



Electronically induced defect formation in Xe-doped solid Kr

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Abstract

Lattice defect formation induced by excitation of excimer-type molecular centers in the Kr matrix is studied by the luminescence VUV spectroscopy method. The samples are excited by slow electrons. It is established that the trapping of electronic excitations in the regular lattice regions produces the formation of permanent point defects. The experimental data on the “ground state” mechanism of defect formation associated with radiative decay of electronic excitations and some supporting evidence for the existence of an “excited state” mechanism are obtained. The efficiency of the latter mechanism is found to correlate with the lifetime of electronic excitation of the molecular centers. This mechanism is shown to be electronically thermal. A model of defect creation and stabilization in the excited state is proposed which consists in that the molecular center is displaced to a noncentrosymmetric position followed by its reorientation. The model parameters for the center Kr_2^* are estimated.

1. Introduction

Rare gas solids (RGS) are widely used as inert matrices to isolate atoms, molecules, radicals and ions and to study chemical reactions [1]. The renewed interest in this subject has been stimulated by development of a powerful XeF-doped solid Ar excimer laser [2] and advances in modern photochemistry [3–6] which are based on the excitation of initial and intermediate products. The electronic excitation energy in a crystal relaxes by radiative and nonradiative transitions. The nonradiative transitions are commonly followed by small (as compared to the lattice parameter) oscillations of a great number of atoms, i.e. by a heat release. There exists, however, a peculiar type of nonradiative transitions that features large displacements of a small number of atoms accompanied by the creation of lattice defects.

This paper deals with the electronically induced permanent lattice defect formation (LDF), when matrix or impurity atoms are displaced from their sites to

defect positions. The inclusion of this phenomenon is of fundamental importance in elucidating the mechanisms of mass diffusion, desorption and solid-phase chemical reactions. The basis for the physics of the phenomenon is the electron–nuclear subsystem transport of energy. The mobile band excitations (free electrons, holes, excitons) cannot provoke immediately a lattice destruction because their lifetime at a lattice site $\tau_s \sim B^{-1}$ (B is the halfwidth of the corresponding band) is much less than the characteristic time of atomic displacement, $\tau_D \sim \omega_D^{-1}$ (ω_D is the Debye frequency). On trapping, the situation changes essentially and τ_s becomes equal to the total lifetime τ_e of the trapped electronic excitation in the crystal. If the energy ΔE released in the vicinity of the trapped excitation on its decay or transformation is higher than the threshold energy E_d essential for the atom to be displaced to an interstitial position, a stable long-lived defect may be generated in the lattice. It should be noted that only point defects are formed on electronic excitation trapping. In the sample bulk these are Frenkel pairs (vacan-

cies and interstitials) with different separations between the components of genetically coupled pairs. Thus, the energy and time criteria of the electronically induced LDF are [7]

$$\Delta E > E_d, \quad (1)$$

$$\tau_s \gg \tau_D. \quad (2)$$

The efficient processes of exciton self-trapping [8–11] into atomic and molecular states accompanied by a considerable energy release to the lattice contribute to a manifestation of this channel of electronic energy dissipation in RGS.

The electronically induced LDF was first observed spectroscopically in a neon matrix containing impurities of heavy rare-gas atoms [12,13]. It was found that permanent lattice defects develop on excitation of both the electronic subsystem of an impurity and the matrix. Other atomic impurities (C, O, N) in the Ne matrix were studied in Refs. [14,15]. The excitation trapping by atomic centers into large-radius states was shown to produce a build-up of permanent point defects in the sample. The mechanism of LDF proposed in Ref. [16] consists in that a microcavity is formed around the atomic center due to predominant repulsive forces. A severe local deformation around the microcavity relaxes through the formation of Frenkel pairs. This mechanism is typical of cryocrystals of light rare-gas elements possessing a negative electron affinity. The radiation-induced formation of Frenkel pairs was observed in cryocrystals of heavy rare-gas elements by using X-ray structure analysis [17] and absorption spectroscopy [18]. The inelastic nature of LDF on electronic excitation of Xe and Kr cryocrystals was first substantiated in Refs. [19–21], where the samples were excited by slow electrons of an energy insufficient to displace an atom from the lattice site by elastic collisions (under “subthreshold” excitation). It was found that the self-trapping of triplet excitons into excimer-type molecular states (M-STE) is a stimulating factor [20–23]. This was verified by experimental data on selective excitation of Xe to the lowest exciton band $\Gamma(3/2)$, $n=1$ [24]. Since both intrinsic and extrinsic self-trappings are possible, it remains to be seen where the LDF occurs – in the regular lattice areas or at the initial preradiation defects. Besides, we must find the answer to the question at which stage of the self-trapping to the molecular states the defects are formed. In

Ref. [17] it has been suggested that the defects are formed after the radiative decay of excimer molecules. The theoretical consideration [16] also implies the possible formation of permanent lattice defects in the excited state. Low-temperature luminescence spectra of M-STE in solid Xe [20] and Kr [21] display spectroscopic manifestations of two mechanisms of permanent LDF induced by self-trapping of excitons into molecular states. One of these is associated with excimer dissociation after radiative decay (a repulsive “ground state” mechanism). It is supposed that the second mechanism of LDF is realized in an excited state (an “excited state” mechanism). Based on qualitative analysis of radiation-induced modification in the luminescence spectra, a simple model was proposed which consists in a displacement of the excited molecular center from the centrosymmetric position in the lattice by overcoming of the potential barrier.

