Defect-formation induced by electron transitions in solid argon

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Results on the first spectroscopic observations of defect formation induced by the excitation of the electronic subsystem are presented. Evidence of charged and neutral defect formation is obtained. A combination of luminescence and thermal activation spectroscopic techniques is used. © *1996 American Institute of Physics.* [S1063-777X(96)01610-6]

1. INTRODUCTION

The excitation of the electron subsystem of atomic cryocrystals causes a considerable rearrangement of the crystal lattice and leads to the formation of stable point defects in the structure.[1-6] The physics of this phenomenon is based on the localization of excitation in a certain limited region of the crystal with subsequent transfer of energy from the electron subsystem to the nuclear subsystem. Defect-formation induced by self-trapping of excitons at atomic-type states was discovered in neon cryocrystals.[1,2] Structural defect-formation caused by self-trapping of excitons at molecular type states was observed in cryocrystals of heavy inert elements xenon[3,4] and krypton.[5,6] It was shown that the defects emerge as a result of decay of self-trapped excitons as well as during the lifetime of the excited states.

Investigations of defect-formation induced by electron transitions in solid argon are of special interest since argon is characterized by a strong electron–phonon interaction, a low coupling energy and a rich variety of self-trapping channels for electron excitations. This paper is devoted to the first spectroscopic observation of defect-formation induced by electron transitions in solid argon.

2. EXPERIMENTAL TECHNIQUE

Experiments were carried out on samples with different concentrations of initial defects before irradiation, which are determined by the sample growth conditions and the concentration of oxygen-containing impurities. Oxygen was used as a deep trap for electrons. Dissociation of molecular oxygen in the matrix leads to the emergence of fragments of atomic oxygen which is known to be an effective trap in view of its high affinity to the electron ($\chi = 1.465$ eV).[7] Argon of 99.9995% purity was condensed from the gaseous phase in a special cryogenic cell[3] with an electromagnetic shutter separating the volume in which the crystal was grown from the volume of the experimental chamber, thus making it possible to grow samples at temperatures much higher than the sublimation threshold. The quality of the samples, which were optically transparent large-block condensates, was controlled by measuring the emission intensity of free excitons and from thermoluminescence spectra. The concentration of the pre- irradiation defects in the samples was varied by varying the condensation temperature T_{cond}. Vacancies are the main initial defects in cryocrystals.[8] Samples grown at $T_{cond} = 60$ K contained the minimum number of defects (the equilibrium concentration of vacancies at this temperature was $\sim 3 \cdot 10^{-7}$). The sample thickness varied in the interval 10^2–10^4 nm. After condensation, the sample was slowly cooled to 5 K, the shutter of the cell in the high-vacuum chamber was opened and irradiation by an electron beam in stationary regime was carried out. Electrons with energy $E_e = 1$ keV, which is lower than the threshold energy E_e^{thr} of electrons causing the formation of defects as a result of elastic collisions between electrons and lattice atoms, were used. The threshold energy for Ar is $E_e^{thr} = 4.8$ keV. The current density in most experiments was $j_e = 0.1$ mA/cm^2. Luminescence of solid argon was analyzed with the help of a vacuum monochromator with a *sun-blind* photomultiplier at the outlet. The irradiation was recorded at a spectral width of the slit equal to 0.16 nm. The dependence of the spectral distribution of the intensity of the quasimolecular radiation band on dose was studied. After each irradiation cycle, the glow curve was recorded while heating the sample to 27 K. The principal glow peak associated with the release of electrons from vacancies lies in this temperature range.[9] The experimental technique is described in detail in Refs. 3 and 9.

3. DISCUSSION OF EXPERIMENTAL RESULTS

The quasimolecular radiation band M of solid argon, which is connected genetically with the transitions $^{1,3}\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ of the excimer molecule Ar_2^*, which lie in the vacuum ultraviolet region of the spectrum. This band was discovered in early works on luminescence properties of atomic cryocrystals[10] and is the strongest singularity in the glow spectrum of bulk samples. Studies on the dependence of spectral distribution of radiation on sample thickness[11] and experiments with samples whose surface is covered by a film of another inert gas[12] show that irradiation centers of the M-band are located in the bulk. The spread of the data presented by various authors[10] on the position of the peak and half- width of this emission band points toward its complexity and a possible dependence of its contour on the sample structure and the excitation mode.

