THERMOLUMINESCENCE STUDIES OF UNDOPED LiF CRYSTALS. 2. THE OSCILLATOR-LIKE REGULARITY IN TRAP ACTIVATION ENERGIES

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The spectrum of activation energy of traps in undoped LiF crystals has been studied in detail by the method of thermoluminescence (TL) in the temperature range 80—500 K. The parameters of traps which are responsible for an intense complicated TL peak at 141 K have been studied in Part I. In this part, the energy spectrum of traps responsible for TL peaks in a higher-temperature range 150—450 K has been studied using the method of fractional curves. The activation energies of traps were found to form an oscillator-like series $E_n = \hbar\omega_{\mathrm{TL}} n$, with $\hbar\omega_{\mathrm{TL}} = 0.1617$ eV (1304 cm^{-1}). However, contrary to other crystals studied earlier, n can be both integer and half-integer. A possible origin of this regularity has been proposed. Basing upon the estimation of the statistical sum of oscillator states, a conclusion has been drawn that TL in LiF occurs through the tunneling of charge carriers from the excited vibration levels of traps to the excited states of luminescence centers. In this case, the trap activation energy is a multiple to the number of vibration quanta. But if the band mechanism is responsible for delivering a charge to the recombination center, the activation energy is described by the noticed oscillator formula with half-integer n's. This situation takes place in the case of destroying V_k-centers in LiF, as well as in all crystals studied by us earlier. Contrary to the Raman spectra of other crystals with complex lattices which were studied by us earlier, the corresponding Raman line $\hbar\omega_{\mathrm{RS}} = \hbar\omega_{\mathrm{TL}}$ was found neither in the LiF spectra nor in the spectra of other alkali halides (NaCl and KCl). Basing upon the correlation between the values of $\hbar\omega_{\mathrm{TL}}$ in LiF, NaCl, and KCl and the corresponding anion masses, we have suggested that this frequency corresponds to a local vibration mode of the halide molecule X_2^-.

1. Introduction

While investigating the energy spectra of traps in various crystals ($Ba_2NaNb_5O_{15}$ [1], $CsCdCl_3$ [2], $Y_3Al_5O_{12}$ [3], $ZnWO_4$ [4], $CdWO_4$ [5], Al_2O_3 [6], etc.), we have found that the energies of thermal activation of traps in them can be fitted by the oscillator-like regularity

$$E = \hbar\omega_{\mathrm{TL}} \left(n + \frac{1}{2}\right), \tag{1}$$

where n is an integer. Depending on the material, one (e.g., in AL_2O_3) to five (in $Y_3Al_5O_{12}$) series of lines were observed, with a relevant value of the vibrational quantum energy $\hbar\omega_{\mathrm{TL}}$ corresponding to each of them. Most of those values coincide with the energies of separate high-energy lines in the basic Raman spectrum of the first order ($\hbar\omega_{\mathrm{TL}} = \hbar\omega_{\mathrm{RSI}}$), while the others correspond to the energies of additional lines with low intensities which are not predicted by the theoretical group analysis (Raman lines of the second order, local modes, and lines prohibited to appear in Raman spectra by selection rules).

We became interested in the question whether a similar regularity exists for crystal structures with a simple cubic lattice, where vibration modes, being active in Raman spectra, are absent. The classical examples of such structures are alkali halide crystals (AHCs). Our research of NaCl crystals [7, 8] revealed the oscillator-like regularity (1) for them with the vibrational quantum energy $\hbar\omega_{\mathrm{NaCl}} = 0.112\,\mathrm{eV}$ $(904\,\mathrm{cm}^{-1})$ which considerably exceeds the energy of the single fundamental optical mode $(162\,\mathrm{cm}^{-1})$, being active in IR absorption; this means that this value corresponds to a certain local vibration mode.

LiF crystals were selected as the next objects to be searched for the oscillator-like regularity. Ions Li^+ and F^- have considerably smaller masses as compared to those of ions Na^+ and Cl^-. Therefore, the local frequency in LiF was expected to be substantially higher. The