The paper is concerned with successive consideration of the possibility of LDF at all stages of electronic excitation relaxation of molecular centers. Particular attention is given to the “excited state” mechanism of LDF. The object of the experiments is a Kr matrix doped with Xe which is a substitutional impurity. The difference in atomic radius between Kr and Xe is modest, so the lattice is deformed around the impurity with no change of the number of nearest neighbors. The exciton self-trapping and the excitation trapping by the impurity centers in this system cause Kr_2^* and Xe_2^* excimers and $(\text{XeKr})^*$ exciplex to be formed. The above centers served as probes to give information on distortion of the crystal lattice in the nearest surroundings. The radiation-induced changes in the luminescence spectra were studied under conditions that exclude a knock-on mechanism of LDF. To separate the LDF processes in the regular lattice areas, a series of measurements on samples with different content of initial defects were performed. Such a working temperature range was chosen which enabled us to eliminate the contribution of common thermally activated LDF in the unradiated regular lattice areas and separate thermally activated processes in the electronic excitation-distorted lattice. The effects of excited state radius and lifetime on LDF efficiency were studied. The effect of the first factor could be traced by comparing the radiation-induced changes in the spectra of Kr_2^* , $(\text{XeKr})^*$ and Xe_2^* . The internuclear separation, r_e , that corresponds to the minima of the lowest excited elec-

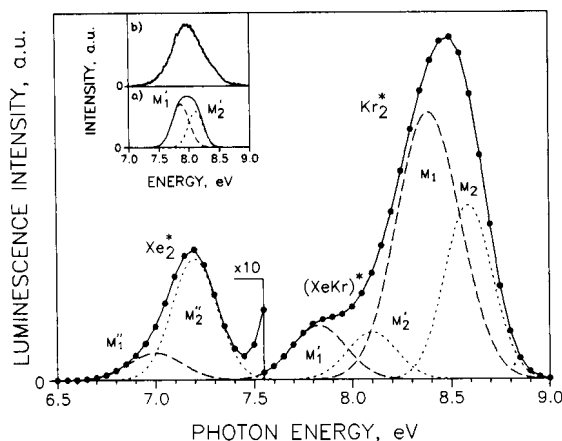


Fig. 1. The molecular luminescence spectrum of the Xe/Kr system. (—) Experiment. The bands obtained by decomposition of the luminescence spectrum into components: (---) defect components; (.....) emission components of the molecular centers in the regular lattice. In the inset compared are the emission bands of the molecular center (XeKr)*: (a) reconstructed by the data given in the paper; (b) measured in Ref. [31].

tronic states increases successively for the above centers: $r_e = 0.285$ nm for Kr_2^* [8], $r_e = 0.301$ nm for $(\text{XeKr})^*$ [25] and $r_e = 0.31$ nm for Xe_2^* [8]. The lifetime of the lowest triplet state of the excimer centers relative to radiation decay was varied by changing the sample temperature [11].

2. Experimental procedure

Spectroscopic study of Kr–Xe mixtures has some interesting features. Xe in the Kr matrix quenches the matrix luminescence very efficiently if the Xe content is higher than 0.1% [26]. Moreover, one can observe an effective exciton-induced diffusion for concentrations of $\sim 10^{-2}\%$ in the Kr–Xe system [27]. These factors limit the impurity content range to low concentrations. In our experiment we used krypton gas with 0.005% Xe to grow the samples. The polycrystalline samples were grown in a special cell attached to the substrate of the He cryostat [20], the cell separating the space where the crystal was grown from that of the experimental chamber. This made it possible to condense Kr under optimum conditions [28], at $T \approx 80$ K and $P \approx 10$ Pa, where one can obtain samples of excellent optical quality with a low initial content of defects.

The amount of defects in the samples could be changed by varying the condensation conditions: temperature, pressure and rate of deposition. The sample quality was controlled by the ratio of luminescence intensities of free and self-trapped excitons. For the most perfect samples the luminescence intensity of free excitons at the band maximum was comparable to that of the M–STE states. The measurements were carried out on samples ~ 1 μm thick.

The experiments were performed at temperatures ranging between 5 and 50 K where the concentration of thermodynamically equilibrium vacancies, $C_{0v} \sim \exp(-h/kT)$, was not higher than $C_{0v} \approx 10^{-9}$ at 50 K ($h = 0.086$ eV/mol is the enthalpy of vacancy formation in Kr [29]) and decreased exponentially with temperature. The samples were excited by an electron beam of energy $E_e \approx 1$ keV insufficient to form defects by elastic collisions. The threshold electron beam energy, E_e^{thr} , above which the lattice atom is displaced from the site due to the electron–atom head-on collision can be given as follows:

$$E_e^{\text{thr}} = \varepsilon_c \frac{(m + M_A)^2}{mM_A}, \quad (3)$$

where m and M_A are the electron and atom masses, respectively, ε_c is the bond energy equal to 0.115 eV in Kr [8]. Estimation by (3) gives $E_e^{\text{thr}} \approx 18$ keV. The irradiation was performed under steady-state conditions, permitting us to detect permanent lattice defects. We used a method of sensitized luminescence when the excitation energy is transferred to the defects by free excitons, followed by “extrinsic” self-trapping. The associated components of the molecular luminescence spectrum were resolved in preliminary experiments (Section 3.1). The luminescence spectra were analyzed with a vacuum monochromator. The signals were recorded with a solar-blind photomultiplier operating in a single quantum mode. The experiment is described in detail in Ref. [20].