Spectroscopic studies of defect-formation stimulated by electron transitions requires in the first place the isolation of spectral singularities associated with structural defects. For this purpose, we made a detailed study of the dependence of the spectral distribution of the intensity of the M-band on the

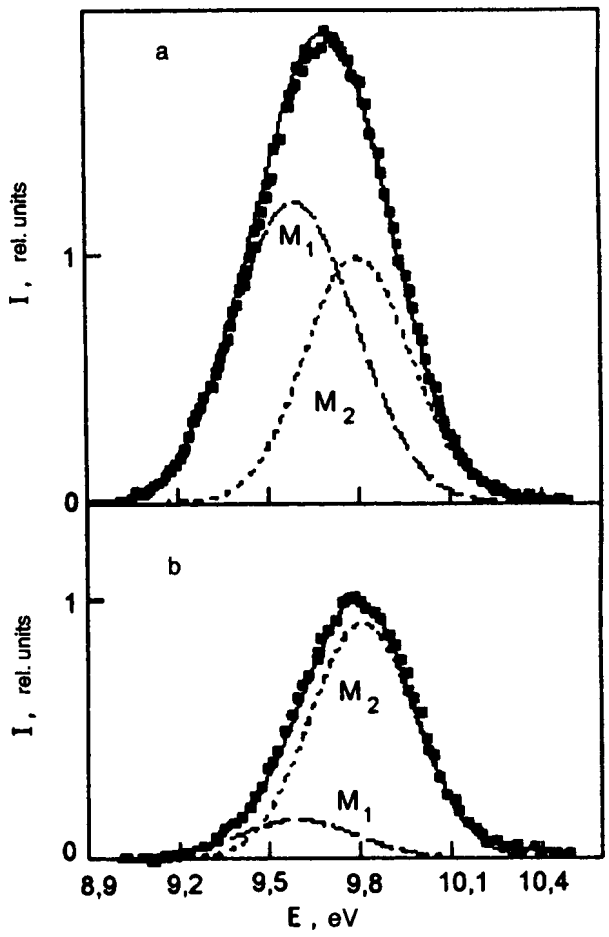

FIG. 1. M-band of argon radiation at 5 K for samples with a high (a) and low (b) concentration of defects.

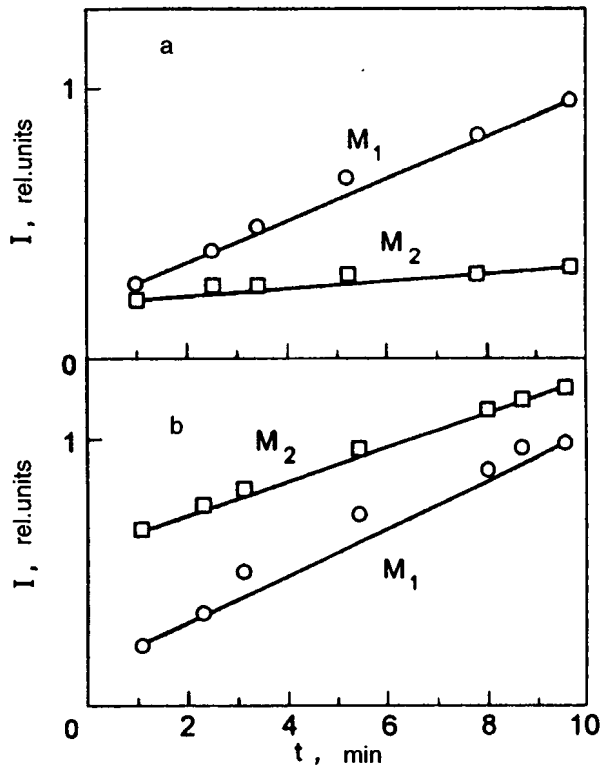

FIG. 2. Intensities of the components M_1 and M_2 as functions of argon irradiation time at 5 K for samples with a high (a) and low (b) concentration of defects.

