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Radiation Effects in Solid Nitrogen and Nitrogen-Containing Matrices: Fingerprints of N_4^+ Species

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ABSTRACT: The radiation effects and relaxation processes in solid N_2 and N_2-doped Ne matrices, preirradiated by an electron beam, have been studied in the temperature range of 5−40 and 5−15 K, respectively. The study was performed using luminescence methods: cathodoluminescence CL and developed by our group nonstationary luminescence NsL, as well as optical and current activation spectroscopy methods: spectrally resolved thermally stimulated luminescence TSL and exoelectron emission TSEE. An appreciable accumulation of N radicals, N^+, N_2^+ ions, and trapped electrons is found in nitrogen-containing Ne matrices. Neutralization reactions were shown to dominate relaxation scenario in the low-temperature range, while at higher temperatures diffusion-controlled reactions of neutral species contribute. It was conceived that in α-phase of solid N_2, the dimerization reaction ($N_2^+ + N_2 \rightarrow N_4^+$) proceeds: "hole self-trapping". Tetranitrogen cation N_4^+ manifests itself by the dissociative recombination reaction with electron: $N_4^+ + e^- \rightarrow N_2^*(a'^1\Sigma_u^-) + N_2 \rightarrow N_2 + N_2 + h\nu$. In line with this assumption, we observed a growth of the $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ transition intensity with an exposure time in CL spectra and the emergence of this emission in the course of electron detrapping on sample heating in the TSL and NsL experiments.

Graphical abstract:

Dimerization reaction:

$N_2^+ + N_2 \rightarrow N_4^+$
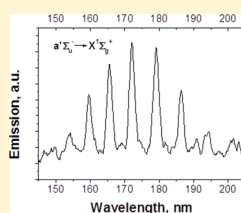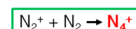
is followed by neutralization:

$N_4^+ + e^- \rightarrow N_2^*(a'^1\Sigma_u^-) + N_2 \rightarrow$
$\rightarrow N_2 + N_2 + h\nu$
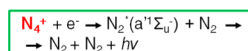
Dissociative recombination of N_4^+ and electron

Exoelectron emission

■ INTRODUCTION

Radiation effects and relaxation processes in solid nitrogen are of high interest in quite diverse fields of science. It is known that so-called nitrogen and nitrogen-containing ices are present in large abundance in cosmic space,[1] being exposed to solar wind and galactic cosmic rays. Another aspect of this interest is related to application of nitrogen and nitrogen compounds as high-energy density materials HEDMs.[2] A lot of effort was directed toward producing high concentrations of reactive nitrogen species in cryogenic solids, for instance in "impurity-helium condensates" (IHCs).[3−6] Concentrations as high as 5×10^{19} nitrogen atoms per cm^3 could be obtained in such porous nitrogen−helium nanocondensates.[7] Films of solid nitrogen also attracted attention for practical applications in material science (e.g., the original technique for surface modification based on laser ablation of nitrogen films was suggested in ref 8). Employing the plume from laser ablation of solid nitrogen film, the authors were able to produce the carbon nitride C_3N_4 and silicon nitride Si_3N_4 species in the surface layers of highly oriented pyrolitic graphite (HOPG) and of silicon plate, respectively. The laser ablation of solid nitrogen film was monitored by UV−visible optical emission spectroscopy, and the modified surface was analyzed by X-ray photoelectron spectroscopy, XPS. On the basis of their results, the authors concluded that the main component of the ablation plume are

neutral N atoms, with traces of molecular nitrogen, evidenced by the Vegard−Kaplan system phosphorescence emission.

Despite a long, 90-year history of solid nitrogen spectroscopy[9−22] there are still open issues, in particular the problem of ionic species generation, stability, and their reactions. Up to very recently, all the results obtained were discussed solely in terms of neutral species reactions. Recent experiments[23] have, however, revealed strong thermally stimulated exoelectron emission TSEE from preirradiated solid nitrogen layers, suggesting a prominent part played by radiation-induced charged species in the energy storage and relaxation processes. Emission of electrons was also detected upon warm-up of nitrogen-containing IHCs.[24] The IR and UV absorption measurements of the electron-bombarded solid nitrogen demonstrated the production of ionic species N_3^+.[25]

The distinctive feature of irradiated solid nitrogen, known from the early studies,[26] is the long afterglow associated with $^2D \rightarrow {}^4S$ atomic transition. In Pimentel's laboratory[27] a thermally stimulated luminescence TSL from solid nitrogen preirradiated by electrons was observed. The authors attributed

the TSL detected to the recombination of ^4S nitrogen atoms due to diffusion stimulated by heating. TSL of solid nitrogen condensed from discharge was registered on $^2D \rightarrow {}^4S$ atomic transition.[28] The structure of the glow curve was interpreted as originating from different trapping sites of atoms. Another possible interpretation, namely TSL of preirradiated solid nitrogen as the result of charge recombination reactions, was not considered. With an extensive range of solid nitrogen emissions (from IR to VUV) taken into account, the need of spectrally resolved TSL study in the wide range of spectrum is obvious.

In order to clarify the question on the intrinsic charged species generation in solid nitrogen, elucidate their stability, and restore the relaxation scenario, we used the CL method and concurrently both the optical (TSL) and current (TSEE) activation spectroscopy technique. In addition, to probe charged species, we employed the nonstationary luminescence NsL method, developed by our group. We started the study with matrix-isolated nitrogen molecules going to pure solid nitrogen. The measurements of CL spectra and spectrally resolved TSL of nitrogen-containing Ne matrices and solid nitrogen preirradiated with an electron beam were performed in the visible, near UV, and VUV range. The whole complex of methods used enabled us to establish which species are produced and survive irradiation and to find limits of their stability. On the basis of the spectrally resolved TSL and NsL data in VUV range, we suggest the hole self-trapping in α-phase N_2 with tetranitrogen cation formation: $N_2^+ + N_2 \rightarrow N_4^+$. Tetranitrogen cation N_4^+ manifests itself by products of the dissociative recombination reaction with electron released from trap upon heating $[N_4^+ + e^- \rightarrow N_2^* (a'^1\Sigma_u^-) + N_2 \rightarrow N_2 + N_2 + h\nu]$.