3. Results and discussion

3.1. Luminescence spectra

The typical low-temperature spectrum of molecular luminescence taken from the samples grown in the cell is shown in Fig. 1. Dominant in the spectrum is a lumi-

Table 1
Parameters of molecular luminescence spectrum

Center	Component	Position (eV)	Halfwidth Δ (eV)
Xe_2^*	M_1''	7.0	0.31
	M_2''	7.23	0.27
$(\text{XeKr})^*$	M_1'	7.85	0.33
	M_2'	8.1	0.29
Kr_2^*	M_1	8.38	0.37
	M_2	8.6	0.28

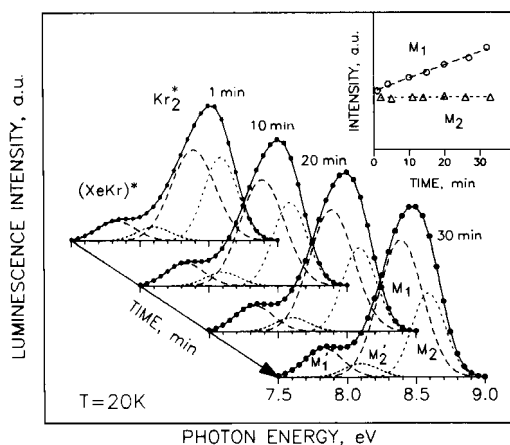


Fig. 2. Modification in the luminescence spectrum in the 7.5–9.0 eV region with exposure time (dose). The inset shows the dose dependences of the components M_1 and M_2 of the luminescence band of Kr_2^* .

nescence band of the centers of Kr_2^* in the region of 8.5 eV. The red shoulder nearby 8 eV is due to the radiative decay of the $(\text{XeKr})^*$ exciplex. The low-energy region of the spectrum displays a weak band which is assigned to the emission of the dimers Xe_2^* in the matrix. As suggested in Refs. [24,26,27], the luminescence band of the matrix is contributed by the luminescence of the center Xe^* ($^3\text{P}_{1,2}$). The measurements of the concentration dependence of the luminescence spectra of the system Xe/Kr [26,27] demonstrate that the contribution of Xe^* luminescence to the total contour of the molecular luminescence band of self-trapped excitons of the Kr matrix is negligible for a Xe content of about $10^{-3}\%$. It should be noted that the luminescence intensity of the matrix is not monotonically dependent on Xe concentration. For low concentrations up to $C \approx 5 \times 10^{-2}\%$ it increases but then decreases as

the Xe content is further increased. The increase in the luminescence intensity of the matrix for low concentrations can be attributed to the free exciton scattering by the impurity centers, stimulating self-trapping [26]. The experiments performed on samples with different amount of defects revealed that all the bands were not elementary. Each of the bands can be well approximated by two Gaussians (two components in the Kr_2^* emission were identified in [30]). The components with subscript "2" (M_2, M_2', M_2'') are dominant in the luminescence of more perfect samples. The spectra of samples with a great number of initial defects are determined mainly by components with subscript "1". This suggests that maxima "2" are due to trapping by the host and the impurity molecular centers in the regular lattice regions while maxima "1" are due to trapping that occurs with the lattice imperfections involved.

The observed bands of the excimer-type centers are identified as $^1,^3\Sigma_u^+ - ^1\Sigma_g^+$ transitions. The $(\text{XeKr})^*$ exciplex emission arises from the decay of the lowest excited molecular states $1(^3\text{P}_2)$ and $0^+(^3\text{P}_1)$ to a repulsive part of the $0^+(^1\text{S}_0)$ state. The positions of components "1" and "2" and their halfwidths estimated by comparing the spectra of samples with different amount of defects are listed in Table 1 for $(\text{XeKr})^*$, Kr_2^* and Xe_2^* .

This spectral band deconvolution is in good agreement with the data given in Ref. [31] where the application of selective excitation has made it possible to produce a luminescence of $(\text{XeKr})^*$ free of superimposition of the matrix molecular continuum. This is illustrated in the inset of Fig. 1 where the resulting curve of components M_1 and M_2 of the stationary luminescence spectrum measured by us is compared to the spectrum of a slow component of the center $(\text{XeKr})^*$ [31]. Maximum position 7.99 eV and halfwidth 0.62 eV (curve b) from Ref. [31] are close to our values (curve a). The same is true for the molecular luminescence band of Kr_2^* .

3.2. Dose dependences of spectra

In order to examine the LDF processes at different stages of excitation energy relaxation of the molecular centers, we studied the behaviour of spectral characteristics of Kr_2^* , $(\text{XeKr})^*$ and Xe_2^* on controllably irradiated samples with small contents of initial defects. Transformation of the luminescence bands of the cen-

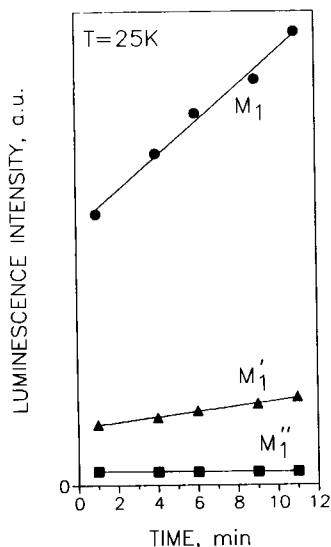


Fig. 3. The dose dependences of component "1" for the molecular centers Kr_2^* , $(\text{XeKr})^*$ and Xe_2^* – M_1 , M_1' and M_1'' , respectively.

