectroscopy cannot be fully realized with only conventional continuous-wave (CW) EPR. Continuous-wave EPR and pulsed magnetic resonance (EPR) are complementary, and the application of both gives a total picture of the spin phenomena under investigation. In the CW EPR, the magnitude of the magnetic field B_0 (static magnetic field) is swept, while the amplitude of the microwave field B_1 is constant with time. In the pulsed EPR experiments (time-resolved experiments), a time-dependent microwave pulse B_1 is applied in addition to a static magnetic field B_0 . In the pulsed EPR spectroscopy, relaxation times can be directly measured by monitoring the magnetization on the same timescale in which relaxation occurs. The advantage of pulsed operation in addition to the recording of the relaxation times is that it is also possible to study photoexcited paramagnetic species including paramagnetic excited states (e.g., excitons) in combination with pulsed lasers. Moreover electron nuclear double resonance (ENDOR) experiments will become feasible in a much wider temperature range than for CW operation. ENDOR technique developed by Feher and Mims [6, 23] is very useful in the systems with not resolved hyperfine structure and makes possible the detection of nuclear magnetic resonance (NMR) through its effect on the electron paramagnetic resonance signal, thus using a high EPR sensitivity as compared with the NMR. The hyperfine coupling constants could be measured with much higher precision as compared with the EPR.

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