■ EXPERIMENTAL METHODS

The experiments were performed using facilities at TUM and ILT. The experimental techniques developed were described in more detail in ref 29 and Ch.7 (by Savchenko) in ref 30 and are therefore only briefly discussed here. High-purity gases, (99.999%) Ne and (99.995%) N_2, were used to grow films of uniform thickness (100 μm) by deposition from the gas phase on a metal substrate cooled to 6 K. The film thicknesses and the deposition rates were determined by measuring the pressure decrease in a known volume of the gas-handling system. Concentration of N_2 in Ne films was varied over a wide range (0.005−5%). The sample growth procedures were kept identical in the experiments carried out at both facilities in order to yield consistent results. A base pressure in the vacuum chambers was ~10^{-8} mbar. The samples were irradiated using an electron beam whose energy could be varied from 500 eV to 2 keV, and whose current density could be adjusted between 30 μA cm^{-2} up to 7 mAcm^{-2}. The luminescence spectra were recorded repeatedly on an exposure time to monitor the dose dependence of excited species formation and accumulation. In addition, the spectra provided information about the presence of impurities in the films. The VUV spectra in the range 100−300 nm were recorded (at ILT) with a modified VMR-2 monochromator, while visible spectra between 200 and 800 nm were concurrently recorded with an MDR-12 monochromator. A multichannel S2000 Spectrometer Ocean Optics based on CCD detectors operating in the range of 170−1100 nm was used in the experiments performed at TUM. Upon completion of the irradiation, the Ne films doped with nitrogen as well as the pure nitrogen films exhibited the well-known long afterglow

at the wavelength of the forbidden atomic transition $^2D \rightarrow {}^4S$.[17,31] Coincidentally, with the afterglow we observed "afteremission" of electrons with similar characteristic decay times. When the afterglow intensity dropped almost to zero, the films were allowed to warm up at a constant rate, measuring the temperature using a calibrated silicon diode sensor, mounted on the substrate. A programmable temperature controller LTC 60 allowed us to maintain desired temperatures during the deposition, irradiation, and to control the desired heating regime. In the experiments performed at ILT, the spectrally resolved TSL was monitored concurrently in VUV and visible range at chosen wavelengths. Using the setup at TUM, we were able to record the entire TSL spectra and monitor their temporal evolution during heating over the entire operating range of the spectrometer. The yields of spectrally resolved TSL and TSEE were detected in time-correlated fashion. The exoelectron current was measured with an Au-coated Faraday plate maintained at a small positive potential of +9 V and connected to a current amplifier FEMTO DLPCA 100. In addition to activation spectroscopy experiments, we used the method of nonstationary luminescence NsL. The main aim of the method is the elucidation of the emissions observed associated with ionic species. The method assumes the generation of charged species with an intense electron beam followed by probe of species under study with a low-density beam on gradual linear heating of the sample. In so doing, we induce "internal electron emission" - release of electrons from progressively deeper traps, enhancing their recombination with positively charged ions. Correlation of NsL intensity with TSEE or TSL yields indicates contribution of charge recombination reactions.

■ RESULTS AND DISCUSSION

Nitrogen-Doped Ne Matrices. Irradiation of nitrogen-containing Ne films with an electron beam results in the generation of electron−hole pairs, molecule fragments, dopant ionic centers, and structural defects distributed throughout the target. The Ne^+ holes are self-trapped within 10^{-12}s of their formation,[32] forming intrinsic ionic centers of dimer configuration Ne_2^+. These centers are then stable as long as the film is maintained cold. Due to the negative electron affinity of solid neon, $E_a = -1.3$ eV,[32] electrons in solid Ne exhibit a freelike behavior[33] but can be trapped by impurities with positive electron affinity (E_a) or by defects such as vacancies, vacancy clusters, or pores. Owing to the wide band gap of neon (21.58 eV), Ne films are capable of storing a large variety of ionic species, many of which were extensively studied by the matrix-isolation technique (e.g., ref 34 and references therein). In particular, considering that the ionization potentials of the N atom, N_2 molecule, and $(N_2)_2$ dimer are 14.53, 15.58, and 14.6 eV, respectively,[2,35] one could expect the formation of the corresponding N^+, N_2^+, and N_4^+ cations. Note that $^{14}N_4^+$ and $^{15}N_4^+$ cations were detected in Ne matrix both by IR absorption[36] and by the ESR technique.[37] Neutralization of ionic species by recombination with electrons and subsequent relaxation can result in their dissociation, the so-called dissociative recombination. Luminescence spectra recorded during the beam irradiation contain "fingerprints" of the species formed and of the relaxation processes which follow excitation.

Figure 1 shows the energy scheme of Ne matrix and potential curves of N_2 molecule. Irradiation with an electron beam generates electron−hole pairs which then relax to exciton
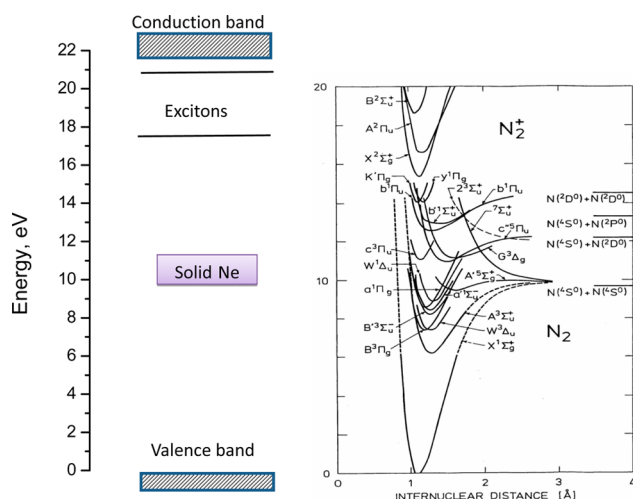
Figure 1. Energy band scheme of solid Ne (left); selected potential curves of N_2 molecule by ref 38 (right).

states. Matrix-isolated N_2 molecules are excited mainly by energy transfer from matrix excitons. The emission spectra of Ne matrix doped with nitrogen (0.1%) are presented in Figure 2 (visible and near UV range) and Figure 3 (VUV).
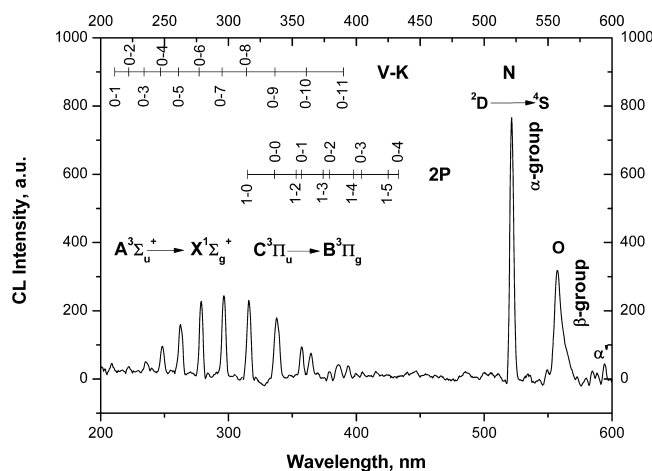

Figure 2. Cathodoluminescence spectrum of nitrogen-doped Ne matrix in the visible and near UV range.

Two molecular progressions are observed: the Vegard–Kaplan system ($A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$) and the second positive bands ($C^3\Pi_u \rightarrow B^3\Pi_g$), in agreement with the earlier study.[17] Note that the $C^3\Pi_u \rightarrow B^3\Pi_g$ system is characteristic for Ne matrix, but it is usually not detected in other rare-gas matrices. The most prominent feature in the visible spectrum (shown in Figure 2) is the doubly forbidden $^2D \rightarrow {}^4S$ transition of atomic nitrogen at 521 nm, referred to as "α-emission" in the paper by Bass and Broida.[11] Three other bands of atomic nitrogen N in the VUV range are shown in Figure 3: transitions $2p^4\,^4P \rightarrow 2p^3\,^4S$, $3s\,^4P \rightarrow 2p^3\,^4S$, and $3s\,^2P \rightarrow 2p^3\,^2P$ (at 112.5, 119.5, and 173.9 nm, respectively), all being slightly shifted with respect to their positions in the gas phase.