ters Kr_2^* and $(\text{XeKr})^*$ with exposure time is shown in Fig. 2. A distinct increase in the intensity of components "1" for Kr_2^* and $(\text{XeKr})^*$ can be observed with increasing exposure time (Fig. 3). As for components "2", they remain unchanged but the free exciton luminescence intensity decreases. The test experiments demonstrate that the exposure of the samples in a vacuum without irradiation does not result in any redistribution of the component intensities. For the centers Xe_2^* , the M_1 and M_2 intensities are independent of exposure time within the accuracy of the experiment. The increase in the intensity of "defect" components "1" with dose suggests that the defects are accumulated. The defects are Frenkel pairs, as in Xe [23]. It should be noted that the defect creation is stimulated by exciting the electronic states of both the host and the impurity excimer-type centers in the matrix.

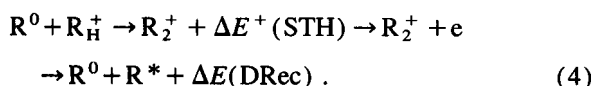
Considering that defects can be formed both in the regular lattice and in different initial lattice imperfections, we performed a series of measurements of dose dependences on samples with different contents of initial preradiation defects. In polycrystalline RGS there are grain boundaries, twins, stacking faults, dislocations and vacancies. And what is more, the main preradiation defects are vacancies [29]. The spectra of imperfect samples consisted mainly of component "1" characterized by a considerable inhomogeneous broad-

ening. Increase in exposure time caused no increase in their intensity. We observed only a broadening of the band. It appears very likely that in samples of high initial defect content these defects undergo a radiation-induced transformation. Let us estimate a possible contribution of vacancies to the LDF processes. The impurity Xe atoms produce, on growing, no "impurity–vacancy" complexes because of a small difference in atomic radii. The vacancy diffusion coefficient, $D_v = D_0 \exp(-Q/kT)$, is small and for $T = 50$ K it is $D_v \approx 10^{-22}$ cm²/s when taken into account that the activation energy of diffusion, Q , is equal to that of vacancy migration (0.22 eV/mol [29]). The time τ_v of arrival of a vacancy at the impurity center is given by [13] $\tau_v = (4\pi d N_0 C_v D_v)^{-1}$ ($d = 0.399$ nm is the nearest-neighbour distance in the Kr lattice, N_0 is the number of atoms per unit volume). If we assume that the vacancy concentration $C_v = C_T \sim 10^{-3}$ is frozen in the crystal on condensation, then for $T = 50$ K $\tau_v \sim 10^7$ min, much higher than the exposure times. The coefficient of diffusion of the Xe atoms in the Kr matrix that proceeds by the vacancy mechanism [32] and is estimated by using the data of Ref. [29] amounts to $D_{\text{im}}^v \sim 10^{-30}$ cm²/s at $T = 50$ K. It follows that the vacancy mechanism of the impurity atom diffusion cannot produce a substantial redistribution of these atoms through the sample with time. The exciton-induced diffusion [27] also gives no rise to a dimerization for the impurity concentration of the order of 10^{-3} . Indeed, the estimations made with the use of the coefficient of exciton-induced diffusion of the Xe atoms in the Kr matrix determined in Ref. [27], $D_{\text{im}}^* \sim 10^{-16}$ cm² s⁻¹, demonstrate that covering a distance equal to the linear separation between the impurity atoms requires no less than 200 min, which is more than the typical exposure times. That is why we did not observe an increase in the luminescence band intensity of Xe_2^* . So, we can state with assurance that in our case where the initial defects are "frozen" and produce no complexes with the impurity atoms the processes of LDF stimulated by excitation of the electron subsystem of the host and the impurity centers in the regular lattice are observed in the most perfect samples.

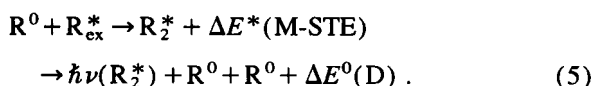
3.3. Temperature effects and mechanisms of lattice defect formation

For an excitation energy higher than the energy of the forbidden band, E_g , there appear charged states in

the crystal, viz., electrons (e) and holes (R_H^+) which can be self-trapped in the regular lattice attended by the energy release ΔE^+ (STH). Dissociative recombination of self-trapped holes (R_2^+) with electrons is also followed by the energy release ΔE (DRec). This can be given by the reaction



Here R^* and R^0 are the atoms in the excited and the ground state, respectively. Population of the exciton (R_{ex}^*) states of Kr, followed by self-trapping, gives rise to a generation of molecular R_2^* centers (M-STE states). The exciton self-trapping is accompanied by the energy release ΔE^* (M-STE) to the lattice. The corresponding reaction is of the form



Here $\hbar\nu(R_2^*)$ are the radiative transitions of the molecular center to the ground state. At the final stage of reaction (5) the centers R_2^* decay into two atoms in the ground state, attended by the energy release ΔE^0 (D) to the lattice. In view of the high quantum yield of luminescence the processes of defect formation under nonradiative decay of the excited molecular states can be neglected.