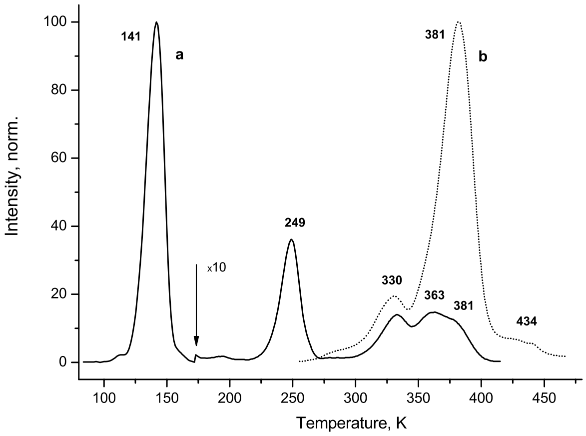

Fig. 1. Examination TL curves of LiF (see explanations in the text)

parameters of traps in LiF, which are responsible for the complex TL maximum at 141 K, were studied in the previous work [9]. These are quoted in the four top lines of the table. In this work, we studied the energy spectra of traps which are responsible for the TL peaks in the range 200—500 K. It turned out that the values of the trap energies in LiF satisfy the regularity which can be described by the generalized formula

$$E = \hbar\omega n, \tag{2}$$

Parameters of the TL spectrum lines of LiF: n is the quantum number, E_{exp} — experimental energy value, E_{calc} — energy calculated by formula (2), T_m — the temperature of the peak maximum, p_0 — the frequency factor

n	E_{exp}, eV	T_m, K	p_0, s^{-1}	E_{calc}, eV
		Our data		
1.5	0.25±0.01	113	3×10^9	0.243
2	0.323±0.003	∼146	5×10^9	0.324
2.5	0.404±0.001	141	1.3×10^{13}	0.405
3	0.48±0.005	165	1.9×10^{13}	0.486
5	0.815±0.001	249	9×10^{13}	0.810
6	0.968±0.007	330	1.2×10^{13}	0.972
7	1.135±0.003	360	2.3×10^{13}	1.134
7	1.138±0.003	381	2×10^{13}	1.134
8	1.292±0.006	434	1.7×10^{13}	1.297
		Data of work [14]		
9.5	1.530	443		1.539
10	1.611	483		1.620
10.5	1.695	508		1.701
11	1.792	533		1.782
12	1.962	558		1.944
13	2.095	558		2.106
13.5	2.186	618		2.187
14	2.272	643		2.268

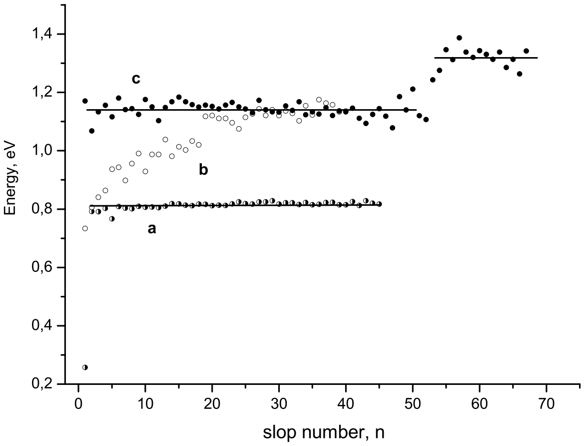

Fig. 2. Fractional glowing of TL peaks at $T = 249$ (a), 330 and 363 (b), and 381 and 434 K (c)

where n, contrary to the substances studied by us earlier, can accept both half-integer and integer values. Below, we propose a probable mechanism of such a regularity.

2. Equipment and Specimens

The studies were carried on in the temperature interval 200–500 K, using the undoped LiF crystal that had been used earlier for studying TL in the range 80—200 K [9]. Specimens were excited by X-ray radiation (BSV-2, W, 30 kV, 10 mA). The rate of their heating was 0.2 K/s. The linear growth of temperature and the data recording were controlled by a computer program.

The trap energies were determined by the fractional curve method. The experimental procedures and the method of data treatment were considered in detail in our previous works [5–8]. We did not use dosimetric-grade material LiF:Mg:Ti (TLD-100), because we had been convinced by many examples that, provided a significant concentration of impurities ($10^{17} - 10^{18}$ cm^{-3}), the trap energies cease to be discrete.

3. Experimental Results

In Fig. 1, curve a displays the TL spectrum of the researched specimen without previous heat treatment. Curve b obtained for the specimen previously annealed at 400 °C for 1 h and then rapidly cooled down to and excited at 20 °C contains a maximum at 434 K which was absent on the unannealed specimen. An increase of the intensity of separate maxima after the specimen having been treated thermally was used to enhance the sensitivity of fractional TL.

The results of calculating the energies from the fractional data are shown in Fig. 2. They are presented as the plots of the energy values versus the serial number of the fractional curve. The activation energies $E_{\rm exp}$ were determined as the ordinates of the shoulders of those dependences (not all of them are depicted). The values of $E_{\rm exp}$, the temperatures of the maxima T_m, and the frequency factors p_0 are quoted in the table. The error was estimated as the mean-square deviation of fractional energies on a shoulder.