Additional weaker "β-band" at about 557 nm stems from the $^1S \rightarrow {}^1D$ transition of atomic oxygen, which is invariably present as a minor impurity in the samples. As depicted in Figure 3, weak O bands were also detected in the VUV range. The VUV spectrum is dominated by a strong emission from the
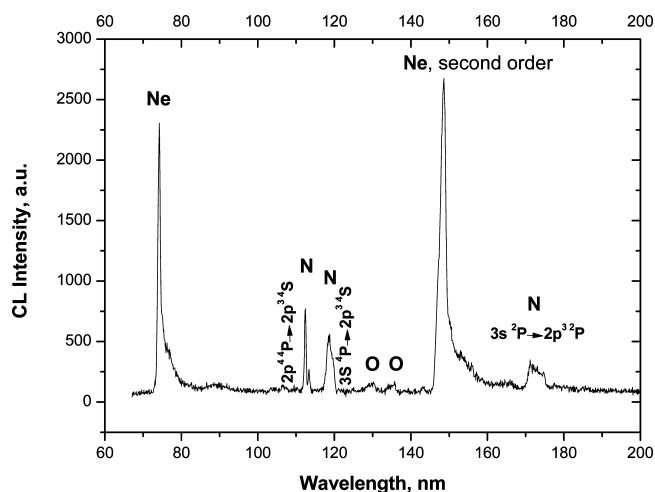

Figure 3. Cathodoluminescence spectrum of nitrogen-doped Ne matrix in the VUV range.

intrinsic Ne centers in the film. This consists of the pronounced atomic type band of complex structure (not shown in the Figure) at about 74 nm and a weak red sideband related to the vibrationally hot luminescence of molecular type centers Ne_2^*.[39] The emitting centers are in fact the well-known self-trapped excitons STE[32] which can be considered as "matrix-isolated" within their own host film. Specific feature of both types of the STE centers is a "bubble" formation around them because of negative electron affinity E_a of solid Ne. This feature results in defect formation via STE and desorption of excited Ne atoms and molecules from the surface.[32,39,40]

Upon completion of irradiation, some part of the absorbed energy remains stored in the matrix in the form of self-trapped holes, trapped electrons, radicals, ionic species of the dopant and its fragments, as well as defects. When the sample is then gradually heated, different processes are "activated" with a part of the stored energy being released. The electrons promoted to the conduction band from shallow traps start to move through the film, and some can then escape from the surface and be detected as thermally stimulated exoelectron emission TSEE, as reported earlier.[41,42] A competing relaxation channel is recombination of the released electrons with positively charged ionic species: self-trapped holes and different cations. Such neutralization is usually accompanied by an emission of photons, so-called thermally stimulated luminescence TSL. Spectrally resolved TSL provides one with information about the ionic species survived in the preirradiated matrix and relaxation processes. It is pertinent to note that TSL may result also from recombination of neutral atoms mobilized by heating. With this in mind, we measured TSL yield from nitrogen-doped Ne matrix at the wavelength corresponding to the nitrogen atomic transition $2p^4\,^4P \rightarrow 2p^3\,^4S$ observed in the VUV range concurrently with TSL detected at the molecular transition $A^3\Sigma_u^+(0) \rightarrow X^1\Sigma_g^+(9)$. Figure 4 shows the glow curves obtained. In this case a layer of Ne containing 0.03% of N_2 was deposited at 5 K and then irradiated with 1 keV electron beam. With irradiation of the sample completed, its temperature was linearly raised at about 7 K/min, while monitoring the TSL yields. Both curves show steep rise exhibiting a clear peak at about 7.5 K followed by slow increase in the range of 8.5−10.5 K. At higher temperature, the TSL yields of atomic and molecular emissions exhibit different behavior: the atomic
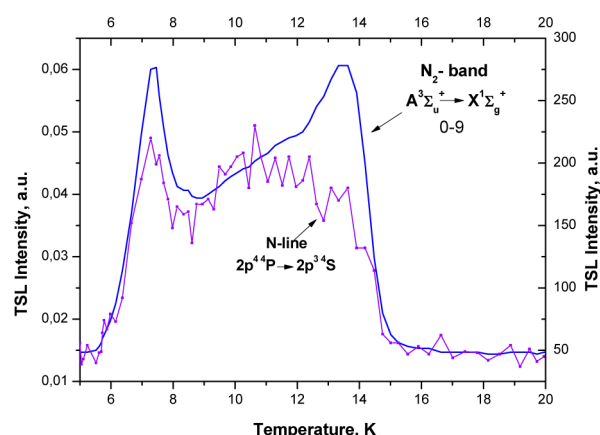
Figure 4. Glow curves of nitrogen-doped Ne matrix detected synchronously at wavelength of the $2p^4\,^4P \rightarrow 2p^3\,^4S$ transition of N atom and at the $A^3\Sigma_u^+(0) \rightarrow X^1\Sigma_g^+(9)$ transition of N_2.

Figure 5. TSEE yield taken from nitrogen-doped Ne matrix and TSL yield measured at the wavelength of the intrinsic atomic type emission of self-trapped excitons in the Ne matrix.

emission decreases slowly, whereas the molecular emission increases and peaks at 13.5 K.

At 15 K, the film is lost and the signals disappear. The features observed point to different relaxation processes contributing the TSL yields. At low temperatures, when diffusion of atoms is frozen, only charge recombination reactions determine the TSL. N^+ ionic centers formed under the electron beam are neutralized by the reaction:

$$N^+ + e^- \rightarrow N^* \rightarrow N + h\nu_1 \qquad (1)$$
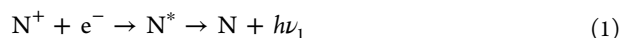
Note that another source of excited atoms can be the reaction of dissociative recombination of N_2^+ with electron:

$$N_2^+ + e^- \rightarrow N^* + N \rightarrow N + N + h\nu_2 \qquad (2)$$
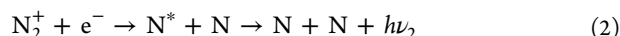
For N_2^+ in the ground vibrational state (level v = 0), there are three dissociation limits of reaction 2: $N(^4S) + N(^2D)$, $N(^4S) + N(^2P)$, and $N(^2D) + N(^2D)$.[43] The atomic emission chosen for measurement in the VUV range and shown in Figure 4 does not fit the limits; that is to say, it is the result of reaction 1. Ions N_2^+ in solid matrix could relax yielding molecular emission:

$$N_2^+ + e^- \rightarrow N_2^* \rightarrow N_2 + h\nu_3 \qquad (3)$$
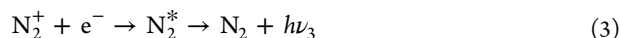
Neutralization of molecular ions initially results in population of high "Rydberg" states, which then rapidly relax. This cascade eventually populates the lower valence states, such as $A^3\Sigma_u^+$ which decays with photon emission. Correlation of atomic and molecular TSL yields in the low temperature range (5−11 K) suggests common TSL mechanism—neutralization reactions. The similar trends, predominance of neutralization reactions at low temperatures, were found in Ar films doped with nitrogen and preirradiated with an electron beam.[44,45]

Interesting question is what kind of electron traps is responsible for the neutralization. In order to clear up the question, we measured the spectrally resolved TSL yield of charge recombination emission of the intrinsic Ne centers shown in Figure 5 together with the TSEE yield.