The lowest excited electronic state of the matrix which is populated in the course of energy relaxation is the M-STE state. It is precisely the self-trapping into the M-STE state that is the factor which stimulates the defect formation. Taking into account the fact that the excitation is transferred to the impurity centers by the matrix free excitons [26], the electronically induced LDF in this case may be treated with due regard for only the trapping into the lowest molecular states similar to the reaction (5). The estimations of energy release made with the use of spectral data and those on potential curves of molecular centers [8–11] show that the energy criterion (1) of LDF is met for each of the centers both at the stage of excitation trapping and after its decay.

We now consider successively the possibility of LDF at different stages of exciton energy relaxation. Test of the suggestion that the defects are generated at the first stage of self-trapping during formation of the center Kr_2^* of symmetry D_{2h} has demonstrated that this stage

of self-trapping is followed by a reversible distortion of the lattice. Its associated component M_2 has no relation to the defects and is dominant in the molecular luminescence spectra of more perfect samples. Despite the fact that the energy criterion (1) is fulfilled, the lack of LDF at this stage implies that the processes of atomic configuration rearrangement followed by transition of atoms to a stable defect position are not manage to occur in the self-trapping time τ_{STE} . Using the values of self-trapping velocity $\Gamma_{STE} \sim 10^9 \text{ s}^{-1}$ [24], we can roughly estimate the time τ_{df} of permanent LDF: $\tau_{df} > 10^{-9} \text{ s}$. Taking into account the high velocities of exciton trapping by the impurity centers in the Kr matrix [26] (according to Ref. [24] $\Gamma_{ET} \sim 10^9 \text{ s}^{-1}$) the first stage of trapping would be expected not to be followed by permanent LDF too. That is why the high-energy components of the impurity molecular luminescence, M_2' and M_2'' , also show no relation to defects and are dominant in the spectra of more perfect samples.

The origination of defects after radiative decay of the molecular centers under transitions to a repulsive part of the potential curve of the ground state followed by dissociation (by the ‘‘ground state’’ mechanism) is supposed in Refs. [17,18,20,21]. The concentration of permanent defects N_{df}^0 originated per unit time by the ‘‘ground state’’ mechanism is determined by the probabilities of self-trapping P_{STE} (or trapping at an impurity P_{TE}), radiative transition to the ground state P_r and transition from the ground state term to a local defect level P_0 :

$$N_{df}^0 \sim P_{STE} P_r P_0 . \quad (6)$$

In such a process there appear ‘‘hot’’ atoms in the lattice whose energy is much higher than the thermal one, and the transition to a local defect level with the probability P_0 is of athermic nature. In view of the high quantum yield of luminescence $P_r \sim 1$. Therefore, according to (6), the temperature dependence of the probability of defect formation by the ‘‘ground state’’ mechanism is given by $P_{STE}(T)$. Under our experimental conditions with electron irradiation the self-trapping occurs in the course of energy relaxation. In this case the branching of the excitons to the molecular states takes place in the vicinity of a self-trapping barrier top [33,34], and P_{STE} is weakly dependent on temperature.

The defects that remain in the lattice after excitation decay are detected with the participation of free excitons. In this case the temperature dependence of the

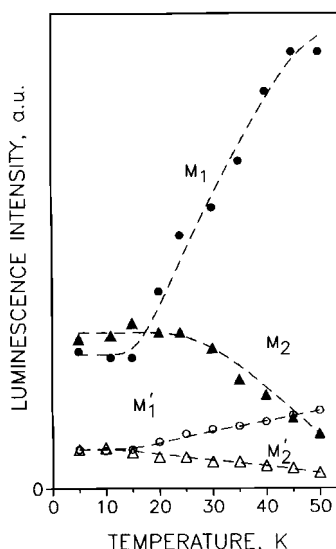


Fig. 4. The temperature dependences of luminescence intensity of the Kr_2^* and $(\text{XeKr})^*$ components.

defect component intensity is determined by the coefficient of their diffusion, $D_{\text{ex}}(T)$. As is shown in Ref. [34], $D_{\text{ex}}(T)$ remains unchanged in the region of low temperatures, up to a certain critical temperature $T_c = 30$ K for Kr, and then decreases by the relation $D_{\text{ex}}(T) \sim T^{-1}$. Thus, the change of the efficiency of detection of permanent defects with varying temperature can be given as follows:

$$\left. \frac{dI_1}{dt}(T) \right|_{\text{gs}} \sim C_1 \Phi(T_c - T) + \frac{C_2 \Phi(T - T_c)}{T}, \quad (7)$$

where C_1 and C_2 are the scale factors; $\Phi(x)$ is the asymmetric singular step function ($\Phi(x) = 1$ for $x > 0$, $\Phi(x) = 0$ for $x \leq 0$). The weak temperature dependence of the defect accumulation rate in the temperature range of 5 to 15 K for Kr [21] is interpreted by us as a manifestation of the “ground state” mechanism. The athermal behaviour of LDF in this temperature region establishes that the “ground state” mechanism is pure electronically induced in nature, i.e. the lattice rearrangement is accomplished only at the expense of released excitation energy. This interpretation is consistent with the observed correlation in the temperature behaviour of the components M_1 and M_2 (Fig. 4) in the 5–15 K range where the diffusion coefficient of free excitons remains unchanged. The same behaviour is typical of the components M_1' and M_2' of the lumines-

cence band of the center $(\text{XeKr})^*$. It should be noted that for the center Xe_2^* the intensity distribution in the band M'' is independent of exposure time within the accuracy of the experiment, i.e. a peculiar “cage effect” is observed. This fact, however, does not eliminate the LDF by the “ground state” mechanism because the defect configuration may be formed by the matrix atoms to which the Xe atoms transfer the energy upon relaxation through the repulsive term. Considering that the energy release ΔE^0 in this process is high, one would expect the emergence of a defect separated from the center by a distance larger than the nearest-neighbour distance. In particular, the formation of a crowdion is likely to occur. In this case the defects are supposed to show up in the luminescence band of the matrix. Note that addition of Xe to Kr matrix that involves an extra channel of free exciton trapping which competes with the trapping at defects causes the efficiency record of defect accumulation at low temperatures to decrease. This favours the view that for $T < 15$ K the defects are formed after decay of the excited molecular centers.

