ТРУДЫ

IV МЕЖДУНАРОДНОЙ НАУЧНОЙ КОНФЕРЕНЦИИ
"РАДИАЦИОННО-ТЕРМИЧЕСКИЕ ЭФФЕКТЫ И ПРОЦЕССЫ В НЕОРГАНИЧЕСКИХ МАТЕРИАЛАХ"
12–19 августа 2004 г.
Томск, Россия

IV INTERNATIONAL SCIENTIFIC CONFERENCE
"RADIATION- THERMAL EFFECTS AND PROCESSES IN INORGANIC MATERIALS"
12–19 August 2004
Tomsk, Russia
The fundamental excitation of non-metallic solids by photons and beams of particles with kinetic energy below the threshold of knock-on of atoms from lattice sites — subthreshold excitation — is a powerful tool for materials modification by selective removal of material, controlled changes in selected regions, altering the balance between process steps, quantum control etc. [1]. The scission of the bonds, stabilising the ground-state configuration, by transfer of electronic excitation energy to the lattice requires the trapping or self-trapping of the electronic excitations. However the range of materials, which exhibit inelastic processes induced by electronic excitation, is limited to specific classes of materials, such as alkali halides, alkali earth fluorides and fused quartz [1].

Recently the atomic cryocrystals — solid xenon, krypton, argon and neon (rare-gas solids) — manifests themselves as a new class of insulators, which demonstrates pronounced electronically induced defect formation and desorption processes [2]. As a consequence of the closed electronic shells, the atomic cryocrystals are the simplest solids known to us with smallest binding energy between atoms in the lattice. On the other hand, solid argon and neon have band-gap energies exceeding that of LiF and may be cited as widest band-gap insulators. Therefore, atomic cryocrystals — model systems in condensed matter physics — are very promising systems for investigation the mechanisms of subthreshold inelastic electronically induced processes.

Cryocrystals exist only at cryogenic temperatures and most of the optical spectroscopy of electronic processes must be done in the vacuum ultraviolet. It requires from experiment the indispensable combination of liquid-helium equipment with window-less VUV-spectroscopy devices and synchrotron radiation as a photon source. To investigate the electronic excitation energy pathways and variety of subthreshold inelastic
radiation induced processes in cryocrystals we used the complementary advantages of cathodoluminescence (possibility to vary the excitation depth beneath the sample surface) and photoluminescence (selective-state excitation by synchrotron radiation at high-flux SUPERLUMI-station at HASYLAB, DESY, Hamburg) [2].

The electronic properties of atomic cryocrystals have been under investigation since seventies [3] and now the overall picture of creation and trapping of electronic excitations is basically complete. Because of strong interaction with phonons the excitons and holes are self-trapped in atomic cryocrystals, and a wide range of electronic excitations coexist: free excitons (FE), several types of atomic-like self-trapped excitons (A-STE), several types of molecular-like self-trapped neutral and charged centers — excitons (M-STE) and holes (STH) with intrinsic structure, and electrons trapped at lattice imperfections [4]. The coexistence of free and trapped excitations and, as a result, the presence of a wide range of luminescence bands in the emission spectra enable one to reveal the energy relaxation channels and to detect the elementary steps in lattice rearrangement [5].

The interatomic bond scission in the crystal lattice may be stimulated either by elastic encounters between atoms composing solids and incoming particles or by creation of electronic excitations which transfer the energy to a specified crystal cell [1]. Local elastic and inelastic lattice deformation around trapped electronic excitations, population of the antibonding electronic states during relaxation of the molecular-like centers, and excitation of the Rydberg states of guest species are the moving force of point defect formation in the bulk of the samples and desorption of atoms and molecules from the surface of cryocrystals [2]. The energy stored by electronic excitations in cryocrystals is much higher than the binding energy $\varepsilon_b$ [3], and various trapping processes concentrate the energy within a volume of about a unit cell. The extremely high quantum yield of luminescence allows one to neglect non-radiative transitions, and the population of antibonding $^1\Sigma_g^+$ ground molecular state is usually considered as a main source of kinetic energy for a large-scale movement of atoms finishing in the Frenkel defects or desorption of atoms in the ground state — ground-state (GS) mechanism. On the other hand, the processes of formation of A-STE and M-STE centers themselves are accompanied by a considerable energy release to the crystal lattice, which also exceeds the binding energy $\varepsilon_b$. Such an excited-state (ES) mechanism of the large-scale atomic movement was the subject of our recent investigations. The ES-mechanism of M-STE to Frankel-pair conversion consists of three stages (Fig.1) [6]. The process is supposed to occur by (stage 1) self-trapping of an
exciton (Fig.1a→b) with a subsequent displacement (stage 2) of M-STE from the centrosymmetric position in the <110> direction (Fig.1b→c) followed by (stage 3) reorientation to the <100> direction (Fig.1d) to stabilize the defect.

The radiative decay of the stabilized excimer (Fig.1d) results in the creation of a stable point defect, Frenkel-pair, in the lattice, whereas the radiative decay of M-STE in the off-center position (Fig.1c) returns the lattice into the initial (Fig.1a) state without permanent defect. Thus, the state Fig.1c may be considered as a metastable short-lived lattice defect, which, together with stable defects, emits the "defect" $M_I$-subband of $M$-luminescence band, but is not accumulated in the crystal lattice [4].

The Frenkel-pair formation induced by excitation of Rydberg states of atomic-like centers was studied both for the intrinsic process of lattice degradation (exciton self-trapping in solid Ne) and for the extrinsic process of lattice degradation induced by excitation of impurity atoms (trapping of exciton at Ar impurity in Ne matrix and selective photoexcitation of Xe impurity in Ar matrix). The strong repulsion of the Rydberg electron with a closed shell of surrounding atoms induces a substantial local lattice rearrangement. In solid Ne and Ar, which have a negative electron affinity, the free exciton self-trapping in the bulk results in a cavity ("bubble") formation around A-STE (Fig.2a). After the

---

**Figure 1.** Scheme of ES-mechanism of Frenkel-pair formation induced by exciton self-trapping into quasi-molecular state in atomic cryocrystals.

---

**Figure 2.** Scheme of inelastic processes induced by A-STE in atomic cryocrystals: (a→b) – Frenkel-pair formation; (c→d) – desorption of excited atoms.
bubble formation the surrounding ground state atoms appear to have moved to the second shell. It was found that the second-nearest neighboring vacancy-interstitial pairs could create the permanent defects, which remain in the lattice after exciton annihilation. At the surface the short-range repulsion is no longer spherically symmetric like in the bulk but effectively directed outside the surface, leading to the ejection of the excited atom (Fig.2d) or excimer by "cavity-ejection" mechanism.

The radiation-induced scission of selected intramolecular bond in molecular cryocrystals (condensed films of simplest molecular gases like CO, O₂, N₂, H₂O, CO₂ etc.) is effectively stimulated by core photoexcitation. Such "molecular scalpel" technique by synchrotron radiation excitation of core states of N and O was recently applied to study the dynamics of hydrogen desorption from thin films of NH₃ and H₂O molecular cryocrystals condensed on monocrystal Ru(001)-substrate [2]. The scission of hydrogen–nitrogen bond is a key stage in the process of low-temperature ammonia oxidation to different NOₓ nitrogen oxides [7]. The selective enhancement of H⁺ yield in comparison to H₀ desorption yield occurs because of delocalization of excited electron from the 4a₁ orbital into the matrix during the lifetime of the O₁s and N₁s core holes [8]. The similar technique was used to investigate the atom-selective bond breaking in a N₂ cryocrystal films on Ru(001) by core photoexcitation [9].