50 years of persistent spectral hole burning

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50 years ago, in 1974, two pioneering papers[1, 2] appeared, introducing the phenomenon of persistent spectral hole burning (PSHB). The observation was that in the absorption (excitation) spectra of impurities in solids quite narrow bands of decreased absorption (spectral holes) may appear under monochromatic (laser) excitation. This opened quite appealing prospects for the PSHB spectroscopy, not speaking about the applications in the processing of optical signals. The versatility of the method stems from the facts, that (i) the spectral holes may be quite narrow (down to kHz-range in RE ions), (ii) under appropriate conditions (low temperatures) their lifetimes may be quite long, and (iii) a number of different micromechanisms can result in the formation of spectral holes (photoionization, dissociation, photoinduced proton transfer etc.). Three different types of PSHB experiments can be envisaged: (I) measurements at fixed conditions (temperature, pressure), (II) burning and recording at different conditions (pressure, electrical field), and (III) with excursions of environmental conditions between burning and recording. By now, the total amount of works on PSHB goes in thousands. This report gives a selective overview of the main result obtained, focusing on the research done in Tartu.

Optical dephasing of impurity transitions in crystals[3].
The main result of these studies was the demonstration of the leading role of interaction with pseudolocalized vibrations in the thermal broadening of the zero-phonon transitions in impurities. They also demonstrated, that at the lowest temperatures the homogeneous linewidth approaches the valued determined by the lifetime of the excited electronic state. However, it was also revealed, that there exists a drastic difference between the optical relaxation in crystalline and glassy matrices[4] even of the same chemical composition[4].

Pressure effects on impurity transitions in amorphous solids (reversible and irreversible processes)[5-7]**.**
Pressures up to 10 kbar have been applied to study the low-temperature dynamics of polymer glasses. A modification of the soft potential model was proposed to account for the experimental observations.

Phase transitions and partially ordered systems. The phase transition in *p*-terphenyl was demonstrated to show up in the pressure dependences of the holewidth[8]. Peculiarities in the dynamics of low-temperature incommensurate phases of biphenyl are demonstrated by PSHB in the dopant spectra[9].

High-temperature SHB in diamond has been demonstrated in the spectra of radiation defects[10, 11].

PSHB studies of chlorophyll and photosynthesizing systems. PSHB turned out to be a versatile method for the studies of photosynthesizing pigments[12]. The based on PSHB differential-FLN spectroscopy was developed and applied to the studies of different pigment-protein complexes of plant and bacterial origin[15-17]. This enabled the first time to measure accurately the shape of the phonon sidebands in the site-selective spectra and to determine the Huang-Rhy factors for the respective transitions.

Eventually the development of methods of spectral hole burning led to realization of the single molecule spectroscopy and based on it the high-resolution (sub-λ) microscopy, crowned by the Nobel Prize in chemistry of 2014 to W. E. Moerner.

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