As is shown in Ref. [21], for Kr the rate of permanent defect accumulation which is determined by dI_1/dt is nonmonotonically dependent on temperature above $T = 15$ K (Fig. 5). Upon reaching the maximum at $T = 25$ K the rate of defect accumulation reduces and for $T = 50$ K becomes vanishingly small. One might suggest that the increase in dI_1/dt by (6) is related to that in the probability of self-trapping P_{STE} . But the intensity of the component M_2 which defines P_{STE} decreases monotonically with increasing temperature.

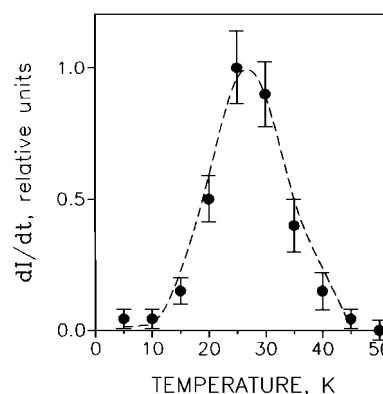


Fig. 5. The temperature dependences of defect accumulation rate. The dashed line shows the results calculated by (10).

So, we cannot treat the full set of experimental data by invoking merely the “ground state” mechanism.

From our observation of the two components in the luminescence spectra of the molecular centers, it might be assumed that in addition to the centrosymmetric configuration of the M-STE which is metastable, there exists a lower-energy noncentrosymmetric one. The severe anisotropic distortion of the lattice that accompanies the self-trapping is evidence of a latent anisotropy [35] and causes the instability to the transition of the excited molecular center to the noncentrosymmetric position. Considering that both of the components M_1 and M_2 are observed simultaneously in the luminescence spectrum, it is believed that the noncentrosymmetric configuration lying in another sheet of the adiabatic potential is separated from the centrosymmetric one by a barrier H_{dc} . We assume that the conversion to the noncentrosymmetric state occurs by activation overcoming of the barrier with the probability $P_{dc} \sim \exp(-H_{dc}/kT)$ [21]. For a face-centered cubic lattice, the noncentrosymmetric configuration is most likely to be formed through the displacement of the self-trapping center along the molecular bond at which the excitation is concentrated (Fig. 6c). In this case the symmetry of the M-STE is lowered from D_{2h} to C_{2v} .

To gain a better insight into the “excited state” mechanism of LDF, we consider now the temperature dependences of defect component intensity, $I_1(T)$, and defect accumulation rate $dI_1(T)/dt$. The behaviours of these curves similar at low temperatures become qualitatively different beginning with $T \approx 25$ K (Figs. 4 and 5). We suggest that this is due to the ratio redistribution between short- and long-lived Frenkel pairs. The curve $I_1(T)$ shows the variation in the defect concentration N_{df} with temperature ($I_1(T) \sim N_{df}$). The conditions of measurement of this dependence were chosen in such a way as to minimize the error due to the radiation-induced defect accumulation. Hence, one may think that $I_1(T)$ at each point contains both the contribution of pre-irradiation defects which remains unchanged up to $T \approx 50$ K and that of defects formed in the excited state lifetime. In other words, $I_1(T)$ reflects the process of defect formation by the “excited state” mechanism, short-lived pairs being detected along with the stable ones. The processing of the curve $I_1(T)$ for the M_1 band in Fig. 4 gives the activation energy of the process $H_{dc} \approx 7.3 \times 10^{-3}$ eV. The dependence $dI_1(T)/dt$

reflects the variation in the rate of permanent defect accumulation ($dI_1(T)/dt \sim dN_{df}/dt$). The decrease in the defect accumulation rate under their generation at $T > 25$ K suggests that the formation of permanent lattice defects requires that the defects be stabilized.

Taking into account the calculations [36] by which the only stable form of an interstitial atom is the split $\langle 100 \rangle$ “dumb-bell” form, one might suggest that the defect stabilization occurs through the reorientation of the excited molecule (Fig. 6d). Thus, in the model proposed the radiation-induced defect is a Frenkel pair—the interstitial of “dumb-bell” configuration $\langle 100 \rangle$ and the vacancy. It should be mentioned that the component M_1 involves the contributions of both the displaced and reoriented molecular centers with the vacancy in the nearest environment. This results in a shift of the component M_1 against M_2 and in its broadening. The spectrum of transient absorption of solid Kr due to the ${}^3\Sigma_u^+ - {}^3\Pi_g$ transitions displays two bands with a separation of 0.16 eV [37] close to that between the components M_1 and M_2 (0.22 eV). It appears very likely that the splitting in the transient absorption spectrum induced by the electron beam excitation is associated with the transitions from the long-lived state ${}^3\Sigma_u^+$ of the molecular center in the regular lattice and at the defect position.