High TSEE current detected on heating of the preirradiated film points to an appreciable accumulation of trapped electrons in Ne matrix. An estimate of the lower limit of the electron density by the yield of TSEE gives 10^{14} electron cm^{-3}. The TSL was observed at the wavelength of the atomic transition, about 74 nm. Atomic Ne centers, so-called self-trapped excitons,[32]
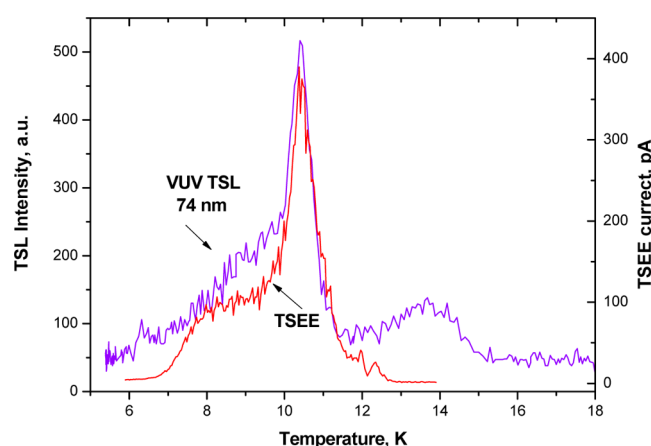
appear as a result of the dissociative recombination reaction of self-trapped holes Ne_2^+ with electrons released from traps on heating:

$$Ne_2^+ + e^- \rightarrow Ne_2^* \rightarrow Ne^* + Ne \rightarrow Ne + Ne + h\nu_4 \qquad (4)$$
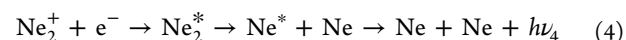
For Ne centers, there is no distinct peak at 7.5 K. The glow curve shows slow rise with a shoulder in the range of 8−9.5 K related to surface traps and a prominent peak at about 10.3 K connected to the radiation-induced defects in Ne films.[41,42] Weak maximum about 14 K can be induced by the chemiluminescent reaction 5 of N atom recombination which is followed by photon emission, discussed below. It was demonstrated that reactions of this kind can dislodge electrons from traps stimulating their recombination with positively charged centers, including intrinsic ones.[46]

Comparison of the spectrally resolved TSL yield of charge recombination emission of the Ne matrix with TSL yields measured at the wavelengths of atomic and molecular nitrogen species reveals a distinction of glow curves. Unlike shape of TSL curves for Ne and nitrogen centers suggests that different groups of electron traps are responsible for the neutralization of nitrogen ionic centers and ionic centers of matrix Ne_2^+. In the case of nitrogen, the traps providing electrons for reactions 1 and 2 are supposed to be spaced closely to the centers and do not contribute to the TSEE yield from the Ne matrix. The most likely, these shallow traps are formed by defects that arise in close proximity of the dopant in Ne film. One of the possible channels of defect formation could be the reaction of dissociative recombination of dopant (2) which yields "hot" N atoms with kinetic energy above 1 eV (1.06−3.45 eV depending on the atomic state of products)[43] that is more than 1 order of magnitude larger than the binding energy of 26.5 meV per atom for solid Ne.[32] Such energetic atoms could produce defects in the solid through minicascades.[47] Another possible mechanism of defect formation is the mechanism similar to that found in Ne matrix—rearrangement of the surrounding atoms in response to the repulsive interaction with the excited electron of dopant.[39,41]

Let us take up the "high temperature" part of the TSL curves (Figure 4) corresponding atomic and molecular emissions. The peak of molecular nitrogen emission at 13.5 K appears within the temperature range where the yield of TSEE from Ne film shown in Figure 5 drops to zero. It arises close to the

temperature where diffusion of N atoms occurs, resulting in N_2^* molecule formation followed by its radiative decay:

$$N + N \rightarrow N_2^* \rightarrow N_2 + h\nu_S \tag{5}$$

Note that in fact the only molecular state which can be populated in such a process is the triplet state $A^3\Sigma_u^+$, the upper state of Vegard−Kaplan series (as seen in Figure 1). Antibate behavior of atomic and molecular TSL yields in the range of 11−13 K supports the scenario discussed. Note that such antibate behavior clearly manifests itself in the range of low concentrations (0.005−0.1%), where the temperature-induced diffusion of nitrogen atoms is essential. An important point is that the neutralization reactions also contribute to the TSL yield at "high" temperatures, indicating presence of nitrogen ionic species in the film up to complete loss of the sample. Similar multipeak glow curves for atomic and molecular nitrogen emissions were detected in the concentration range of 0.005−0.1%; however, relative intensity of the peaks varied with concentration. As the nitrogen content increased, the 7.5 K peak of the molecular emission decreased in its intensity with respect to the 13.5 K peak. At a concentration of 1%, the structure of glow curves became blurred with a dominating central peak at about 11 K. The feature of the TSL curves taken from the sample with 1% of nitrogen is close correlation of TSL yields for the atomic $^2D \rightarrow {}^4S$ transition and the triplet molecular emissions $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ over the entire temperature range. The spectrum evolution in the range 7−15 K, demonstrating the effect for the whole molecular series and for the atomic $^2D \rightarrow {}^4S$ transition is shown in Figure 6. This
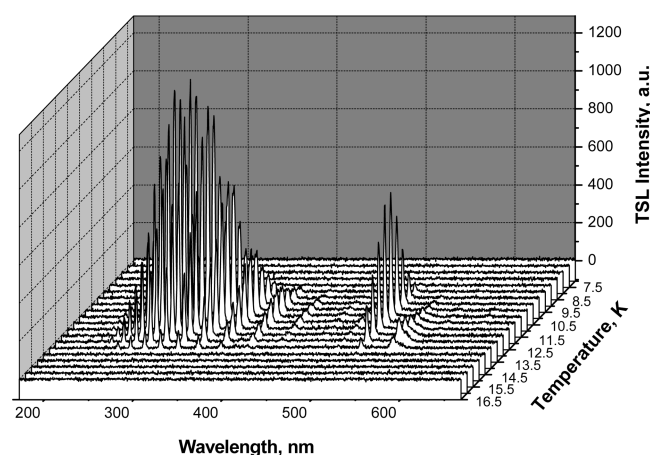

Figure 6. 3D plot of TSL spectra taken from Ne matrix doped with 1% of N_2.

correlation suggests that $N(^2D)$ atoms could be produced by neutralization reactions 1 and 2. On detrapping, electrons became mobile, so they might recombine with any cations present in the solid, producing neutrals in excited states.

