

## Thermoactivation spectroscopy of solid Ar doped with N<sub>2</sub>

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A new modification of low-temperature activation spectroscopy technique for real-time correlated study of relaxation processes in cryogenic solids was developed. This enabled us to measure simultaneously thermally stimulated exoelectron emission (TSEE) and spectrally resolved thermally stimulated luminescence (TSL) in the range from 200 to 1100 nm. This paper presents the results on TSL and TSEE from solid Ar doped with N<sub>2</sub> exposed to irradiation by low-energy electron beam (500 eV) during deposition. The TSEE and TSL yields were measured at the heating rate of 3.2 K/min. The emissions of molecular ( $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  transition) and atomic ( ${}^2D \rightarrow {}^4S$  transition) nitrogen in the TSL spectra and their temperature behavior were studied. Drastic changes in the intensity distribution of the molecular progression were observed with temperature rise. In low-temperature range «hot» vibrationally unrelaxed transitions were detected in contrast to «cold» vibrationally relaxed transitions observed in «high» temperature TSL. The mechanisms of the processes resulting in TSL in whole temperature range of Ar solid occurrence are suggested.

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### Introduction

Studies of luminescence from rare gas solids subjected to high-energy irradiation extends back more than eighty years to the work of Vegard, who hoped to gain this way understanding of auroral glow and its spectrum. Interestingly, the most prominent spectral features observed from solid argon were due to minor impurities, the so-called «auroral» line at 557.7 nm due to the forbidden  ${}^1S-{}^1D$  transition of O atoms, as well as lines due to atomic and molecular nitrogen [1]. In particular, a prominent system of strong lines in the UV range, today called Vegard–Kaplan bands, was later identified as the  $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  phosphorescence of molecular N<sub>2</sub>. The pioneering studies of Vegard led to the realization that low temperature solids, and in particular rare gases, provide an excellent medium for studies of free radicals and ionic species, and moti-

vated the development of matrix isolation spectroscopy as a useful spectroscopic technique [2], which was discussed in a number of review articles [3,4].

The energetic radiation impinging on the solid results in excitation, break up, or ionization of the species present, as already shown by Vegard, and part of its energy thus remains stored in the solid in the form of defects, vacancies and interstitial atoms, as well as impurity atoms, radicals or ions. In 1962, Brocklehurst and Pimentel [5] investigated emission of such an irradiated solid during its subsequent warmup, a study which can be viewed as an early example of the so-called «activation spectroscopy», a method which is becoming a useful tool in studies of radiation «damage» in a variety of materials. As the temperature of the pre-irradiated sample is gradually raised, a number of processes are triggered or «activated»: elec-

trons can be promoted to the conduction band and become mobile, they can recombine with any positive ions present, or exit the solid, and also atoms can be ejected from the sample surface. At higher temperatures, atoms and small radicals can start to diffuse through the solid, and these microscopic processes can then result in a number of observable macroscopic effects: recombination and neutralization of the fragments may result in an emission which can be spectrally- and time-resolved and studied as the so-called TSL, thermally stimulated luminescence; electrons leaving the solid can be detected as an «exo-electron» current, thermally stimulated exoelectron emission (TSEE), and atoms ejected from its surface result in a rise in pressure. Conversely, observation of these macroscopic effects can provide a detailed insight into the microscopic processes in the solid, and a number of such studies have been reported.

While most previous studies have concentrated on just one of these «activation spectroscopy methods», obviously a most detailed information can be gained by examining all the observable effects concurrently, on the same sample. For this purpose we have recently designed and constructed an apparatus which can, under computer control, arbitrarily choose the heating regime, and simultaneously record the spectrally resolved TSL and TSEE during warmup, while recording the pressure and sample temperature. In the present study, we use this apparatus to study pre-irradiated solid argon samples doped with molecular nitrogen.