Note that the separation between the “dumb-bells” atoms in Kr [36] is 0.339 nm, only slightly greater than r_c of the molecular centers. Therefore, the Frank–Condon transition to the ground state is supposed to correspond practically to the transition of the center to the stable defect level with almost no change in the internuclear separation. In this case the electronic excitation disappears and “the memory” of it is retained in the lattice in the form of permanent defect. The model in question is in agreement with the results the paper [38] where the interstitials of such configuration were revealed by diffuse X-ray scattering method in irradiated RGS.

It is also interesting to estimate the size of the crystal region where the direct annihilation of genetically coupled Frenkel pairs is quite possible. For the elastic vacancy–interstitial atom coupling [39], using the potential [40]

$$U_{iv} = \frac{GV_i V_v}{r^3},$$

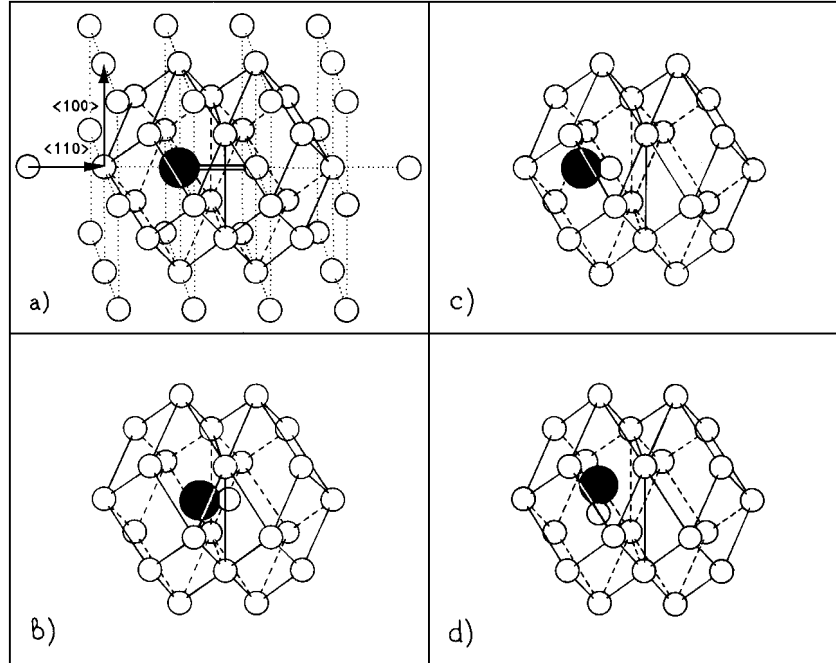


Fig. 6. Scheme of the “excited state” mechanism of defect formation. (a, b) The centro symmetric configuration formation; (c) the M-STE displacement from the centrosymmetric position; (d) the M-STE reorientation.

we can obtain a separation r_0 with the first stable position of the interstitial atom in the vacancy elastic field:

$$r_0 = \left(\frac{3GV_i V_v a}{U_m} \right)^{1/4},$$

where G is the shear modulus, V_i and V_v are the variations in the crystal volume caused by the interstitial atom and the vacancy; a is the lattice parameter; and U_m is the migration energy of a movable defect in the lattice. For krypton $a = 0.5646$ nm, $G = 1.158 \times 10^{10}$ dyne/cm² [41], $V_i = 0.75V_a$, $V_v = 0.92V_a$ [36] ($V_a = a^3/4$ is the volume per atom). Since for Kr the vacancy is more labile in the v-i pair [29], we set $U_m = Q$. In this case $r_0 = 0.594$ nm. Hence, the direct annihilation of the genetically coupled v-i pairs may occur only within the crystal unit cell. The application of the continuum elastic interaction of point defects is, to be sure, a very rough approximation, especially at distances of the order of the lattice constant, therefore the estimate of the instability region size is only tentative.

Further evidence for the proposed model is provided by the analytical treatment of the temperature behav-

our of the defect accumulation rate. The concentration of stable defects N_{df}^* originated per unit time by the “excited state” mechanism is determined by the probabilities of defect creation P_{dc} and defect stabilization P_{ds} :

$$N_{df}^* \sim P_{STE} N(\tau_{df}) P_{dc} P_{ds}. \quad (8)$$

The factor $N(\tau_{df})$ defines the variations in the excited state population in a time τ_{df} required for the permanent defect configuration to be formed. Assuming that P_{dc} and P_{ds} are described by the thermally activated processes in the electronic excitation-modulated lattice, we have

$$N_{df}^* \sim P_{STE} \exp\left(-\frac{\tau_{df}}{\tau_r}\right) \exp\left(-\frac{H_{dc} + H_{ds}}{kT}\right), \quad (9)$$

where H_{dc} and H_{ds} are the barriers for defect creation and stabilization, respectively. In accordance with (9) we may expect a sharp increase in the rate of defect formation with temperature. At low temperatures where the barrier H_{dc} is not transparent this mechanism is blocked and makes no contribution to the spectral distribution of intensity. The rate of defect accumula-

tion increases drastically with increasing temperature up to $T = 25$ K (Fig. 5).

The decrease in the radiative lifetime τ_r of the excited state with increasing temperature [11] results in a reduction of the permanent defect concentration at $T > 25$ K by (9). The short-lived pairs annihilate, not managing to be stabilized. It is just the factor $N(\tau_{df})$ that accounts for the competition of the processes of LDF and radiative decay of the M-STE centrosymmetric configuration. That is why we observed the decrease in defect accumulation rate with increasing temperature beginning with $T = 25$ K (Fig. 5).

