Nanostructures and impurity centers in cryogenic environment

Studies of materials at low temperatures play a prominent role in the progress of condensed matter physics and chemistry. Impurity centers and nanostructures nowadays turn into the most hot objects of physical and chemical investigations. In a broad sense, impurity centers include both — dopants and radiation-induced species generated in solids. The whole field of low-temperature research related to impurity centers developed in the «matrix isolation» physics and chemistry as it was called by George Pimentel. The condensed gases (Ne, Ar, Kr, Xe, N_2 etc.) used as matrices are characterized by weak interatomic interactions that together with low temperatures greatly simplify the guest spectra and make them easily tractable theoretically. The applications of matrices today extend over a variety of fields ranging from creation of high-energy density materials, laser technique, catalysis, cryochemistry, to study of reactions occurring in the interstellar space as related to the fundamental question of the origin of life on Earth.

This special issue, which is published in the journal FNT/LTP v. 45, Nos. 6, 7, comprises a selection of original research papers to provide some overview of the current research in this field with emphasis on low-temperature studies involving impurity centers in cryogenic matrices and nanostructures. Of course, the entire field cannot be covered in a single issue but we hope that this «snapshot» will give readers an impression of cryogenic studies of impurity centers, which have become one of the objects of modern physics and chemistry.

Researchers used as matrices not only classical solidified gases but also polymers, ~~or~~ carbon nanobundles, ~~or~~ quantum hosts such as solid hydrogen and superfluid helium, He droplets; several of the manuscripts in this issue deal with these hosts, e.g., Gil *et al.*, Feodosyev *et al.*, Strom *et al.*, Meraki *et al.*, Gutiérrez-Quintanilla *et al.* A broad repertory of techniques has been employed apart of traditional Fourier transform infrared (FTIR) spectroscopy with isotopic analysis: VUV-visible absorption and luminescence, laser induced fluorescence and two-dimensional mapping of emission spectra (Endo *et al.*), fluorescence line narrowing (FLN) technique and excitation spectroscopy (Gil *et al.*), lifetime measurements by time correlated single photon spectroscopy (Kleshchina *et al.*). Along with spectroscopic methods, EPR (ESR) techniques were applied (Dmitriev, Benetis and Meraki *et al.*). Methods of scanning electron microscopy SEM (Karachevtsev *et al.*), mass spectrometry have also been utilized. Technique of thermoluminescence (TL) was implemented by Meraki *et al.* and Ostapenko *et al.* Experiments were performed not only in matrices, but also in supersonic jet (Oswald and Coussan) and cryogenic plasma (Boltnev *et al.*). Different sources of excitation were employed — lasers, ion and electron beams, e.g., ion beam lines at the GANIL, and at GSI (Bibang *et al.*), multiply charged ions (Ban *et al.*), electron beam (Khyzhniy *et al.*), and discharge (Kołos, Meraki *et al.*). The most of studies were supported by theoretical approaches, from *ab initio* quantum calculations to molecular dynamics simulations.

Laboratory experiments are of high importance to investigate astrophysical questions, to test or probe astrochemical processes, to solve astrophysical problems. Among them, experiments playing with molecular structures in cryogenic solids are fully pertinent, either to mimic the processes occurring in interstellar grains or to give access to the characterization of exotic structures discovered or assumed to be present in the interstellar medium. This special issue begins with two short reviews related to astrophysics. Kołos summarizes the recent investigations on long polyynic nitrile chains with the matrix isolation technique. Carbon chains and especially cyanopolyynes form prominent families of molecules in space. Longer and longer chains are found to be produced by UV excitation of smaller precursors in the matrix, allowing their characterization. The synthesis of complex organic molecules (COMs) in the Interstellar Medium is a key point in exobiology. Rothard and co-workers review their results of radiation effects on molecular ices which are potential astrophysical ices, using ion beams at GANIL. The formation of COMs was obtained. Moreover, the experiments provide a tool to study their radiosensitivity. The cyanopolyyne family is also at play in the paper of Mouzay *et al.* The authors prove the formation of HC_3N and HCN from irradiation of C_2N_2–C_2H_2 complexes isolated in solid argon at the Lyman α wavelength. Both precursors are important components of Titan's atmosphere and the matrix results bring information on possible photochemical processes in this planetary atmosphere. Krim and Jonusas explored the photochemistry of methane ices doped with water in order to pave the way of the formation of COMs in molecular ices relevant to cometary, planetary or interstellar ices. The IR spectroscopy of VUV irradiated ices reveals the formation of many products and among them oxygenated hydrocarbons, even in the presence of only traces of water.

Infrared spectroscopy combined with matrix isolation is a very powerful tool to identify new products, new molecular structures, as shown in the previously cited works. It is also at play in the following papers devoted to the characterization of complexes and especially important, hydrogen bonded complexes, as well as to environment effects. Platakyte *et al.* explored the isomers of trifluoroacetylacetone stabilized in argon and nitrogen matrices, complexed or not with water. The trifluoroacetylacetone has two chelated enol forms, slightly differing in energy. Thanks to weak additional bands in the IR spectra, the authors conclude to the existence of both isomers in nitrogen or when complexed with water whereas only the most stable is trapped in argon. Doroshenko *et al.* studied water