Note that $N(^2D)$ atoms could also be formed due to energy transfer from the N_2 molecule in the triplet state $A^3\Sigma_u^+$ to N atom in the ground state with its excitation to the ^2D state, the process akin to that discussed in solid nitrogen:[13]

$$N_2(A^3\Sigma_u^+) + N(^4S) \rightarrow N(^2D) + N_2(X^1\Sigma_g^+) \tag{6}$$
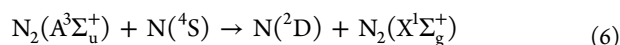
The TSL spectrum in the range of α-line and the Vegard−Kaplan system recorded at 11 K is presented in Figure 7. A weak feature related to oxygen atoms ($^1S \rightarrow {}^3P$ transition) is
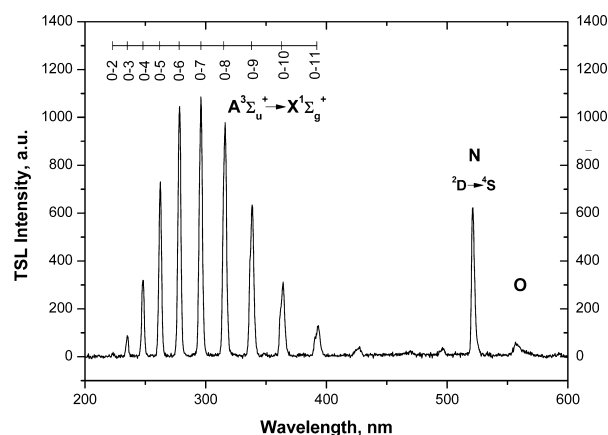

Figure 7. 2D cut through the 3D plot (Figure 6) at 11 K.

also observed. The mechanisms of its formation are similar to those for $N(^2D)$ atoms: reactions 1, 2, and 6. Interesting that the intensity of the atomic $^2D \rightarrow {}^4S$ line in the TSL spectra appears to be much lower than the intensity of a prominent band of the $A^3\Sigma_u^+(0) \rightarrow X^1\Sigma_g^+(7)$ transition in contrast to the pattern observed in the luminescence spectra recorded under irradiation (Figure 2).

A weak TSL was revealed on the $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ molecular transition after irradiation of Ne film containing 5% of nitrogen. Taking into account a poor solubility of nitrogen in solid Ne, one can expect appearance of the phase areas of pure nitrogen.

Solid Nitrogen. We measured luminescence spectra of solid nitrogen grown at 5 K over a broad wavelength range, from the visible to the VUV. The luminescence spectrum in the visible and near UV range is consistent to that obtained earlier.[14−16] The spectrum is quite similar to the spectrum observed in nitrogen-doped Ne matrix (shown in Figure 2). The most intense emission is the α-line around 523 nm related to the $^2D \rightarrow {}^4S$ transition of N atom studied in detail in ref 13. Note that the molecule fragmentation is one of the main channels of radiation, induced defect formation in molecular solids. If such an event happens near the surface, ejection of particles can take place. The study of electronically induced desorption of solid nitrogen revealed an ejection of atoms and molecules.[48−52] Molecular luminescence in the visible range of spectra, the second positive system ($C^3\Pi_u \rightarrow B^3\Pi_g$), is much weaker. The distinctive feature of this system is the coincidence of the observed bands with those detected in the gas phase spectra within the accuracy of our measurements. As has been found in our recent experiments, the second positive system is emitted by N_2^* molecules desorbed from solid nitrogen. This issue will be addressed in a subsequent publication. In the VUV range, luminescence spectrum of solid nitrogen is dominated by the $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ molecular progression (system of Ogawa−Tanaka−Wilkinson−Mulliken) shown in Figure 8. Also present in the spectrum are the Vegard−Kaplan ($A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$) bands and the atomic line $3s\ ^4P \rightarrow 2p^3\ ^4S$. Note that both molecular systems exhibit the luminescence rise with an exposure time. The inset in Figure 8 demonstrates as an example the effect for the $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ progression.

Enhancement of the luminescence indicates accumulation of primary centers responsible for the emissions observed. The most likely is that these primary centers are of ionic nature.

After irradiation, we observed the well-known intense afterglow on the wavelength of the forbidden atomic transition, the $^2D \rightarrow {}^4S$ together with after emission of electrons,
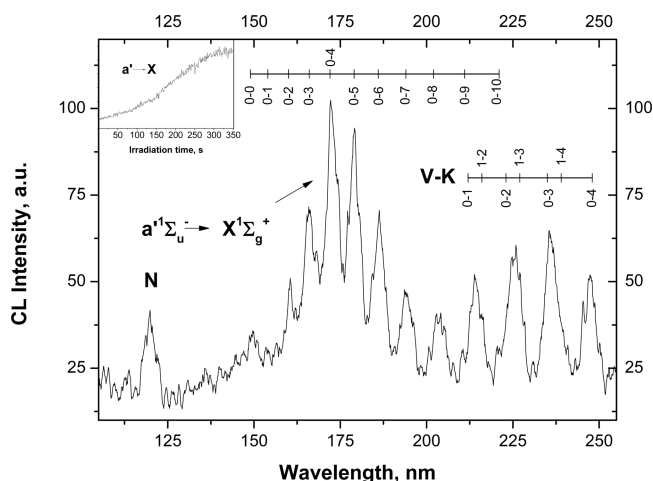
Figure 8. Cathodoluminescence spectrum of solid nitrogen in the VUV range. Dose behavior of the CL intensity for $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ progression is shown in the inset.

indicating electrostatic charging of nitrogen films. The afterglow decayed exponentially with a characteristic time τ about 37 s in agreement with ref 31 and our previous measurements.[23] The current decay can be fitted by a sum of two exponents with decay times 37 and 216 s. An existence of long exponent might be connected with the recapture of electrons. When the afterglow decayed to zero, that is to say, all long-lived $N(^2D)$ atoms returned to the ground ^4S state, we started to heat the sample, detecting the yields of TSL. It has been found that the preirradiated solid nitrogen exhibits a TSL not only in the visible range (at the α-line and at the bands of Vegard-Kaplan progression) but also in the VUV range—emission from the $a'^1\Sigma_u^-$ state (Figure 9).
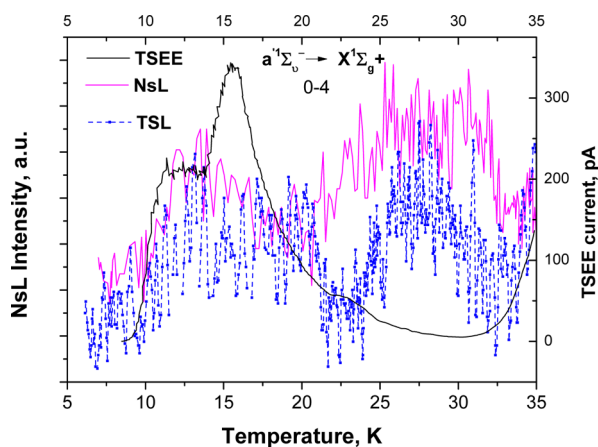

Figure 9. TSL of solid nitrogen: total yield and spectrally resolved one detected at a wavelength of the 0−4 band of $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ molecular transition.