### Experimental

A schematic of our new experimental setup is shown in the Fig. 1. The work is carried out in a fairly conventional matrix isolation cryostat, cooled by a closed cycle Leybold RGD 580 cryostat. The bottom temperature is about 6 K, the base pressure in the vacuum shroud is around  $10^{-8}$  mbar. In the present experiment, a sample of argon doped with 1% of nitrogen is deposited on a copper substrate coated with thin layers of Au and  $MgF_2$ . The gas flow rate during deposition controlled by means of a Brokhorst Gas Flow Controller was 2 ml/min; the sample thickness, typically 100  $\mu\text{m}$ , could also be independently determined by observing the pressure drop in the gas handling system of a known volume. Concurrently with the deposition, the sample was irradiated by a 600 eV electron beam with a current density of about  $30 \mu\text{A}/\text{cm}^2$  (see Fig. 2). The source of electrons was a heated 2.2 V tungsten filament with the beam being focused on the sample by a special electromagnetic lens. After the deposition is complete, the substrate was turned to the position for spectral measurements (see Fig. 3), and the heating of the sample was carried out using a digital programmable controller Leybold LTC 60, with the temperature being monitored

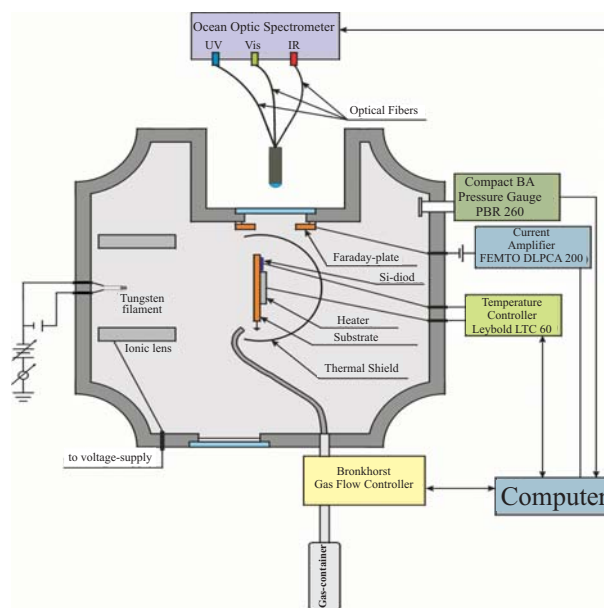


Fig. 1. Schematic of the experimental setup used for time-correlated simultaneous measurements of TSEE and of spectrally resolved TSL.

by means of silicon diodes located on the back side of the substrate.

The TSEE signal was detected by a Faraday plate kept at +9 V, and amplified by a FEMTO DLPCA 200 current amplifier. A hole in the middle of the Faraday plate permitted detecting and recording the TSL luminescence. The optical signal could, when desired, be spectrally resolved, and recorded in the range from 200 nm to 1100 nm by an Ocean Optics S2000 spectrometer. In order to carry out measurements of all the effects and parameters simultaneously and in real time, we had to develop a special software to control the entire apparatus. The program also allowed us to enter the parameters of the desired heating regime into the temperature controller, which in turn was connected to a computer via a GPIB interface. All signals

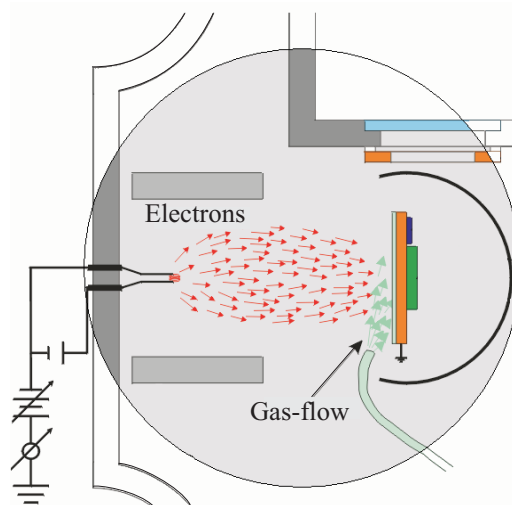


Fig. 2. Substrate in position for sample deposition.