The registration of the peak at 249 K, as well as that of the peak at 141 K [9], was accompanied by a background glowing, the intensity of which faded with increase in the number of the fractional curve and disappeared in the last curves. In order to obtain correct values for the fractional energies, the background was excluded by subtracting the identical values from the experimental intensities. The routine was stopped after achieving the minimal mean-square deviation of the experimental intensities from the straight-line dependence $\ln I = \ln I_0 - E/kT$. The procedure of excluding the background was described in detail in works [7, 8]. In higher-temperature peaks, the TL background is absent.

All the experimental energies agree well with the generalized oscillator formula (2) (see column $E_{\rm calc}$ in the Table) for the quantum energy $\hbar\omega_{\rm TL} = (0.1617 \pm 0.0004)$ eV (1304 $\rm cm^{-1}$). The trap energies in LiF appeared to be a multiple of $\hbar\omega_{\rm TL}$, except that for the peak at 141 K (a V_k-center) which corresponds to the fractional value $n = 2.5$ and, probably, for the peak at 113 K ($n \approx 1.5$).

The literature data concerning the trap energies in LiF are rather ambiguous. For example, in work [10], the energy of the peak at 141 K estimated by five different methods changes within the interval 0.143—0.226 eV. In work [11], the energy value deduced from the shape of the TL curve amounts to 0.276 eV, and to 0.434 eV if calculated from the initial slope. The nearest to ours are the results of work [12], where the energy of the basic peak is 0.36 eV, and of the next one 0.32 eV. A significant discrepancy of energy values, which depends on the method of their definition and on a specific specimen, is brought about first of all by ignoring the intense background and the fact that the peak is not elementary. The TL peak at 249 K is elementary and rather solitary. Therefore, the dispersion of energies is considerably narrower for it: 0.765 [11], 0.74 [12], and 0.59—0.82 eV [10], depending on the method applied. The value of 0.815 eV obtained by us exceeds those results to some extent owing to the account made for the background. The TL peaks in the range 300—500 K overlap one another rather essentially, and their intensities depend on the temperature prehistory of the specimen. These circumstances, together with various rates of heating applied by researchers, make the identification more complicated. In work [25], the estimation of the energy gave the values of 0.22 (T_m = 340 K), 0.69 (T_m = 368 K), and 0.4 eV (T_m = 398 K). Much closer to ours are the results obtained in work [13]: 1.18 (374 K), 1.23 (390 K), and 1.56 eV (423 K). Taking into account the results obtained earlier [1—8], we may assert that the validity of the oscillator-like regularity for LiF is an additional evidence for the reliability of the results obtained by us.

The data presented in the bottom section of the table were taken from work [14], where the TL of LiF (TLD-100) has been studied in detail within the temperature interval 300—650 K using the monochromatic light with the energy of quanta of 3.01 eV and, in less details, using the additional low-intensity bands of emission of 2.90- and 2.71-eV quanta. In work [14], the trap parameters were determined by the method of the best fitting of experimental TL curves using a computer. The table data are the averaged energy values obtained in work [14] for different doses of γ-radiation at the operating emission band of 3.01 eV. These values also obey oscillator-like dependence (2), and the frequency $\hbar\omega = (0.162 \pm 0.001)$ eV determined from them coincides with the frequency obtained by us.

The fourth column of the table contains values of the frequency factor p_0. Five of them are practically identical. The average value $\langle p_0 \rangle = 1.5 \times 10^{13}\ \rm s^{-1}$ is close to the frequency of a vibration quantum: $\langle p_0 \rangle = 0.5\nu_{\rm TL}$ and $\nu_{\rm TL} = 2.94 \times 10^{13}\ \rm s^{-1}$. The dependence of the energy on the temperature of the peak maximum is represented in Fig. 3. The straight line is drawn through the points which correspond to identical values of the frequency factor. The equation of this line is

$$E = 34kT_m. \qquad (3)$$

The TL peak at 249 K, with $E = 0.815$ eV, does not satisfy dependence (3). The calculation of its energy by formula (3) gives 0.73 eV, which corresponds to the value $E = 0.729$ eV calculated by Eq. (2) where $n = 5.5$. Concerning the TL peak at 113 K which also drops out of this dependence, we have, according to Eq. (3), $E = 0.33$ eV, i.e. $n = 2$.