The TSL was detected at wavelengths corresponding to transitions from several vibronic levels of the $a'^1\Sigma_u^-$ state. Figure 9 presents as an example the TSL yield detected at a wavelength of the $a'^1\Sigma_u^-(0) \rightarrow X^1\Sigma_g^+(4)$ molecular transition in comparison with the TSEE yield.

The TSEE yield shows a pronounced peak at about 16 K with a weak shoulder near 13 K. The TSL detected at the wavelength of the 0−4 band of $a' \rightarrow X$ molecular emission exhibits a wide feature in the temperature range of 12−18 K.

Correlation of the molecular band with TSEE yield at low temperatures (up to 22 K) suggests that primary ionic centers responsible for the $a' \rightarrow X$ molecular emission are neutralized by detrapped electrons. Taking into account localized character of positive charge carriers in solid nitrogen,[53] it seems most likely that holes are self-trapped due to interaction with phonons. In other words, the dimerization reaction,

$$N_2^+ + N_2 \rightarrow N_4^+ \tag{7}$$

efficiently proceeds with N_4^+ cation formation. The dimerization reaction with N_4^+ formation was observed in supersonic nitrogen jet below 20 K.[54] Note that an observation of neutral $(N_2)_2$ in free icosahedral nitrogen clusters formed in supersonic jet was also recently reported.[55] There is additional argument in favor of hole self-trapping, which comes from the experiments on electronically stimulated desorption of solid nitrogen.[40,49] Absence of high-energy tail of N atoms in the energy distribution of electron-irradiated solid nitrogen was attributed to the dimerization reaction 7 with $(N_2)_2^+$ formation. At low temperatures survived after irradiation, self-trapped holes (N_4^+) remain stable as long as electrons are trapped elsewhere. Detrapping of electrons by heating initiates the neutralization reaction which usually occurs by the dissociative recombination:[2]

$$N_4^+ + e^- \rightarrow N_4 \rightarrow N_2^* + N_2 \rightarrow N_2 + N_2 + h\nu_8 \tag{8}$$
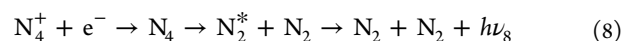
It is worth noting that in TSL experiments, initial state of N_4^+ for reaction 8 is vibrationally relaxed ground state of N_4^+. The energetically lowest-lying state of N_4^+ corresponds to a linear centro-symmetric geometry $D_{\infty h}$ with a $^2\Sigma_u^+$ ground electronic state.[2] This geometry was confirmed by the ESR study,[37] where $^{14}N_4^+$ and $^{15}N_4^+$ were generated by the ion-neutral reaction 7 and isolated in the Ne matrix at 5 K. Neutralization of N_4^+ results in population of excited N_4^* molecular states. Relaxation could occur via transition structures for fragmentation.[2] For triplet state it could result in $^3\Sigma_u^+$ population, for singlet state relaxation terminates in the lowest singlet excited state $a'^1\Sigma_u^-$, which then decays radiatively. It should be mentioned that the height of barrier for fragmentation varies with the electronic states of N_2 involved. In particular, the theoretical study of the ground and excited states of $N_4(D_{2h})$[56] predicted an absence of the barrier for the state with dissociation limit $N_2(a'^1\Sigma_u^-) + N_2(a'^1\Sigma_u^-)$. Observation of TSL at the $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ transition as the result of a neutralization reaction indicates formation of tetranitrogen cations N_4^+ viz. the self-trapped holes, which are the primary ionic centers formed in solid nitrogen exposed to ionizing radiation.

A second peak in the TSL at 28 K has no analogue in the TSEE yield. The question arises as to how the $a'^1\Sigma_u^-$ state observed in TSL is populated at higher temperatures ($T > 22$ K). The $a'^1\Sigma_u^-$ state is a lowest singlet excited state, and its dissociation limit is formed by two nitrogen atoms in excited states: $N(^2D) + N(^2D)$.[31] However, formation of an $a'^1\Sigma_u^-$ state via recombination of two excited atoms in the ^2D state in a preirradiated sample is unlikely. So the 28 K peak cannot be attributed to atom−atom recombination. One may assume that this peak stems from neutralization of close ion-electron pair $N_4^+ + e^-$, a process that does not contribute to TSEE.

To test the hypothesis, we performed experiments using the NsL method described in brief above. Solid nitrogen film was first irradiated with a 1 keV electron beam (6 mA cm^{-2}) to generate ionic species and then was probed with a 1 keV beam

of 1 mA cm^{-2} upon gradual heating. The yield of NsL detected at the same wavelength as in the TSL measurements is shown in Figure 9. Clear correlation with TSL was observed supporting connection of the radiative a$'^1\Sigma_u^-$ → X$^1\Sigma_g^+$ transition with the neutralization reaction 8.

CONCLUSIONS

We employed the combination of cathodoluminescence CL and nonstationary luminescence NsL with current and optical activation spectroscopy methods to study radiation effects in solid α-N$_2$ and in N$_2$-doped Ne matrix with a focus on nitrogen ionic species, electron-driven reactions, and relaxation paths. Harnessing spectrally resolved thermally stimulated luminescence TSL in wide spectral range together with exoelectron emission TSEE enables us to probe reactions of neutral and charged species and to restore the relaxation scenario. An appreciable accumulation of trapped electrons (up to 10^{15} cm^{-3}), radicals, and ionic species was found. It was shown that the neutralization reactions dominate in the low-temperature range. As the temperature increases, diffusion-controlled reactions of atom−atom recombination contribute to TSL. Strong evidence in favor of hole self-trapping with tetranitrogen cation N$_4^+$ formation − N$_2^+$ + N$_2$ → N$_4^+$ was derived from the spectrally resolved TSL and NsL study in the VUV range in combination with TSEE measurements. "Fingerprints" of N$_4^+$ were found as products of the dissociative recombination reaction observed on heating: N$_4^+$ + e$^-$ → N$_2$*(a$'^1\Sigma_u^-$) + N$_2$ → N$_2$ + N$_2$ + $h\nu$.

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REFERENCES

(1) Clark, R. N.; Carlson, R.; Grundy, W.; Noll, K. Observed Ices in the Solar System. In *The Science of Solar System Ices*; Gudipati, M. S., Castillo-Rogez, J., Eds.; Astrophysics and Space Science Library, Springer: New York, 2012; Vol. 356, pp 3−46.

(2) Nguyen, M. T. Polynitrogen Compounds. 1. Structure and Stability of N$_4$ and N$_5$ Systems. *Coord. Chem. Rev.* **2003**, *244*, 93−113.

(3) Khmelenko, V. V.; Krushinskaya, I. N.; Boltnev, R. E.; Bykhalo, I. B.; Pelmenev, A. A.; Lee, D. M. Dynamics of Thermoluminescence Spectra of Impurity-Helium Condensates Containing Stabilized Nitrogen and Oxygen Atoms. *Low Temp. Phys.* **2012**, *38*, 688−699.