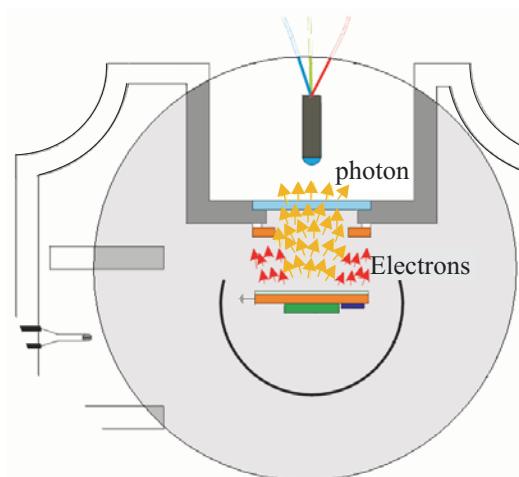


Fig. 3. Substrate rotated for TSEE and TSL measurements.

were digitized and recorded using a 16 channel BNC2110 analog/digital converter.

### Results and discussion

Spectrum of nitrogen in the solid rare gases is a convenient model system which, following the early studies by Vegard in the 1920's, was reexamined by a number of investigators. In the 1968 study by Tinti and Robinson [6] some 70 spectral bands were observed and identified, and a number of subsequent detailed investigations made N<sub>2</sub> one of the molecules, whose matrix spectra are best known and understood. Also the TSL «glow curves» of irradiated N<sub>2</sub> in rare gases were previously reported; yet, studied alone and without spectral resolution they yield little insight into the microscopic processes occurring in the solid. We have therefore applied our new apparatus to reexamine this system.

As we have previously shown, besides luminescence, the sample warm-up often results in electrons being emitted, and we show in the Fig. 4 a typical TSEE curve. In this case a layer of solid argon doped with about 1% of molecular N<sub>2</sub> was deposited at 6 K, with a concurrent 500 eV electron irradiation. After rotating the sample to the position for spectral acquisition, its temperature was then linearly raised at about 3.2 K/min, while monitoring the current of electrons exiting the sample. The curve shows that the electron current starts to rise sharply around 8 K, exhibiting several distinct maxima. The strongest one at 11 K has a shoulder around 13 K, the current then decreases sharply, another strong maximum appearing near 37 K. Above about 43 K the sample is lost, and the signal disappears. The curve is similar to the previously reported TSL «glow curves», when the intensity of the total sample luminescence as a function of temperature is monitored.

As noted above, a more detailed insight is obtained in a spectrally resolved TSL experiment, where the entire

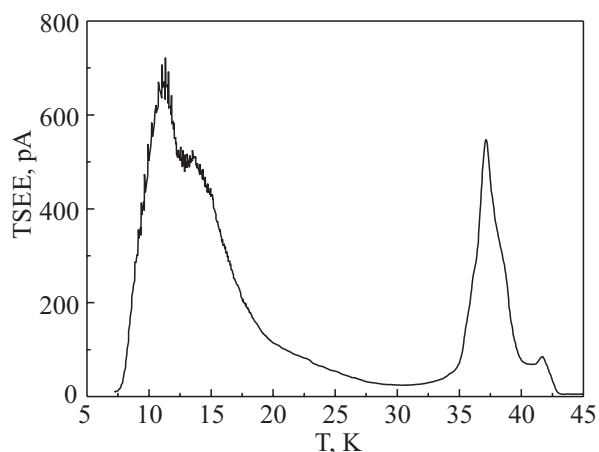


Fig. 4. TSEE curve of solid Ar doped with 1% of N<sub>2</sub>.

thermo-luminescence spectra, and their changes, are repetitively recorded and stored as the temperature rises. The spectrum between 15000–50000 cm<sup>-1</sup> recorded with the sample at 11 K shown in the Fig. 5, *a* exhibits as its most prominent feature the doubly forbidden <sup>2</sup>D→<sup>4</sup>S transition of atomic nitrogen at 19119 cm<sup>-1</sup>. Several progressions of rather intense bands are clearly due to the molecular N<sub>2</sub>, the Vegard–Kaplan A<sup>3</sup>Σ<sub>u</sub><sup>+</sup> → X<sup>1</sup>Σ<sub>g</sub><sup>+</sup> phosphorescence. Additional, weaker series of bands can be identified with the molecular NO a<sup>4</sup>Π → X<sup>2</sup>Π transition [7]. These are undoubtedly due to a small oxygen impurity, which is invariably present in the samples. Most of the spectral features observed in our TSL study were observed and assigned previously, and a list of the lines seen in our experiment and their respective assignments are presented in Table 1.