Since the accumulation of long-lived defects, no matter what the mechanism of their formation, is detected with the participation of free excitons, the total variation in the M_1 intensity per unit time (as a function of temperature) is, in view of (7) and (9), of the form:

$$\begin{aligned} \frac{dI_1(T)}{dt} \sim & \left(C_1 \cdot \Phi(T_c - T) + \frac{C_2 \Phi(T - T_c)}{T} \right) \\ & \times \left[1 + C_3 \exp\left(-\frac{\tau_{df}}{\tau_r(T)}\right) \exp\left(-\frac{H_{df}}{kT}\right) \right. \\ & \left. - C_4 \exp\left(-\frac{H_{da}}{kT}\right) \right], \end{aligned} \quad (10)$$

where C_3 and C_4 are the scale factors; the effective value of the barrier is $H_{df} = H_{dc} + H_{ds}$. Note that τ_{df} also has the meaning of effective time which characterizes both defect creation and their stabilization. The last term in square brackets accounts for the contribution of thermally activated annealing of the stable radiation-induced defects. According to Ref. [42], the annealing temperature of the most movable long-lived radiation-induced defects in Kr is not under $T = 40$ K.

In Fig. 5 the dashed line shows the results calculated by (10). The calculated curve describes well the experimental dependences $dI_1(T)/dt$ for the following values of the parameters: $H_{df} = 1.12 \times 10^{-2}$ eV, $H_{da} = 1.29 \times 10^{-2}$ eV and $\tau_{df} = 4.2 \times 10^{-7}$ s. For $\tau_r(T)$ we used the data on temperature dependence of the $^3\Sigma_u^+$ state given in Ref. [11]. The long time τ_{df} is in agreement with our two-step model of LDF in the excited state attended by the defect stabilization.

The ‘‘excited state’’ mechanism in question is electronically thermal. The electronic excitation trapping into the predefect M-STE causes a severe lattice distortion, resulting in a considerable reduction of the LDF

threshold energy ($H_{df} \ll E_d \approx 0.6$ eV). In so doing, the thermally activated processes of LDF begin to show up at such low temperatures where the common thermal fluctuation LDF in undistorted lattice is ‘‘frozen’’.

It should be mentioned that the ‘‘excited state’’ mechanism of DF suggests anticorrelation in the behaviour of the components M_1 and M_2 of the molecular luminescence, as evidenced by the picture observed in the experiment for $T > 15$ K (Fig. 4). Typical regions of correlation and anticorrelation of the bands with subscripts ‘‘1’’ and ‘‘2’’ can be observed for Kr_2^* and $(\text{XeKr})^*$. The intensity distribution through the luminescence band of the center Xe_2^* remains unchanged within the 5–45 K temperature range. In the context of the model under consideration this result may be treated as a decrease in the probability of displacement to the noncentrosymmetric position with increasing impurity center radius. This suggestion is consistent with the behaviour of the dose curves for the above centers (Fig. 3). In the case of Xe_2^* a defect accumulation was not detected. Additional evidence for the model of LDF in the excited state is provided by the experiments with samples of high preradiation defect content described in Section 3.2. The electronic excitation trapping at the molecular centers near the lattice defects allows, from the outset, for the noncentrosymmetric configuration, i.e. the mechanism of LDF through the off-center displacement is precluded by the experimental conditions. In this connection the temperature behaviour of the components M_1 and M_2 changes qualitatively. The curves $I_1(T)$ and $I_2(T)$ show no redistribution in intensities of the M_1 and M_2 components which in more perfect samples is related to the overcoming barrier H_{dc} between centro- and noncentrosymmetric states. These dependences remain unchanged at $T = 5$ –45 K, and a typical dose dependence is not observed.

4. Summary

Reliable data have been obtained which suggest that permanent point defects are formed on trapping of electronic excitation at the molecular centers in the regular lattice regions of Kr. It has been shown that the local distortion of the lattice at the self-trapping of exciton into centrosymmetric configuration is reversible and corresponds to a predefect state. Additional evidence on the electronically induced defect formation under

radiative decay of excited excimer-type molecular centers has been obtained.

A model of the “excited state” mechanism of lattice defect formation has been developed which proposes that the defects are created and stabilized over the electronic excitation lifetime. There is experimental evidence indicating that short-lived Frenkel pairs make a contribution to the defect formation process. The microscopic model of the “excited state” mechanism consists in that the molecular center is displaced from the centrosymmetric position in the direction $\langle 110 \rangle$. On reorientation of the excited molecular center that follows the molecule axis is aligned with the $\langle 100 \rangle$ direction which coincides with that of the stable “dumb-bell” defect configuration in Kr. The main model parameters – the time of stable lattice defect formation and the necessary activation energy – have been estimated. The efficiency of defect formation in the excited state has been found to be determined by lifetime and temperature. To test the model the potential surface of the lowest M-STE state should be calculated.

It is interesting to note, that during the defect formation process the molecular center occupies a new radiation induced position in the lattice. In this regard the inclusion of the above mechanisms may appear to be useful in studying the radiation-induced mass diffusion in rare gas matrices and desorption. It is of interest that similar mechanisms of defect formation were observed in ionic crystals [7,43–45] with pronounced self-trapping effects.

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