Low Temperature Spectroscopy and Radiation Effects

To the anniversary of E.V. Savchenko

Excited electronic states and their dynamics form the basis of new processing methods in modern Material Science. Better and deeper understanding of the basic processes of energy transfer and conversion is the way to enable controlled modification of materials – to enhance selectively, to favor specific reaction channels or inhibit troublesome excitations. Electronic excitations possess advantages to arrange the spatial localization of excitation and spectral selectivity. The key ideas of electronically induced modification of materials are charge and energy localization. A lot of vitally important information may be gained using spectroscopic methods, especially at low temperatures.

Solidified noble-gases, or cryocrystals – the simplest model solids, play a growing role to elucidate the diversity of physical and chemical phenomena in condensed media in general. Due to their simple structure, weak interatomic forces and strong electron–phonon interaction they offer unique opportunity to study electronically induced phenomena and unveil elementary processes, branching and cross-connection of different relaxation channels.

Professor Dr. Elena Savchenko dedicated most of her scientific career to electronic excitations and their dynamics in cryocrystals. She is an experimentalist with high technical skills in synchrotron radiation studies, tunable excitation spectroscopy, laser and electron beam techniques, low temperature and vacuum ultraviolet techniques, luminescence, absorption and activation spectroscopy. The high skills in combination with a deep theoretical background and creativity enabled her to perform research on radiation-induced inelastic processes in cryocrystals and discover a number of new effects and phenomena.

A comprehensive study of the electron excitation dynamics revealed regular trends in electron–phonon interaction in this class of solids and disclosed different channels of the self-trapping and trapping in noble-gas solids. The result on the coexistence of free excitons with atomic type (one center) and molecular type (two-center) self-trapped excitons on one hand confirmed the theory of self-trapping and on the other hand gave impetus to further development of the theory. Based on these studies and employing the synchrotron radiation technique Savchenko's group solved a nontrivial task to separate the processes of exciton trapping on defect sites and exciton self-trapping in the own lattice due to electron–phonon interaction.

E. Savchenko pioneered the study of radiation-induced lattice rearrangement in cryocrystals. New "excited state" mechanisms of Frenkel pair formation stimulated by self-trapping of excitons into atomic and molecular type states were discovered and models of atomic processes of lattice rearrangement in the course of relaxation were proposed in the studies of her group. The knowledge of these processes on a microscopic level is of fundamental importance for deeper understanding of a variety of radiation-induced physical and chemical processes in condensed matter: first of all, mass diffusion, molecular fragmentation, solid-state chemical reactions and production of novel chemical compounds based on noble-gas atoms. The results obtained promoted the development of the theory of radiation-induced nonequilibrium processes.

A novel approach to investigate ionic species in cryogenic materials has been developed. This is based on "pump-probe" experiments (pumping with electron beam or high energy radiation) in conjunction with controlled *in situ* injection of electrons via their release from traps. This method could be extended to a large number of insulating materials and semiconductors. The effect of hole self-trapping was clearly demonstrated. It was shown that in contrast to the excitons, the holes are "self-localized" in the lattice in the barrier-free process. Electronic structure, atomic configuration and stability of ionic centers were clarified using the technique of plasma cryocondensation combined with the "matrix-isolation" technique and optical spectroscopy as well as the activation spectroscopy methods.

The achievements of Savchenko on Spectroscopy of Solids were awarded the Prize of Antonina Prikhot'ko – a famous Ukrainian spectroscopist, "mother" of cryocrystals.

After the dissolution of Soviet Union, it was a hard time for her and her Institute, she has been very eager to collaborate with many well-known scientific centers. Among them are synchrotron centers at Deutsches Electronen Synchrotron (DESY, Hamburg) and Institute for Molecular Science (UVSOR, Okazaki), with Technical University of Munich (TUM), University of Helsinki, Gakushuin University (Tokyo), etc. Her brilliance has stimulated every researchers working with her. Her worldwide activity made her a top-notch scientist with excellent international reputation.

The studies of Savchenko's group performed in collaboration with Prof. Dr. V.E. Bondybey have led to the discovery of thermally stimulated exoelectron emission from cryogenic solids and a novel phenomenon – anomalously strong low-temperature desorption from pre-irradiated solids. The recent results on interconnection between atomic and electronic processes in cryocrystals – possibility of relaxation cascade stimulation via chemiluminescent reactions open up new fields in photochemistry and modification of material properties.

As a Guest Editor, E. Savchenko arranged a number of the Special Issues of the journal “Low Temperature Physics” (“Fizika Nizkikh Temperatur”). Her bright lectures in Ukraine and abroad attracted a number of young students and encouraged them to choose the field of Condensed Matter for their further research.