Interestingly and consistent with the previous studies, during the warm-up of the pre-irradiated sample there appear not only vibrationally relaxed lines originating from the v' = 0 level but also «hot bands» originating from upper vibrationally excited levels. In the case of the Vegard–Kaplan transition, the lines up to v' = 6 are

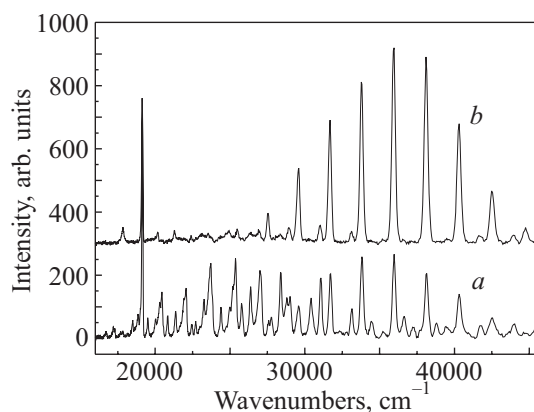


Fig. 5. TSL spectrum taken at 11 K (trace *a*) and 25 K (trace *b*).

Table 1. List of spectral lines observed in our TSL, with their positions determined by derivatives the derivative method

Nitrogen emission									NO		
Molecular						Atomic			$a^4\Pi \rightarrow X^2\Pi$		
$A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$						$2D \rightarrow 4S$					
$v'$	$v''$	$v, \text{cm}^{-1}$	$v'$	$v''$	$v, \text{cm}^{-1}$	$v'$	$v''$	$v, \text{cm}^{-1}$	$v$ ,	$v', \text{cm}^{-1}$	$v, \text{cm}^{-1}$
0	2	44982	2	2	47717	4	8	37355	19119	4	30629
0	3	42688	2	3	45519	4	11	31151(?)		5	28860
0	4	40438	2	4	43309	4	14	25191		6	27131
0	5	38256	2	6	38918	4	15	23309		7	25444
0	6	36061	2	7	36746	4	16	21398		8	23761
0	7	33941	2	8	34589	4	17	19535		9	22090
0	8	31803	2	10	30492(?)	4	18	17699		10	20474
0	9	29701	2	11	28443					11	18887
0	10	27618	2	12	26431	5	11	32445		12	17321
			2	13	24465	5	12	30492(?)			
1	2	46309	2	14	22493	5	16	22727			
1	3	44094				5	17	20846			
1	4	41888	3	11	27813						
1	5	39604	3	12	25844	6	14	27813			
1	7	35354	3	13	23882	6	16	24004			
1	8	33236	3	14	21913	6	18	20279			
1	9	31151(?)	3	15	20058						
1	10	29073	3	16	18189						

clearly identified, indicating that vibrational relaxation in the upper state is slow, even when compared with the very long, many second radiative lifetime of the  $A^3\Sigma_u^+$  excited state. Figure 5 (trace *b*) shows a spectrum obtained similarly but at a higher (25 K) temperature, and it is clear that the spectral distribution has changed appreciably. The spectrum is significantly simplified, with the molecular  $N_2$  emission now being more intense than the atomic  $2D \rightarrow 4S$  line, and the relative intensities of the NO impurity bands are greatly reduced. The most apparent change is, however, that now essentially only the  $v' = 0$   $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  bands are present, with the vibrationally unrelaxed  $v' > 0$  hot bands being almost absent.

The new software written specifically for our new experimental setup makes it possible to display the entire thermoluminescence data in the form of as a three-dimensional wavenumber-temperature-intensity array, as exemplified in Fig. 6. The spectra *a* and *b* presented in the Fig. 5 are simply two-dimensional cuts through the 3-dimensional spectrum of the Fig. 6 at selected temperatures. Obviously, instead of taking 2D cuts through the 3D data

presented in Fig. 6 perpendicular to the temperature axis, that is at a given temperature as shown in the Fig. 5, one can similarly make 2D cuts perpendicular to the wavenumber axis, thus showing the temperature dependent intensity at a given wavenumber, that is of a selected spectral line.