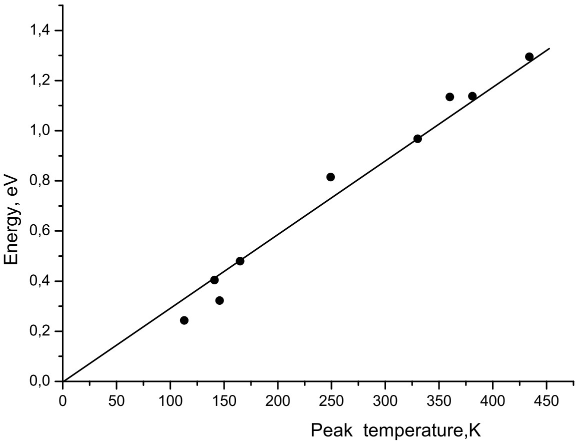

Fig. 3. Dependence of the energies of TL peaks on the temperature of the peak maximum

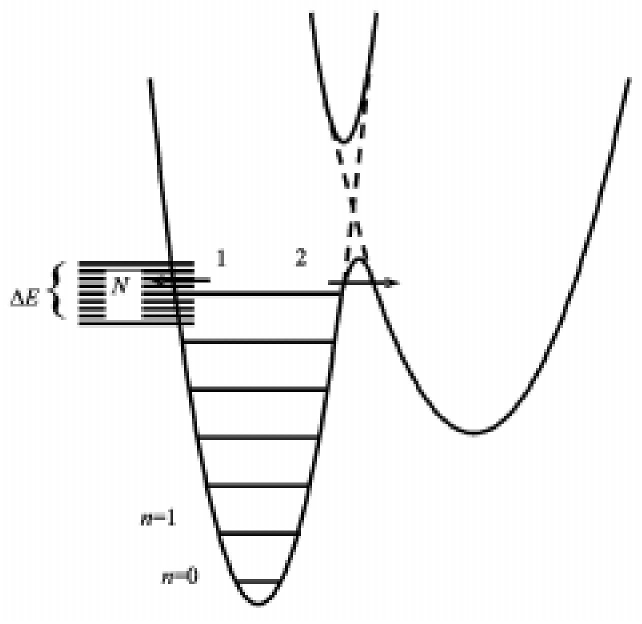

Fig. 4. The model of a polaron trap: *1* — charge transition into the polaron band, *2* — tunneling onto a luminescence center

4. Discussion of Results

4.1. The Polaron Model of Traps

On the basis of the results obtained earlier [1–8], we suggested the model, according to which a filled trap is interpreted as a polaron, either self-trapped or stabilized by the local field of an intrinsic defect or an impurity. Really, the equidistant positions of energies evidence for the elastic character of interaction, which can be provided only by the crystal lattice. If $\hbar\omega_{\mathrm{TL}} = \hbar\omega_{\mathrm{RS}}$, there appear the modes in the energy spectrum of traps which belong to the set of internal vibrations of quasimolecular complexes, being the structural elements of rather complicated lattices of the crystals under study. In the case where $\hbar\omega_{\mathrm{TL}} \neq \hbar\omega_{\mathrm{RSI}}$ (NaCl), a local vibrational mode reveals itself.

When dealing with a polaron state, one must distinguish between optically and thermally induced processes and describe each of them in the framework of different models. In the Lax cascade model [15], both the processes are considered running in the same system of electron levels, because the model is based upon the hydrogen-like model for a defect in a covalent crystal, where the influence of the lattice is taken into account at a macroscopic level, namely, by introducing the dielectric permittivity function. Optical transitions occur between the allowed combinations of energy levels, and thermally activated processes govern the quasiequilibrium population of the levels according to the Boltzmann distribution.

In an ionic crystal, owing to the local polarization of its lattice, a polaron (i.e. a charge with local polarization) moves stochastically by means of thermally induced hopping in the field of a stabilizing center; therefore, the system is not described by "atomic" levels. For example, in an AHC, a hole in the relaxed state has a two-center localization, so that it can be regarded as a monovalent haloid molecule X_2^-. There is a system of electron levels in the molecule, and the transitions between them are observed in optical absorption and emission spectra [16, 17]. For thermally activated processes, crucial are the variations just in the ionic subsystem, which can be imagined as a motion of the molecule X_2^- in the field of some defect which is the stabilizing center of a polaron. Therefore, the polaron trap can be presented as a potential well filled with equidistant vibrational levels (see Fig. 4). The depth of the potential well, i.e. the number of the vibrational level n, from which the charge can escape thermally, is defined by the nature of the defect that traps the hole.