clusters embedded in argon matrices, focusing their theoretical approach on the effect of the argon environment on the clusters structures and IR spectra. Complexes with water have been investigated by Gutiérrez-Quintanilla *et al.* at very low temperature by means of trapping in helium droplets. Experiments on propyne–water complexes give access to very precise infrared frequencies. The comparison with *ab initio* calculations provides the identification of the structure and highlights the effects of the partly superfluid environment on the complex. Chloroform–nitrogen aggregates are explored by Oswald and Coussan in matrices and jet expansion varying the amount of nitrogen in order to investigate the influence of nitrogen on the vibrational frequencies of chloroform. The results exhibit an unusual blue-shift of the C–H stretch involved in the hydrogen bond with the increase of N_2 amount. Costa and Silveira focused on study of the amino acid L-valine that plays an essential role in the dynamics of all living organisms. The study of temperature dependence of absorption spectra and their behavior at thermal excursion revealed that the sample is constituted only by valine zwitterions. Another interesting organic molecule — porphycene — has been thoroughly investigated by Gil *et al.* in polymer samples and nitrogen matrix. An unexpected correlation between the sites in S_1 and S_2 states was observed in glassy polymers in spite of a loss of selectivity upon S_2 excitation. The relation with possible H-transfers in the internal ring is addressed. Hydrogen atoms as impurities are examined in two papers. Based on the EPR study of H(D)/Ne system, Dmitriev and Benetis suggested a new empirical approach relating the hyperfine constant (HFC) matrix shifts of trapped H and D atoms to a combination of the van der Waals and Pauli pair interactions between the H atoms and the host particles. Anderson and co-workers present a study of H atom catalyzed *ortho*-to-*para* H_2 conversion in quantum matrix of *para*-H_2. H-atoms were shown to diffuse by a quantum tunneling mechanism. The analysis of *o*/*p* conversion kinetics compared with H–H recombination suggested that the H atoms diffuse preferentially in regions of high *para*-H_2 content.

The Part II of the issue is opened by papers devoted to metals trapped in rare gas (RG) matrices. Wakabayashi with co-workers reinvestigated the electronic spectroscopy of bismuth dimers trapped in neon. Two-dimensional (excitation-emission) spectra revealed satellite bands accompanying each major band. Based on theoretical calculations, the authors assigned the structures to the formation of Bi_2Ne_n clusters in the matrix (n up to 6), the main carrier being the linear Bi_2Ne complex. Lara-Moreno *et al.* explored the sites occupied by metal atoms (M = Zn, Cd) in various rare gas solids. Absorption ($^1P_1 \leftarrow {}^1S_0$) and emission of the matrix-isolated metal atoms were calculated, taking into account the site occupancies obtained in the simulation of the matrix growth. The results compared well with the recorded spectra of the M/RG solids, allowing a reliable assignment of the experimental trapping sites. Atomic ytterbium isolated in a Xe matrix has been explored by electronic spectroscopy by Kleshchina *et al.* Excitation in the singlet state is followed by emission from the triplet state. The observation of several emission bands differing by their lifetimes revealed multiple trapping sites. The lifetime temperature-dependence in the most stable site was explained by means of electron-phonon coupling enhancing non-radiactive relaxation paths. De Pujo *et al.* present the results of combined experimental and theoretical study of the spectroscopy of Na atom isolated in Xe matrix. Important emphasis here is the effect of spin-orbit (SO) coupling on the band shapes, manifested itself through dynamic Jahn–Teller effect. The SO effect at play is due to the heavy atom (Xe) environment and thus depends on the site occupied by Na.

The following papers describe new highly energetic processes at play in cryogenic solids. Khyzhniy *et al.* deal with radiation effect of a delayed explosive desorption followed by oscillations from solid Ar doped with methane. A decrease of H atoms concentration (monitored via the Ar_2H^* emission band) at higher concentration of CH_4 evidenced bleaching these centers due to recombination of H atoms with energy release. Ban *et al.* report total and partial (ions) desorption yields from condensed Ar and Ne films induced by multiply charged Rg^{q+} ions. A new desorption model, in which the ions were created in the solid by the potential energy of the incident ions and desorbed together with surrounding neutral atoms erupting from the spike region in the solid was suggested. Molecular nitrogen luminescence in cryogenic non-equilibrium He plasma jets has been studied by Boltnev and co-workers. Enhancement of molecular nitrogen luminescence was observed in the afterglow of N_2–He gas mixtures at $T \leq 10$ K. The effect is explained by the increased efficiency of the recombination of N atoms and energy transfer from metastable N_2 and He atoms to nitrogen molecules. Meraki *et al.* examined the dynamics of TL spectra emitted during the heating of nitrogen–neon and nitrogen–argon nanoclusters inside superfluid He. The decisive role of vortices in stimulating recombination reactions of species has been elucidated.

Optical spectra and TL of polygermane and polysilane films and nanocomposites were explored by Ostapenko *et al.* Discrete levels of the carriers activation energy in TL of both polymers were found. Polymer chains of PDHGe confined in the nanopores of SBA-15 silica, in contrast to those of PDHS, have the gauche-conformation. Karachevtsev *et al.* investigated the graphene oxide-single walled carbon nanotube (GO-SWNT) hybrids. The fabricated 3D carbon nanostructures were found to show significantly improved electrical conductivity of GO, which make them very useful for many potential applications. Feodosyev *et al.* considered theoretically defects in linear chains of atoms on the surface of carbon nanobundles. Localized states of defects were found both above and below the quasi-continuous band. The simple analytical expressions to determine these defect parameters were obtained.

We cordially thank all the authors for their contributions to the issue!

Claudine Crépin-Gilbert and Elena Savchenko