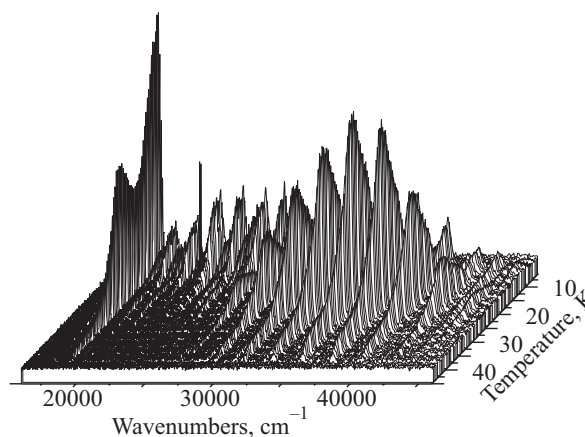


Fig. 6. 3D TSL spectrum of solid Ar doped with 1% of  $N_2$ .

Several examples of such time dependent intensity profiles are presented in Fig. 7, and the results are quite informative. The top panels 7,*a* and 7,*c* represent the intensities of the metastable N-atom line at 19199 cm<sup>-1</sup>, and of one NO  $a^4\Pi \rightarrow X^2\Pi$  impurity emission band. The comparison reveals significant differences, the atomic emission exhibiting a secondary maximum near 25 K, absent in the NO emission profile. To obtain the bottom two panels, 7,*b* and 7,*d*, the intensities of one of the  $v' = 0$   $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  Vegard–Kaplan N<sub>2</sub> bands, and one of the corresponding vibrationally unrelaxed  $v' > 0$  bands, respectively, were monitored. Obviously, the time profiles in 7,*b* are independent of which of the vibrationally relaxed bands was selected, and similarly the «hot band»,  $v' > 0$  emission time profile in 7,*d* is independent of the specific  $v'$  value. The intensity profiles of the unrelaxed  $v' > 0$  bands  $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  are also essentially independent of the specific  $v'$  value.

With the detailed above data, one can try to get a consistent interpretation, and get some insight into the microscopic processes taking place in the solid. The TSEE curve in Fig. 4 reveals a prominent exoelectron current maximum near 11–13 K, indicating that around this temperatures the electrons produced during sample irradiation are promoted from shallow traps into the conduction band, become mobile, and if close to the surface, can be

ejected from the sample. Examination of the four curves in Fig. 7 reveals that each of them exhibits a maximum, or at least a local maximum, at about the same temperature. This suggests strongly that the emission of all these species near this temperature is associated with the mobilization and reactions of the trapped electrons.

Our previous studies have shown that the major effect of electron irradiation of rare gas solids is the ionization of rare gas atoms, followed by a rapid formation of rare gas dimer ions Ar<sub>2</sub><sup>+</sup> in the case of solid argon. These are then effectively indefinitely stable, «self-trapped», as long as the matrix is maintained cold. When the temperature is raised, the electrons can be mobilized and can recombine with these self-trapped holes, populating highly excited electronic states of neutral Ar<sub>2</sub>. These then proceed through a complex cascade of nonradiative relaxation, and eventually relax radiatively to the ground state. This is evidenced by a very intense VUV emission as well as by an anomalous surface atom desorption evidenced macroscopically by a pressure rise. The VUV emission is way outside the spectral range studied, but the results show that also the near UV and visible emission of N atoms and N<sub>2</sub> and NO molecules in this temperature range must be due to similar processes.

The ionization potentials of gas phase Ar atoms, N atoms and N<sub>2</sub> molecules are 15.755, 14.54 and 15.576 eV.