There are two possible mechanisms of transportation of a thermally escaped charge to the center of luminescence. First, it is the classical band mechanism which takes place in crystals, where polarons do not form self-trapped states [1–6]. Here, the energy of thermal activation of a trap is defined by the vibrational level, from which a charge transits into the polaron band (transition *1* in Fig. 4). Secondly, in alkaline halide and many oxide crystals, the relaxed hole polarons are capable of self-trapping. In this case, a thermally excited charge can tunnel into the next equivalent position in the lattice, provided that there is a corresponding configuration of the ionic environment there, induced by a thermal motion [18]. If the center of luminescence is located near the trap, the tunneling of the excited charge immediately into the excited state of the luminescence center becomes possible (transition *2*).

Let us consider the influence of those mechanisms on the TL kinetics. The energy states of polaron traps of one type with the concentration m are described by formula (1). The quantum number $n = N$ corresponds to the energy level, from which the charge escapes from the trap. Independent oscillators, $m = \sum_{n=0}^{N} m_n$ in total, make up a quantum ensemble that is in quasiequilibrium with a thermostat – the crystal lattice. The probability of filling the state $n = N$ is determined by the Boltzmann distribution

$$w_N = \frac{m_N}{m} = \frac{g_N}{S} \exp\left[-\hbar\omega\,(N+1/2)/kT\right]. \tag{4}$$

Here, g_N is the degeneration degree of the N-th level and S is the statistical sum which is determined from the condition of the probability normalization to unity. The intensity of the TL peak is proportional to the rate of reduction of the filled trap concentration, $I \propto -dm/dt$, i.e. to the rate of charge transitions from the N-th level into the band or onto the center of luminescence:

$$\frac{dm}{dt} = -A_N m_N, \tag{5}$$

where A_N is the probability of the transition from the N-th level. Taking into account Eq. (4), we obtain the equation describing the linear TL kinetics:

$$-\frac{dm}{dt} = \frac{A_N g_N}{S}\ \exp\left[-\hbar\omega\,(N+1/2)/kT\right]\, m. \tag{6}$$

If the band is not engaged into the transition process, the statistical sum is determined by the formula for a one-dimensional ($g_n = 1$) oscillator with a limited number of levels ($n = 0 \ldots N$):

$$S_{\text{osc}} = \sum_{n=0}^{N} \exp\left(-\frac{\hbar\omega\,(n+1/2)}{kT}\right) \approx \exp\left(-\frac{\hbar\omega}{2kT}\right). \tag{7}$$

In the final expression, all other terms are excluded as insignificant. For example, for $\hbar\omega = 0.162$ eV and $T = 141$ K, we obtain $\exp(-\hbar\omega/kT) = 2 \times 10^{-6} \ll 1$. Thus, Eq. (6) becomes

$$\frac{dm}{dt} = -A_N m \exp\left(-\frac{N\hbar\omega}{kT}\right), \tag{8}$$

i.e. it describes TL with the energy of activation multiple of $\hbar\omega$ and with the frequency factor $p_0 = A_N$.

If the band mechanism is in action, then it is necessary to take into account the hybridization of band states when calculating the statistical sum. First of all, this concerns the level $n = N$, from which the charge escapes into the band. Making allowance for the band-assisted character of the process, one can admit $g_N \sim 10^{22}$, whereas $g_{n<N} \sim 1$. The statistical sum now contains two components: $S = S_{\text{osc}} + S_{\text{band}}$, where S_{osc} is determined by formula (7) with $n = 0 \ldots N-1$. Since $g_N \gg 1$, the band component should exceed considerably the oscillator one, i.e. $S \approx S_{\text{band}}$. Thus, the quantity S does not include multiplier (7), and TL is described by the expression

$$\frac{dm}{dt} = -\frac{A_N g_N}{S} m \exp\left(-\frac{\hbar\omega\,(N+1/2)}{kT}\right). \tag{9}$$

The frequency factor is described, in the case of the band mechanism, by the the formula

$$p_0 = A_N g_N / S.$$

Thus, the charges that thermally escape from traps with the energy multiple of (8) are tunneling, without passing into the band state, into the equivalent neighboring crystalline environment which has been created as a result of temperature fluctuations and reach the center of luminescence after several similar hops; or they tunnel immediately into the excited state of a recombination center, if there is any one about. If the trap energy corresponds to a half-integer value of the quantum number (9), the charge escapes from the trap into the band, which is followed by its recombination with a luminescence center located at any place. The last scenario is realized in all compounds that were investigated by us earlier; it is also valid for the TL peak at 141 K in LiF caused by the destruction of V_k-centers.