(4) Khmelenko, V. V.; Kunttu, H.; Lee, D. M. Recent Progress in Studies of Nanostructured Impurity-Helium Solids. *J. Low Temp. Phys.* **2007**, *148*, 1−31.

(5) Boltnev, R. E.; Gordon, E. B.; Khmelenko, V. V.; Krushinskaya, I. N.; Martynenko, M. V.; Pelmenev, A. A.; Popov, E. A.; Shestakov, A. F. Luminescence of Nitrogen and Neon Atoms Isolated in Solid Helium. *Chem. Phys.* **1994**, *189*, 367−382.

(6) Boltnev, R. E.; Krushinskaya, I. N.; Pelmenev, A. A.; Popov, E. A.; Stolyarov, D. Yu.; Khmelenko, V. V. Study of the Stabilization and Recombination of Nitrogen Atoms in Impurity-Helium Condensates. *Low Temp. Phys.* **2005**, *31*, 547−555.

(7) Bernard, E. P.; Boltnev, R. E.; Khmelenko, V. V.; Lee, D. M. Stabilization of High Concentration of Nitrogen Atoms in Impurity-Helium Solids. *J. Low Temp. Phys.* **2004**, *134*, 199−204.

(8) Niino, H.; Sato, T.; Narazaki, A.; Kawaguchi, Y.; Yabe, A. Laser Ablation and Photo-Dissociation Solid-Nitrogen Film by UV PS-Laser Irradiation. *Appl. Surf. Sci.* **2002**, *197−198*, 67−71.

(9) Vegard, L. The Auroral Spectrum and the Upper Atmosphere. *Nature* **1924**, *113*, 716−717.

(10) McLennan, J. C.; Shrum, G. M. On the Luminescence of Nitrogen, Argon and Other Condensed Gases at Very Low Temperatures. *Proc. R. Soc. A* **1924**, *106*, 138−149.

(11) Bass, A. M.; Broida, H. P. Spectra Emitted from Solid Nitrogen Condensed at 4,2 K from a Gas Discharge. *Phys. Rev.* **1956**, *101*, 1740−1746.

(12) Peyron, M.; Hörl, E. M.; Brown, H. W.; Broida, H. P. Spectroscopic Evidence for Triatomic Nitrogen in Solids at Very Low Temperature. *J. Chem. Phys.* **1959**, *30*, 1304−1309.

(13) Oehler, O.; Smith, D. A.; Dressler, K. Luminescence Spectra of Solid Nitrogen Excited by Electron Impact. *J. Chem. Phys.* **1977**, *66*, 2097−2107.

(14) Fugol, I. Ya.; Poltoratskii, Yu. B.; Savchenko, E. V. Observation of an Exciton Luminescence of Nitrogen Crystals in the region of the Vacuum Ultraviolet. *JETP Lett.* **1976**, *24*, 3−7.

(15) Coletti, F.; Bonnot, A. M. Emission Spectrum of Electron Excited Solid Nitrogen. *Chem. Phys. Lett.* **1977**, *45*, 580−582.

(16) Poltoratskii, Yu. B.; Stepanenko, V. M.; Fugol, I. Ya. Reconstruction of Radiation Spectrum of Solid Nitrogen due to Variation of Exciting Electron Beam Parameters. *Sov. J. Low Temp. Phys.* **1981**, *7*, 60−65.

(17) Tinti, D. S.; Robinson, G. W. Spectroscopic Evidence for Slow Vibrational and Electronic Relaxation in Solids. The Vegard-Kaplan and Second Positive Systems of N$_2$ in Solid Rare Gases. *J. Chem. Phys.* **1968**, *49*, 3229−3245.

(18) Kühle, H.; Bahrdt, J.; Fröhling, R.; Schwentner, N.; Wilcke, H. Vibrational Relaxation and Electronic Energy Transfer of N$_2$ Aggregates in Solid Xe Matrices. *Phys. Rev. B* **1985**, *31*, 4854−4865.

(19) Semling, M.; Jordan, M.; Syassen, K.; Jodl, H. J.; Signorini, G. F. Luminescence Spectra of Matrix Isolated N$_2$ at High Pressure and Low Temperature. *J. Chem. Phys.* **1997**, *106*, 1336−1345.

(20) Hudson, R. L.; Moore, M. H. The N$_3$ Radical as a Discriminator between Ion-Irradiated and UV-Photolized Astronomical Ices. *Astrophys. J.* **2002**, *568*, 1095.

(21) Jamieson, C. S.; Kaiser, R. I. Isotopic Study of the Formation of the Azide Radical (N$_3$). *Chem. Phys. Lett.* **2007**, *440*, 98−104.

(22) Wu, Y.-J.; Wu, C. Y. R.; Chou, S.-L.; Lin, M.-Y.; Lu, H.-C.; Lo, J.-I.; Cheng, B.-M. Spectra and Phtolysis of Pure Nitrogen and Methane Dispersed in Solid Nitrogen with Vacuum-Ultraviolet Light. *Astrophys. J.* **2012**, *746*, 175−186.

(23) Khyzhniy, I.; Savchenko, E.; Uyutnov, S.; Gumenchuk, G.; Ponomaryov, A.; Bondybey, V. Exoelectron Emission from Solid Nitrogen. *Radiat. Meas.* **2010**, *45*, 353−355.

(24) Boltnev, R. E.; Bykhalo, I. B.; Krushinskaya, I. N.; Pelmenev, A. A.; Khmelenko, V. V.; Lee, D. M.; Khyzhniy, I. V.; Uyutnov, S. A.; Savchenko, E. V.; Ponomaryov, A. N.; et al. Comparative Study of Thermostimulated Luminescence and Electron Emission in Nitrogen Nanoclusters and Films. *Low Temp. Phys.* **2013**, *39*, 451−455.

(25) Wu, Y.-J.; Chen, H.-F.; Chuang, S.-J.; Huang, T.-P. Ultraviolet and Infrared Spectra of Electron-Bombarded Solid Nitrogen and Methane Diluted in Solid Nitrogen. *Astrophys. J.* **2013**, *768*, 83−92.

(26) Nelson Wright, A. *Active Nitrogen*; Academic Press Inc.: New York, 1968; pp 602.

(27) Brocklehurst, B.; Pimentel, G. C. Thermoluminescence of Solid Nitrogen after Electron Bombardment at 4,2 K. *J. Chem. Phys.* **1962**, *36*, 2040−2046.

(28) Faure, E.; Tribollet, B.; Vincent, F.; Valadier, F.; Janin, J. Thermoluminescence de l'Azote Actif Condensé à 5 K. *Le Journal de Physique-Letters* **1979**, *40*, L-555−L-557.

(29) Ponomaryov, A.; Gumenchuk, G.; Savchenko, E.; Bondybey, V. Radiation effects, energy storage and its release in solid rare gases. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1329−1340.

(30) Allodi, M. A.; Baragiola, R. A.; Baratta, G. A.; Barucci, M. A.; Blake, G. A.; Brucato, J. R.; Contreras, C.; Cuylle, S. H.; Boduch, Ph.; Fulvio, D.; et al. *Space Sci. Rev.* **2013**, *180*, 101−175.