concentration of pre-radiation defects in the sample. In order to minimize the effect of the radiation dose on the luminescence spectrum and to separate the initial and radiation defects, measurements were made for a low current density of the beam (j_e=0.01 mA/cm^2). A spectral analysis shows that two components can be singled out in the M-band near 9.7 eV, their ratio depending on the defectness of the sample. The form of these components is described quite well by Gaussian curves with peaks at 9.59 eV(M_1) and 9.77 eV(M_2) with half- width 0.47 eV and 0.41 eV, respectively. As an example, Fig. 1 shows the emission spectrum of a defective sample grown at 5 K (a) and a sample with a low concentration of defects obtained as a result of condensation on a substrate at 60 K (b). It can be seen that the shape of the M-band for the more perfect sample is mainly determined by the component M_2, which allows us to associate it with self-trapping in the regular lattice. The atoms displaced from the lattice sites along the direction ⟨110⟩ come closer and form a molecular center Ar_2^* of central-symmetry configuration with a symmetry D_{2h}.[10] As the defect concentration increases, the low-energy component M_1 begins to dominate and serves as an indicator of defects in the sample. Such an interpretation is in accord with the results of experiments on selective photoexcitation,[13] which indicate that the component M_2 is excited in the absorption band of the bulk excitons, while the component M_1 is excited below the bottom of the exciton band. Note that the presence of two components in the emission band M, one of which is connected with defects, is a characteristic feature of the luminescence spectrum of cryocrystals of all heavy inert gases.[3-6]

Experiments on the excitation of solid argon by slow electrons, carried out at 5 K, reveal a transformation of the M-band upon an increase in the irradiation dose, i.e., in time t. The nature of the transformation depends on the structure of the original sample, its thickness, and the impurity concentration. The intensity of the low-energy component M_1, which is connected with the defects, increases in contrast to the intensity of the component M_2 (Fig. 2). Note that samples with low concentration of the initial pre-irradiation defects show an increase in the intensity of both components (Fig. 2b). Upon an increase in the number of structural as well as chemical electron traps in samples (e.g., oxygen impurity), the time dependence of the intensity of the M_2 component becomes weaker (Fig. 2a). The contribution of the pre-radiation defects is determined by extrapolating the dependence on irradiation dose to t=0. An increase in the "defect" component M_1 with irradiation time in the stationary state points toward the emergence and accumulation of stable structural defects in samples. The accumulation of defects upon a low-temperature excitation of samples in "subthreshold" regime allows us to state with confidence that excitation of the electron subsystem is the main stimulating factor. This conclusion was confirmed in experiments on the irradiation of solid argon by synchrotron radiation in the en-

ergy range 5–40 eV.[14] Since the energy of electron excitations is transformed into the kinetic energy of motion of atoms over a limited region of the lattice near the trapping center for the excitation, we can rule out the formation of three-, two-, or one-dimensional defects. In this case, only point radiation defects, viz., Frenkel pairs (interstitial atoms and vacancies) may emerge in the bulk of the crystal.

Let us consider the possible channels of energy relaxation of electron excitations, which may lead to electron-induced defect-formation. As the crystal is excited in the region of interband transitions above E_g (E_g is the forbidden band gap), charged states, viz., electrons (e^-) and holes (Ar_h^+) emerge in the crystal and may be self-trapped in the regular lattice (self-trapping of a hole or STH) with the release of energy ΔE^+(STH):

$$Ar^0 + Ar_h^+ \rightarrow Ar_2^+ + \Delta E^+(\text{STH}). \quad (1)$$

The dissociative recombination (DR) of self-trapped holes (Ar_2^+) with electrons is also accompanied by the release of energy ΔE(DR) which may be spent on the creation of structural distortions:

$$Ar_2^+ + e^- \rightarrow Ar^0 + Ar^* + \Delta E(\text{DR}). \quad (2)$$

The population of exciton states (Ar_{ex}^*) with subsequent self-trapping leads to the formation of the states of molecular (Ar_2^*) and atomic (Ar*) types (states M-STE and A-STE, respectively). Self-trapping is accompanied by the liberation of energy ΔE^*(M-STE) during the formation of a molecular center and ΔE^*(A-STE) during formation of an atomic center. The corresponding reactions have the form

$$Ar^0 + Ar_{ex}^* \rightarrow Ar_2^* + \Delta E^*(\text{M-STE}); \quad (3)$$

$$Ar_{ex}^* \rightarrow Ar^* + \Delta E^*(\text{A-STE}). \quad (4)$$

The final stage of reactions (3) and (4) is accompanied by a radiative decay of the centers, the decay (D) of a molecular (excimer) center is accompanied by the liberation of a considerably large amount of energy ΔE^0(D) in the lattice:

$$Ar_2^* \rightarrow Ar^0 + Ar^0 + \Delta E^0(\text{D}); \quad (5)$$

$$Ar^* \rightarrow Ar^0 + \Delta E^0. \quad (6)$$

Reactions (5) and (6) describe the obtained radiative transitions of molecular and atomic centers to the ground state. Estimates of energy liberation to the lattice in relaxation channels leading to the formation of molecular centers show that $\Delta E^+(\text{STH}) = 1.38$ eV, $\Delta E(\text{DR}) = 1.38$ eV, $\Delta E^*(\text{M-STE}) = 0.9$ eV, and $\Delta E^0(\text{D}) = 0.56$ eV[15] exceed the binding energy $\varepsilon_b = 88.8$ meV.[16] According to the energy criterion,[17] the defect-formation is possible in reactions (1)–(5). A verification of the assumption about the possibility of the emergence of structural distortions at the first stage of reaction (3) shows that the formation of centrally symmetric configuration D_{2h} of a self-trapped exciton is not accompanied by an irreversible lattice distortion, since the M_2-component does not exhibit a direct relation with the defects and dominates in spectra of samples with a more perfect structure. In all probability, the absence of defect-formation at this stage is due to the violation of the time criterion,[17] i.e., the time τ_{df} of defect-formation is larger than the exciton self-trapping time τ_{STE}. At the same time, a redistribution of intensities of M_1- and M_2- components associated with emission from the lowest states of molecular centers points toward the participation of two-center self-trapping channel for excitons in defect-formation. We assumed that like in cryocrystals of heavy inert elements Xe[3,4] and Kr,[5,6] the formation of defects in Ar also occurs at the second stage of reaction (3) during the lifetime of the excited state and after radiative decay of the center Ar_2^* during a transition to the repulsive part of the ground state energy level (reaction 5). According to the model proposed by us in Ref. 6, the most probable pattern of defect-formation is the displacement of an excited molecular center Ar_2^* in the direction ⟨110⟩ followed by a reorientation along the direction ⟨100⟩ as indicated by the data on structural analysis of point defects in x-ray-irradiated argon.[18] Taking into consideration the data on stable configurations of interstitial atoms in the cryocrystals of inert elements,[18] it can be assumed that the configuration of defects emerging in this channel corresponds to a Frenkel pair, viz., an interstitial atom with a dumb-bell configuration ⟨100⟩ and a vacancy. Note that two components corresponding to absorption from the metastable state $^3\Sigma_u^+$ were registered in the transient absorption spectrum of electron-irradiated solid Ar.[19] The energy gap between them is 0.15 eV and is close to the gap between M_1- and M_2-components of the luminescence spectrum (0.18 eV). It is quite likely that the transient absorption spectrum components correspond to the transitions of molecular center Ar_2^* in the regular lattice and at the defect position.