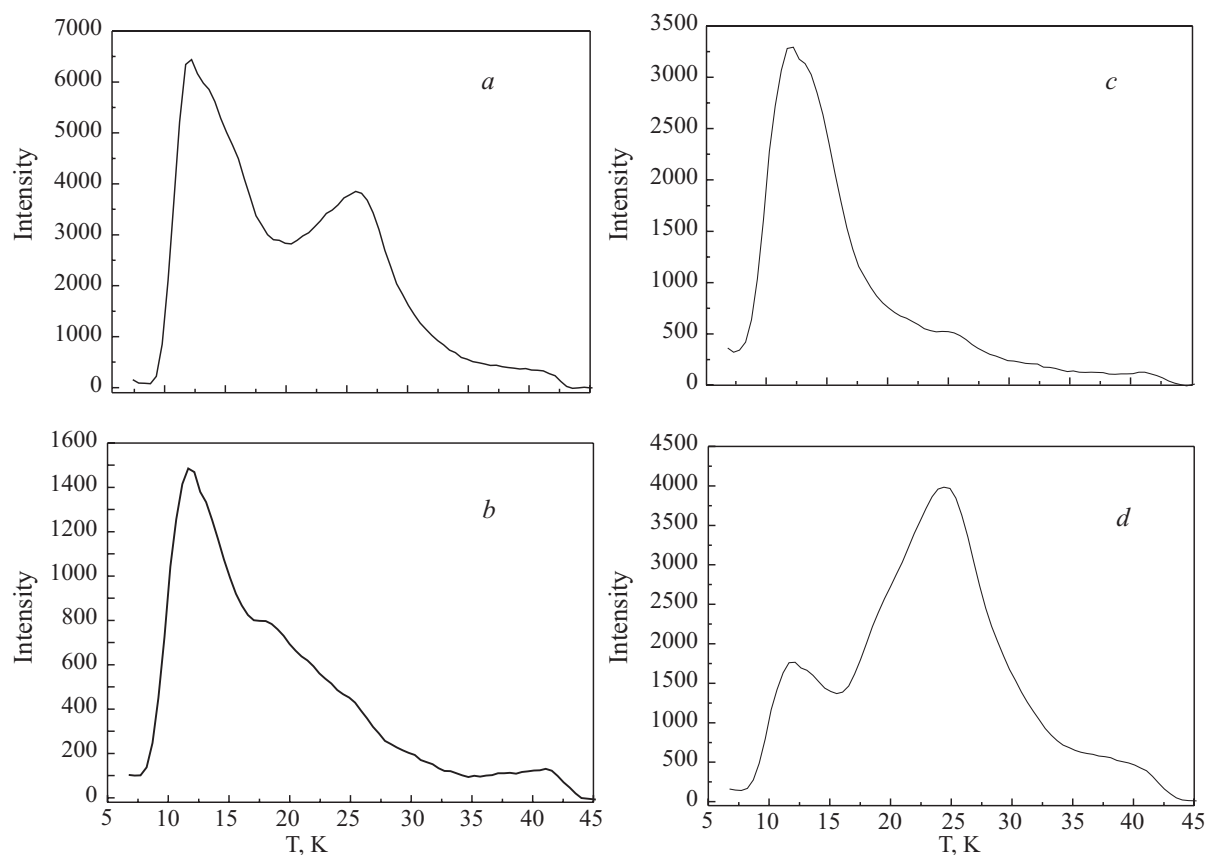
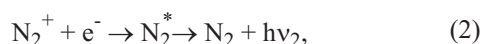
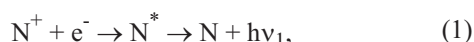


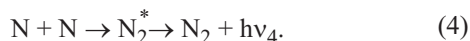
Fig. 7. The temperature dependence of the intensity of atomic nitrogen line (19119 cm<sup>-1</sup>) – trace *a*; «hot» molecular nitrogen line (31151 cm<sup>-1</sup>) — trace *b*; NO line (22075 cm<sup>-1</sup>) — trace *c*; and «cold» molecular nitrogen line (36061 cm<sup>-1</sup>) — trace *d*.

The band gap of solid argon is 14.16 eV, and it is also known that the ionization energies of matrix isolated molecules are similarly lowered by about 1.5–2 eV. It is therefore very likely that under electron irradiation, in addition to self-trapped  $\text{Ar}_2^+$  «holes»,  $\text{N}^+$  as well as molecular ionic  $\text{N}_2^+$  and  $\text{NO}^+$  centers are formed. When around 11–13 K the electrons become mobile, they can obviously recombine not only with intrinsic  $\text{Ar}_2^+$  centers but also with any other cations present in the solid, in general producing the corresponding neutrals in highly excited electronic states and with a large excess of energy. These can then relax radiatively, resulting in photon emissions:



The neutralization of an ion by an electron will initially populate very high «Rydberg» states, which will then rapidly relax. Extensive studies of relaxation processes in the matrix have shown that such a relaxation proceeds efficiently by inter-electronic cascades, often involving several electronic states. This cascade can then eventually populate the lower excited valence states, such as in the present case  $\text{N}_2 A^3\Sigma_u^+$  or  $\text{NO } a^4\Pi$ , and if the vibrational relaxation in these states is also slow [8], vibrationally excited levels can be populated and «hot» bands will appear in the spectrum, as observed.