The traps which produce a continuous distribution of fractional energies within an interval from 0.404 ($n = 2.5$) to 0.322 eV ($n = 2$) were shown in work [9] to be responsible for the TL peak at 141 K in LiF. According to the analysis carried out above, this anomalous dependence (from a greater to smaller energy) can be explained by a gradual transition from the band mechanism of recombination at the initial stages to the jump-like tunneling of the charge at the final stages of the fractional glowing, the jump-like tunneling coming into action owing to the destruction of the polaron band as the temperature grows [18].

4.2. The Nature of Traps Which Are Active in TL

The issue concerning the nature of charges (electrons or holes) which escape in the course of TL in LiF and other AHCs remains disputable till now. An attempt to substantiate the hole origin of traps was made in works [19–22]; the basis for the substantiation was the circumstance that the TL emission spectra of all traps contain an emission band at 400 nm which is connected with the recombination of holes with F-centers. It is important that this band is available in the emission spectrum of the TL peak at 141 K induced by the thermal destruction of V_k-centers [23]. Moreover, the study of the X-ray-induced spectra of optical absorption in Li:Mg shows that the concentration of F-centers undergoes a step-like decrease, and the absorption bands of the Mg^{2+}—cation vacancy complexes in the range 310—380 nm disappear one after one as the annealing temperature of a specimen rises [17, 24]. As was found in work [25], the positions of the maxima of TL peaks coincide with those of the maxima in the derivative $-dn_F/dT$, where n_F is the concentration of F-centers. TL in other AHCs — NaCl [26] and KCl [27] — runs according to the same scenario. The principal reason which forced other researchers to develop the electron model of TL in LiF turned out to be the absence of the hole peak at 141 K in the spectra of photo-induced thermoluminescence (PITL) [10, 13, 19–21, 23, 24, 28]. Nevertheless, the convincing arguments concerning the failure of this model were presented in work [25].

In LiF, as well as in other AHCs, the ionic processes play an important role in thermal, optical, electric, and other phenomena. After the LiF specimen having been irradiated, the intense band of F-absorption appears at 250 nm. Another intense band at 113 nm is connected with anions excited by neighbor haloid vacancies. The existence of these bands means that the relevant number of interstitial atoms and haloid ions stabilized by some defects are available simultaneously. After the recording of the TL curve having been completed, the induced haloid vacancies and the F-centers disappear, which is evidenced for by both the absence of the corresponding absorption bands and the reproducibility of TL curves. In this connection, it becomes obvious that an adequate model of TL in LiF and other AHCs can be constructed only if one takes into account the contribution of the nonequilibrium ionic component to it. Both the electron and hole models do not provide mechanisms for the healing of radiation-induced defects in the course of TL, because the final result, in those cases, is the formation of haloid vacancies and the corresponding number of interstitial anions. So, the adequate model of TL should provide the mechanism for the healing of haloid vacancies by interstitial anions.

The model of TL in AHCs which satisfies this requirement was proposed in works [25–27]. It was supposed that, in the course of TL, haloid interstitials (H-centers) escape from some defects, and, afterwards, their radiative recombination with F-centers occurs. The conclusion concerning the ionic nature of the TL mechanism in AHCs is confirmed by our results. Really, the existence of an oscillator-like regularity in the trap energy dependences in LiF and NaCl with local vibrational frequencies means that every filled trap must include a comparatively isolated ionic component which is connected to the frequency of either 1304 cm^{-1} (0.162 eV) in LiF or 904 cm^{-1} (0.112 eV) in NaCl. The H-center can be such a component. The interstitial haloid atom and the neighbor nodal anion together compose a complex which can be regarded as a molecular ion X_2^- centered at a haloid point. The relaxed hole also has two-center localization, by forming, together with a neighbor anion, a molecular complex X_2^-, with a distance between its components being 28% shorter in LiF [29] than that between neighboring anions in an undistorted lattice. The shortage of the site-site distance may be interpreted as a reason for the appearance of the local vibration frequency, owing to the increase of the force constant. However, the V_k-center is not an ionic defect, so that it does not satisfy the condition stated above.