Apart from neutral structural defects, we also discovered piles of charge centers, viz., electrons in various traps,[9] and self-trapped holes Ar_2^+. Self-trapping of holes in Ar was predicted theoretically,[20] and its experimental manifestation was associated with the low mobility of positive charge carriers. Such centers must be quite stable owing to a high binding energy.[20] However, interaction with slow electrons must lead to recombination of hole centers (reaction 2) and their relaxation to the exciton states followed by self-trapping (reaction 3). There are several factors in favor of the considerable contribution from the recombination channel for self-trapped holes in populating the lowest states of self-trapped excitons responsible for the M-band emission. In the first place, we note that the dose dependences of the M-band component intensities are highly sensitive to the concentration of electron traps in the sample. We considered the effect of two types of traps, viz., the deep traps connected with the oxygen impurity, and the shallow structural traps. Both types of traps effectively capture slow electrons whose participation is essential for recombination processes. Filling of deep traps led to irreversible changes in the dose dependences. Electrons from shallow traps were released as a result of heating of the sample. Cooling followed by irradiation again led to the population of shallow traps and reproduction of dose dependences. Suppression of the recombination processes upon an increase in the concentration of electron traps was accompanied by a decrease in the growth rate for the component M_2 as illustrated in Fig. 2a. Note that the band

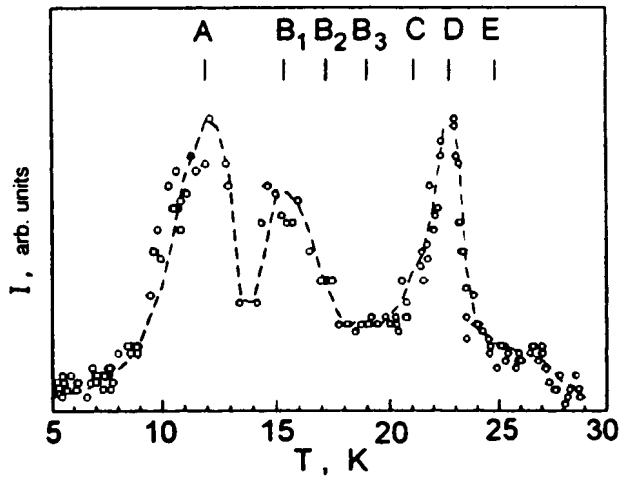

FIG. 3. Argon thermoluminescence in the region of M-band after irradiation of the sample by an electron beam with $j_e = 1$ mA/cm^2 at 5 K during 15 min. The positions of the peaks on the thermal excitation curve are shown at the top.[9]

M is connected with the emission band H(6.2 eV) from the ionic molecular states of argon,[21] one of whose population channels is the excitation of self-trapped holes. Introduction of deep electron traps led to an increase in the intensity of the H-band in the spectrum and to attenuation of the M-band. The discovery of recombination glow in the region of M-band as a result of thermally stimulated liberation of electrons from the traps serves as a direct evidence of the formation of self-trapped holes (Fig. 3). The peaks of the glow curve recorded at an energy 9.7 eV in the region of the M-band repeat the shape of the integral (over spectrum) glow curve.[9] Thermoluminescence was detected after a long time following the irradiation cycle, thus pointing toward the stability of self-trapped holes at low temperatures. An analogous recombination glow in the region of the M-band was observed earlier in solid Kr.[22] The mechanism of participation of charged states in defect-formation at the microscopic level can be determined only after detailed investigations. Note that the ionic states in atomic cryocrystals play a significant role in the process of electron-transition-induced desorption of particles from the surface,[23-27] which can be treated as an analog of the defect-formation process.

CONCLUSION

Formation and accumulation of neutral and charged defects was detected by the cathode-glow and thermoluminescence techniques in the vacuum ultraviolet region in solid argon irradiated by slow electrons at low temperatures. The effect of pre-irradiation defects and oxygenous impurities (which served as electron traps) on the transformation of molecular luminescence band with increasing irradiation dose was studied. The self-trapped holes were found to be stable at low temperatures.

