New emission band of solid Nitrogen

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Nitrogen solids gained general recognition as classical model molecular crystals which attract much attention in diverse fields of science – physics and chemistry of interstellar and solar systems, material science, specifically, the problem of polynitrogen compounds considered as environment-friendly high energy-density materials (HEDM). Energy storage, transformation, and its release are the focus of studies and among the methods used spectroscopy is one of the most effective. Optical spectroscopy of solid nitrogen has a long story and its recent trends were reviewed in [1]. Despite an impressive progress there are still unsolved questions and the most long-standing one concerns identification of, the so-called γ–line, situated in the near infrared (NIR) range. Some hypothesis of its origin was suggested in [2]. According to [2] the γ–line appears as a result of the interaction of mobile electrons and metastable $N(^2D)$ atoms in solid matrices with formation of nitrogen anion N^-. The radiative transition ($^1D \rightarrow {}^3P$) of N^- gives the γ–line. Its red satellite remained unidentified.

Here we present new results on the study of radiation effects in nitrogen solids with a focus on the γ–line. An electron beam of subthreshold energy was used to excite N_2 solids. Relaxation dynamics was monitored by emission spectroscopy – cathodoluminescence (CL) and nonstationary luminescence (NsL), along with current activation spectroscopy. On completion of irradiation correlated in real time measurements of thermally stimulated luminescence (TSL) and exoelectron emission (TSEE) were performed. In the NIR CL spectra of solid N_2 three emission bands were recorded.

Wavelength, nm	794	802	810
Energy, eV	1.56	1.545	1.53
cm^{-1}	12594	12469	12346

The band at 810 nm was detected for the first time. Bands at 794 and 802 nm are close to the observed in the impurity helium condensates [2]. These three bands are characterized by similar behavior and form molecular series with spacing between adjacent vibrational energy levels of the ground state of 125 cm^{-1} and 123 cm^{-1}. These findings call into question the identification of the γ–line as the emission of nitrogen anion N^-. The NsL and TSL measurements along with the TSEE record indicate the connection of the γ–line with the neutralization reaction.

It was found in the theoretical study [3] that there exists a stable isomer N_4 (D_{2h}) with barrier to dissociation and it may be possible to sinthesize it at low temperatures. The lowest optically accesible excited state 1^1B_{3u} lies about 1.6 eV above the ground state ^1A_g. Its geometry is very similar to that of the ground state that results in large Frank-Condon factors for transitions between the two states. The energy of the transition $^1B_{3u} \rightarrow {}^1A_g$ is quite close to the experimental value of the γ–line, however vibrational structure does not coincide with the predicted in [3].Theory gives a spacing between adjacent vibrational energy levels of the ground state of around 500 cm^{-1}, while the experiment gives 125 cm^{-1}. Additional theoretical and experimental studies are needed to solve the problem of the γ–line.

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