The fact that the energy $\hbar\omega_{\mathrm{TL}}$ can be ascribed to vibrations just in the anion subsystem is confirmed by a correlation between the frequency ratio of vibrational quanta in LiF and NaCl ($\hbar\omega_{\mathrm{LiF}}/\hbar\omega_{\mathrm{NaCl}} = 1.44$) and the ratio between the square roots of Cl and F atomic masses ($\sqrt{m_{\mathrm{Cl}}/m_{\mathrm{F}}} = 1.37$). Some discrepancy of these values is even mandatory, because the force constants of those crystals must be somewhat different. In addition, our studies of the trap energy spectrum in KCl [30], which are still in progress, indicate that the oscillator-like regularity (1) is valid for these crystals, as well as in the case of NaCl, with the vibrational quantum energy $\hbar\omega_{\mathrm{KCl}} \approx 0.12$ eV. The proximity of this value to the quantum energy in NaCl does not contradict a conclusion concerning the anionic nature of traps in AHCs. This conclusion is also confirmed by the fact that the values of the frequency $\hbar\omega_{\mathrm{TL}}$ and the activation energy $E = 0.16$ eV needed for the anion interstitials to migrate in LiF [31] coincide.

4.3. Recombination Model of TL

Thus, the analysis shows that at least some of TL peaks (except for the peak at 141 K) possess the ionic nature, i.e. they are induced by the thermal escape of H-centers from defects. Let us consider possible channels of their recombination. An H-center thermally escaped from the trap can recombine in two ways: with an F-center and with an anion vacancy. In the first case, there appears a nodal atom of haloid at the position of the F-center. Such a model has been proposed earlier to explain TL in AHCs [25–27]. The energy of the $H—F$ recombination was supposed to be transformed into the energy of the radiative electron transition. Here, however, one is faced with the problem to substantiate the efficiency of transformation of the energy of ion vibrations into the electron one theoretically. Calculations show [32] that the radiative efficiency of the $F—H$ recombination is extremely low. In addition, this recombination has to differ spectrally from that of a hole with an F-center.

We suggest to extend this model by taking into account that, besides the radiationless $F—H$ recombination, there must be a recombination of H-centers on anion vacancies according to the reaction

$$\mathrm{i}_a^0 + V_a \to \mathrm{X}^- + \mathrm{e}^+. \qquad (10)$$

Here, i_a^0 is the haloid interstitial atom, v_a the anion vacancy, and X^- the nodal anion. The reaction yield consists of the hole and the nodal anion. The hole recombines radiatively with an F-center according to the reaction

$$V_a\mathrm{e}^- + \mathrm{e}^+ \to V_a + h\nu_{\mathrm{lum}}, \qquad (11)$$

where $V_a\mathrm{e}^-$ is the F-center. Those two consecutive reactions result in a quantum of light which corresponds to a band of 400 nm and the healing of one F-center. The concentration of anion vacancies does not change at that.

The account of the recombination on vacancies allows one to explain the identity of the emission spectrum compositions of the hole peak at 141 K and H-peaks. Concerning the PITL, photoillumination of the specimen which has been irradiated preliminary by a radiation dose, with light in the range of the F-band (250 nm) at $T = 80$ K, liberates haloid interstitial atoms and excites F-centers, not ionizing them. Some fraction of H-centers liberated by the F-illumination recombines with F-centers and reduces their concentration, which provokes us to draw conclusion about their ionization by F-light. Indeed, the study of the PITL excitation function and the temperature decay of the absorption F-band [28] showed that F-centers do not play the crucial role in exciting PITL, and the photoassisted transfer of charges into shallow traps proceeds from a defect which is responsible for the absorption band with the maximum at 225 nm, the long-wave wing of this band being imposed on the F-band. Since exciting into the absorption F-band is not accompanied with the generation of free holes, this explains the absence of the 141-K peak at PITL.

Thus, F-centers participate in both the radiationless $H—F$ recombination and the radiative two-stage recombination (10), (11). The existence of competing recombination channels allows the monotonous disappearance of TL peaks, starting from low-temperature ones, with increase in the irradiation dose to be explained, which has not found a satisfactory explanation within the framework of existing models [14, 25]. In addition, a decrease of the intensity of stationary luminescence with the dose was observed [13]. This fact testifies to that the reduction of the TL intensity is brought about by the reduction of the radiative efficiency rather than the trap concentration. It is important that the positive charge of anion vacancies predetermines their effective recombination with anion interstitials, the latter possessing the highest mobility among other intrinsic defects. As a result, the concentration of anion vacancies proves to be negligible in comparison with that of F-centers and saturates quickly as the dose increases, whereas the concentration of F-centers grows linearly with the dose. The higher the irradiation dose, the smaller the ratio between the anion vacancy and the F-center concentrations, and the lower the radiative efficiency. At substantial doses, practically all H-centers thermally escaped from shallow traps recombine in a radiationless manner with F-centers. Therefore, the first TL peak — or, may be, several low-temperature ones — is absent. As the specimen is heated up further, the concentration of F-centers decreases, whereas the concentration of anion vacancies remains constant. The probability of radiative transitions grows, and the intensities of the next TL peaks become sufficient for their reliable registration. At low doses, the concentration of F-centers is still insignificant, whereas the concentration of anion vacancies is close to that in the saturation state. It enables the low-temperature TL peaks to be recorded as well.