While the «glow curves» in panels *a*, *b*, and *d* are rather similar, each exhibiting a strong maximum coincident with the prominent 11–13 K peak in the exoelectron spectrum, curve 7, *c*, representing the vibrationally relaxed  $v' = 0 A^3\Sigma_u^+$   $\text{N}_2$  emission, is clearly different. While also showing a local maximum at 11–13 K, it then starts to rise again above 15 K, reaching a prominent peak near 25 K, within the range where the TSEE curve actually exhibits a deep minimum. This suggests clearly that this second maximum is not connected with the electron-ion neutralization process. It appears, however, close to the temperature where atomic diffusion might start to take place. It seems therefore likely to propose, that the process involved here is the recombination of nitrogen atoms:



Obviously, the energy available in such a recombination process is essentially the dissociation energy of  $\text{N}_2$ , which is more than enough to populate the excited  $A^3\Sigma_u^+$  electronic state. The excess energy is, however, significantly smaller than in the case of ion-electron neutralization, and this may explain why here only – or at least preferentially – the vibrationally relaxed  $v' = 0$  level is populated. Obviously, an alternative but probably less likely interpretation of the absence of  $v' > 0$  bands is the

increased rates of the vibrational relaxation in the  $A^3\Sigma_u^+$  state of  $\text{N}_2$  at higher temperatures.

Interestingly, the atomic N emission line in the Fig. 7, *a* also exhibits a secondary peak near 25 K, which should suggest that the recombination of nitrogen atoms and the formation of  $\text{N}_2$  also results in the production of electronically excited  $^2D$  N atoms. Possible interpretations include reabsorption of the photons emitted through reaction (4) by the ground-state N atoms or, more likely, by a nonradiative, Forster type transfer between the electronically excited  $\text{N}_2$  and nearby N atoms. Clarification of this process would require further studies.

## Summary

We have designed and constructed a new apparatus for «activation spectroscopy» studies, which concurrently records spectrally resolved temperature stimulated luminescence (TSL) as well as exoelectron emission (TSEE) current curves, and we used it for a detailed investigation of pre-irradiated solid Ar solids doped with molecular nitrogen. The samples were prepared by depositing  $\text{N}_2$  doped argon from the gas phase on a 6 K substrate, with a simultaneous irradiation by 600 eV electrons. The lines of atomic N and molecular  $\text{N}_2$ , as well as NO impurity bands are identified in the TSL spectrum which appears when the temperature of the sample is gradually raised. Time correlated recording of both temperature dependent TSEE current and of the TSL «glow» curves at specific wavelengths provides a better insight into the microscopic processes occurring in the solid, subsequently studies using each of the activation techniques individually. At lower temperatures the observed TSL is shown to be mainly due to neutralization of ions produced during the pre-irradiation by detrapped electrons, while above about 20 K the neutral atom diffusion and recombination become important. The study provides a better, consistent understanding of the mechanisms of the release and relaxation of the energy stored in the sample during the electron beam irradiation process.

1. L. Vegard, *Nature* **114**, 357 (1924).
2. E. Whittle, D.A. Dows, and G.C. Pimentel, *J. Chem. Phys.* **22**, 1943 (1954).
3. *Chemistry and Physics of Matrix-Isolated Species*, L. Andrews and M. Moskowits (eds.), North Holland, New York (1989).
4. V.E. Bondybey, M. Räsänen, and A. Lammers, *Ann. Rep. Prog. Chem., Sec. C*, **95**, 331 (1999).
5. B. Brocklehurst and G.C. Pimentel, *J. Chem. Phys.* **36**, 2040 (1962).
6. D.S. Tinti and G.W. Robinson, *J. Chem. Phys.* **49**, 3229 (1968).
7. H P. Broida and M. Peyron, *J. Chem. Phys.* **32**, 1068 (1968).
8. V.E. Bondybey, *Adv. Chem. Phys.* **47**, 521 (1981).