(31) Lofthus, A.; Krupenie, P. H. The Spectrum of Molecular Nitrogen. *J. Phys. Chem. Ref. Data* **1977**, *6*, 113−307.

(32) Song, K. S.; Williams, R. T. *Self-Trapped Excitons*, 2nd ed., Springer-Verlag: Berlin, 1996; pp 404.

(33) Storchak, V. G.; Eshchenko, D. G.; Brewer, J. H.; Cottrell, S. P.; Cox, S. F. J.; Karlsson, E.; Wappling, R. W. Electron Transport in Cryocrystals. *J. Low Temp. Phys.* **2001**, *122*, 527−535.

(34) Jacox, M. E. The Spectroscopy of Molecular Reaction Intermediates Trapped in the Solid Rare Gases. *Chem. Soc. Rev.* **2002**, *31*, 108−115.

(35) NIST Chemistry WebBook http://webbook.nist.gov/chemistry/ (accessed September 11, 2014).

(36) Thompson, W. E.; Jacox, M. E. The Vibrational Spectra of Molecular Ions Isolated in Solid Neon. III. N_4^+. *J. Chem. Phys.* **1990**, *93*, 3856−3861.

(37) Knight, L. B., Jr.; Johannessen, K. D.; Cobranchi, D. C.; Earl, E. A.; Feller, D.; Davidson, E. R. ESR and *ab initio* Theoretical Studies of the Cation Radicals $^{14}N_4^+$ and $^{15}N_4^+$: The Trapping of Ion-Neutral Reaction Products in Neon Matrices at 4 K. *J. Chem. Phys.* **1987**, *87*, 885−897.

(38) Smirnov, B. M.; Yatsenko, A. S. Properties of Dimers. *UFN* **1996**, *166*, 224−245.

(39) Savchenko, E. V.; Ogurtsov, A. N.; Zimmerer, G. Exciton-Induced Defect Formation. *Low Temp. Phys.* **2003**, *29*, 270−273.

(40) Johnson, R. E.; Schou, J. Sputtering of Inorganic Insulators. *Mat.-Fys. Medd.-K. Dan. Vidensk. Selsk.* **1993**, *43*, 403−493.

(41) Grigorashchenko, O. N.; Rudenkov, V. V.; Khizhniy, I. V.; Savchenko, E. V.; Frankowski, M.; Smith-Gicklhorn, A. M.; Beyer, M. K.; Bondybey, V. E. Activation Spectroscopy of Electronically Induced Defects in Solid Ne. *Low Temp. Phys.* **2003**, *29*, 876−879.

(42) Frankowski, M.; Savchenko, E. V.; Smith-Gicklhorn, A. M.; Grigorashchenko, O. N.; Gumenchuk, G. B.; Bondybey, V. E. Thermally Stimulated Exoelectron Emission from Solid Neon. *J. Chem. Phys.* **2004**, *121*, 1474−1479.

(43) Peterson, J. R.; Le Padellec, A.; Danared, H.; Dunn, G. H.; Larsson, M.; Larson, A.; Peverall, R.; Strömholm, C.; Rosén, S.; Ugglas, M.; et al. Dissociative Recombination and Excitation of N_2^+: Cross Sections and Product Branching Ratios. *J. Chem. Phys.* **1998**, *108*, 1978−1988.

(44) Ponomaryov, A. N.; Savchenko, E. V.; Gumenchuk, G. B.; Khizhniy, I. V.; Frankowski, M.; Bondybey, V. E. Thermoactivation Spectroscopy of Solid Ar Doped with N_2. *Low Temp. Phys.* **2007**, *33*, 532−537.

(45) Savchenko, E. V.; Khyzhniy, I. V.; Uyutnov, S. A.; Gumenchuk, G. B.; Ponomaryov, A. N.; Bondybey, V. E. Relaxation of Charged and Neutral Particles in Doped Atomic Solids: TSL, OSL, TSEE, OSEE and their Interconnection. *IOP Conf. Ser.: Mater. Sci. Eng.* **2010**, *15*, 012082 (6 pp).

(46) Savchenko, E. V.; Khyzhniy, I. V.; Uyutnov, S. A.; Gumenchuk, G. B.; Ponomaryov, A. N.; Beyer, M. K.; Bondybey, V. E. Charging Effects in an Electron Bombarded Ar Matrix and the Role of Chemiluminescence-Driven Relaxation. *J. Phys. Chem. A* **2011**, *115*, 7258−7266.

(47) Johnson, R. E.; Liu, M. Molecular Dynamics Studies of Minicascades in Electronically Stimulated Sputtering of Condensed-Gas Solids. *J. Chem. Phys.* **1996**, *104*, 6041−6051.

(48) Ellegard, O.; Schou, J.; Sørensen, H.; Børgesen, P. Electronic Sputtering of Solid Nitrogen and Oxygen by keV Electrons. *Surf. Sci.* **1986**, *167*, 474−492.

(49) Pedrys, R.; Oostra, D. J.; Haring, A.; de Vries, A. E.; Schou, J. Energy Distribution from Electron-Sputtered Solid Nitrogen. *Radiat. Eff. Defects Solids* **1989**, *109*, 239−244.

(50) Hudel, E.; Steinacker, E.; Feulner, P. Kinetic Energy Distribution of Particles Desorbed from Solid N_2, O_2, and NO by Electron Impact. *Surf. Sci.* **1992**, *273*, 405−412.

(51) Rakhovskaia, O.; Wiethoff, P.; Feulner, P. Thresholds for Electron Stimulated Desorption of Neutral Molecules from Solid N_2, CO, O_2 and NO. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1995**, *101*, 169−173.

(52) Shi, H.; Cloutier, P.; Sanche, L. Low-Energy-Electron Stimulated Desorption of Metastable Particles from Condensed N_2 and CO. *Phys. Rev. B* **1995**, *52*, 5385−5391.

(53) Loveland, R. J.; Le Comber, P. G.; Spear, W. E. Charge Transport in the Diatomic Molecular Solids and Liquids: N_2, O_2, and CO. *Phys. Rev. B* **1972**, *6*, 3121−3127.

(54) Randenlya, L. K.; Zeng, X. K.; Smith, R. S.; Smith, M. A. Temperature Dependence of Termolecular Association Reactions $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$ and $O_2^+ + 2O_2 \rightarrow O_4^+ + O_2$ Occuring in Free Jet below 20 K. *J. Phys. Chem.* **1989**, *93*, 8031−8037.

(55) Doronin, Yu. S.; Libin, M. Yu.; Samovarov, V. N.; Vakula, V. L. Spectroscopic Observation of $(N_2)_2$ Dimers in Free Icosahedral N_2 and Ar-N_2 Clusters. *Phys. Rev. A* **2011**, *84*, 023201−023211.

(56) Elesin, V. F.; Degtyarenko, N. N.; Pazhitnykh, K. S.; Matveev, N. V. Modeling of Synthesis and Dissociation of the N_4 Nitrogen Cluster of D_2H Symmetry. *Russ. Phys. J.* **2009**, *52*, 1224−1234.