5. Conclusions

Lithium fluoride has extended the list of crystalline materials which manifest the oscillator-like regularity in their energy spectrum of traps. However, the difference is that the majority of energies in LiF turned out to be multiples of the vibrational quantum energy $\hbar\omega_{\rm LiF} = 0.162$ eV. On the basis of the estimation of the statistical sum for oscillator states, a conclusion has been made that TL in LiF takes place through the charge tunneling from the excited vibrational states of traps into the states of luminescence centers, without a transition into the band state. In this case, the activation energy of a trap turns out to be a multiple of the vibrational quantum energy. If the transport of the charge to a recombination center occurs through the band, the activation energy corresponds to the half-integer number of vibrational quanta. Such a mechanism is realized when the V_k-centers are being destroyed; it is also in action in the crystals investigated by us earlier [1–8].

In the materials investigated earlier, the energies of vibrational quanta coincided with the energies of separate lines in their Raman spectra, whereas these energies in LiF and NaCl correspond to local vibrational modes. Basing on the correlation between the values of $\hbar\omega$ and the anion mass in LiF, NaCl, and KCl, these frequencies can be attributed to a local vibration mode of the haloid molecule (H-center).

The proposed supplement to the ionic model of TL in AHCs [25–27] allows one to explain the existence of the 400-nm band of the emission inherent to all TL peaks, as well as the phenomenon of the gradual decay of low-temperature TL peaks with increase in the irradiation dose.

The main conclusion of the work is that the existence of an oscillator-like regularity in the energy spectrum is caused by the polaron effect. We may guess that this regularity is not a unique feature of the materials investigated by us, but is a universal property of all wide-gap crystals with the mainly ionic type of coupling. In any case, until now, we have not found a material, where this regularity was not observed. In order to establish the fact of the existence of this regularity, precision measurements are needed. In our opinion, only the method of fractional TL can provide the required accuracy, owing to an opportunity to obtain a significant body of data of the same type and to perform their profound mathematical treatment.

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ДОСЛІДЖЕННЯ ТЕРМОЛЮМІНЕСЦЕНЦІЇ НЕЛЕГОВАНИХ КРИСТАЛІВ LiF.
2. ОСЦИЛЯТОРНА ЗАКОНОМІРНІСТЬ В ЕНЕРГІЯХ ПАСТОК

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Резюме

Методом термолюмінесценції (ТЛ) досліджено енергетичний спектр центрів прилипання (ЦП) в спеціально не легованих кристалах LiF. Параметри пасток, які відповідають за низькотемпературний інтенсивний максимум ТЛ 141K, досліджено в першій частині роботи. В цій частині методом фракційного висвічування детально досліджено енергетичний спектр пасток, що відповідають за піки ТЛ у більш високотемпературній області — 150 ÷ 450 K. Їх енергії активації утворюють одну осциляторну серію $E_n = \hbar\omega_{\text{ТЛ}} n$, $\hbar\omega = 0{,}1617$ еВ (1304 см$^{-1}$), і, на відміну від раніше досліджених нами речовин, n набуває як півцілих, так і цілих значень. Запропоновано можливий механізм існування цієї закономірності. На основі оцінки статистичної суми для осциляторних станів зроблено висновок, що в LiF процес ТЛ відбувається шляхом тунелювання зарядів із збуджених коливальних станів ЦП у збуджені стани центрів люмінесценції. В цьому випадку енергія активації пасток кратна цілому числу коливальних квантів. Якщо ж процес доставки заряду до центра рекомбінації відбувається через зонний механізм, то енергія активації описується формулою осцилятора з півцілими n (n+1/2). Такий випадок реалізується при руйнуванні V_k-центрів у LiF, а також у всіх досліджених нами раніше кристалах. На противагу раніше дослідженим кристалам із складною ґраткою, в спектрі КРС LiF не знайдено відповідної лінії, як і в інших лужно-галоїдних кристалах — NaCl, KCl. Виходячи з наявності кореляції між значеннями $\hbar\omega_{\text{ТЛ}}$ в LiF, NaCl, KCl та масами аніонів, припускається, що ця частота відповідає локальній коливальній моді молекули галоїду X_2^-.