Following the contents of this special issue, in paper 1 Wonderly and Andersen have ptotolyzed fully deuterated formic acid in solid parahydrogen and identified HDO, which are suggested to form in a reaction of initially formed OD radical with the host H_2 molecules.

The second paper by Healy, Kerins, and McCaffrey uses pulsed synchrotron radiation to excite luminescence of Mg, Zn and Cd atoms in solid neon. Cd and Zn atoms occupy two distinct sites while Mg only a single site in neon. This experimental behavior is interpreted with simulations.

The study by Khmelenko *et al*. deals with thermoluminescence dynamics during destruction of neon–helium and krypton–helium condensates containing stabilized nitrogen and oxygen atoms. Unusual characteristics of the thermoluminescence spectra were observed, and their changes were explained in terms of the shell structure of impurity nanoclusters which comprised the impurity-helium condensates.

In the study of Dmitriev electron emission was obtained from a solid Ne sample growing from the gas phase on a low temperature substrate with simultaneous irradiation by microwave excited Ne atoms. Addition of D_2 as an impurity influences the electron yield, which is tentatively attributed to the exceptional properties of the neon–hydrogen solids.

The paper by Lindgren *et al*. focuses on spectroscopic behavior of CO isolated in Ar. Interestingly, quite different thermal behaviour is observed in the Raman and IR studies, and crystal field and quantum chemical modeling are used to interpret the disparity between the spectroscopies.

FT-ICR method is employed in the study of Scharfschwerdt *et al*. to study the photodissociation channels of $V^+(H_2O)_n$, n = 1–4, in the 360–680 nm region. Proper agreement with the simulations is found.

Intense phosphorescence of NC_4N is observed in Ar, Kr and Xe matrixes in the study by Turowski *et al*. External heavy atom effect can explain the differencies of the excited state lifetimes of NC_4N in these matrices.

Arabei *et al*. report on absorption, fluorescence and persistent spectral hole burrning in nitrogen matrices, doped with tetrabenzoporphin. Characteristic features of stimulated emission were also observed.

Photoluminescence of C_{60}, saturated with molecular hydrogen was studied by Zinoviev *et al*. in a wide temperature range, from 10 to 235 K. Their study yielded interesting effect of orientational glassification in Fullerite C_{60} saturated with H_2.

Gumenjuk *et al*. have studied charge carrier traps energy spectra in silicon organic polymer poly(di-n-hexylsilane) by fractional thermally stimulated luminescence (FTSL) in the temperature range from 5 to 200 K. Raman active totally symmetric vibrational modes of silicon chain are responsible for the regularities.

Arakawa *et al*. studied photo-stimulated desorption of ions from methane and water hetero-cluster on the surface of solid neon. The yield of the variety of photodesorbed species showed strong dependence on the composition and the size of the mother cluster.

In the study by Kassühlke and Feulner, two-dimensional electron spectroscopy applied to bound and continuum excitations of neon films condensed onto clean metal surfaces results in precise energy values of excitons and ionization potentials for the surface and for the bulk neon atoms.

Kato *et al*. studied low energy electron impact desorption of metastable atoms induced by electronic transitions in solid Ne. Qualitatively reproduction of the annealing effects was obtained by simple trajectory calculation.

de Barros *et al*. review the application of FTIR spectroscopy to study the evolution of the chemical composition of ices containing the most abundant molecular species found in the solar system and interstellar medium, such as H_2O, CO, CO_2 and hydrocarbons.

In his overview, Feldman discusses the rich and diverse radiation-induced (fast electrons and x ray) chemistry in solid xenon, monitored both by IR and EPR spectroscopies.

Szymonski *et al*. investigate desorption of Rb and I atoms from the RbI (100) surface co-irradiated with 1 keV electrons and visible light (with a wavelength corresponding to the F-center absorption band) by mass-selected time-of-flight (TOF) spectroscopy. Thermal dependence of the desorption yield agrees with the defect-mediated desorption model.

A brief review of broad-band light-emitting radiation-induced F_2 and F_3^+ electronic point defects is given by Montereali *et al*. Their formation, properties and applications are discussed.

Baldacchini *et al*. focus their discussion to organic light emitting devices (OLEDs), in particular to Alq3 and its photoluminescence behavior upon temperature.

Loktev and Pogorelov analyze the quasiparticle spectrum of graphene in the presence of different substitutional order, including vacancies. The anomalous character of impurity effects in this system is demonstrated, compared to those in well-known doped semiconductors, and explained in terms of conical singularities in the band spectrum of pure graphene.

We dedicate this special issue of the journal on “Low Temperature Spectroscopy and Radiation Effects” to Elena Savchenko, on the occasion of her 70th birthday and wish her many more productive years in science.

We heartily thank all authors for their contributions to this special issue.

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