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[1] E. V. Savchenko, Yu. I. Rybalko, and I. Ya. Fugol', Pis'ma Zh. Eksp. Teor. Fiz. **42**, 210 (1985) [Sov. Phys. JETP Lett. **42**, 256 (1985)].
[2] E. V. Savchenko, Yu. I. Rybalko, and I. Ya. Fugol', Fiz. Nizk. Temp. **14**, 399 (1988) [Sov. J. Low Temp. Phys. **14**, 220 (1988)].
[3] I. Ya. Fugol', A. N. Ogurtsov, O. N. Grigorashchenko, and E. V. Savchenko, Fiz. Nizk. Temp. **18**, 44 (1992) [Sov. J. Low Temp. Phys. **18**, 27 (1992)].
[4] E. V. Savchenko and A. N. Ogurtsov, Ukr. Fiz. Zh. **38**, 108 (1993).
[5] I. Ya. Fugol', E. V. Savchenko, A. N. Ogurtsov, and O. N. Grigorashchenko, Physica B **190**, 347 (1993).
[6] E. V. Savchenko, A. N. Ogurtsov, O. N. Grigorashchenko, and S. A. Gubin, J. Chem. Phys. **189**, 415 (1994).
[7] A. A. Radtsig and B. M. Smirnov, *Reference Data on Atomic and Molecular Physics*, Springer, Berlin, 1985.
[8] A. V. Chadwick and H. R. Glyde, in *Rare Gas Solids*, Academic Press, London, New York (1977).
[9] A. N. Ogurtsov, E. V. Savchenko, O. N. Grigorashchenko *et al.*, Fiz. Nizk. Temp. **22**, 1205 (1996) (to be published).
[10] E. V. Savchenko and I. Ya. Fugol', in *Cryocrystals* (ed. by B. I. Verkin and A. F. Prikhot'ko) [in Russian], Naukova Dumka, Kiev (1983).
[11] E. V. Savchenko, I. Ya. Fugol', O. N. Grigorashchenko *et al.*, Fiz. Nizk. Temp. **19**, 586 (1993) [Low Temp. Phys. **19**, 418 (1993)].
[12] G. Zimmerer, *Excited State Spectroscopy in Solids*, North-Holland, Amsterdam (1987).
[13] A. Ogurtsov, M. Runne, A. Karl *et al.*, HASYLAB Ann. Report 1995, p. II-77, DESY, Hamburg (1996).
[14] A. Ogurtsov, M. Runne, A. Karl *et al.*, HASYLAB Ann. Report 1995, p. II-79, DESY, Hamburg (1996).
[15] D. C. Lorents, Physica C **82**, 19 (1976).
[16] M. L. Klein and J. A. Venables (Eds.), *Rare Gas Solids*, Vol. 1 and 2, Academic Press, Now York (1976-77).
[17] Ch. B. Lushchik and A. Ch. Lushchik, *Decay of Electron Excitations Accompanied by Defect Formation in Solids* [in Russian], Nauka, Moscow (1989).
[18] R. Balzer, O. Kroggel, and H. Spalt, J. Phys. C **13**, 6349 (1980).
[19] T. Suemoto and H. Kanzaki, J. Phys. Soc. Jpn. **46**, 1554 (1979).
[20] K. S. Song and R. T. Williams, *Self-trapped Excitons*, Springer-Verlag, Berlin, Heidelberg (1993).
[21] O. N. Grigorashchenko, S. A. Gubin, A. N. Ogurtsov, and E. V. Savchenko, *J. Electr. Spectr. Relat. Phenom.* **79**, 107 (1996).
[22] M. Kirm and H. Niedrais, J. Luminesc. **60,61**, 611 (1994).
[23] C. T. Reimann, W. L. Brown, and R. E. Johnson, Phys. Rev. B **37**, 1455 (1988).
[24] D. Menzel, Appl. Phys. A **51**, 163 (1990).
[25] G. Dujardin, L. Hellner, L. Philippe *et al.*, Phys. Rev. B **48**, 14529 (1993).
[26] A. Hoshino, T. Hirayama, and I. Arakawa, Appl. Surf. Sci. **70/71**, 308 (1993).
[27] G. Rocker, P. Feulner, R. Sheuerer *et al.*, Physica Scripta **41**, 1014 (1990).

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