

OSCILLATORY REGULARITY IN THE ENERGY SPECTRUM OF TRAPS IN ORDERED MEDIA.

II. DISCUSSION OF THE MODEL (CRITICAL REVIEW AND THEORETICAL PERSPECTIVE)

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Abstract. This review describes the study of several materials of different types using the improved fractional thermoluminescence method. It is shown that the activation energies of traps exhibit oscillatory regularities, $E = \hbar\omega_{\text{TL}}(n+1/2)$, in which most values of ω_{TL} coincide with the frequencies of the Raman spectrum lines. Part I of the review describes the applied thermoluminescence (TL) methods and presents experimental results. We formulated the polaron trap model. Part II describes the TL mechanisms corresponding to the proposed model in different material types studied. The reasons for activation energies that are integer or half-integer multiples of $\hbar\omega_{\text{TL}}$ are discussed. The concept of the frequency factor was clarified, and its influence on TL processes was described.

Keywords: thermoluminescence, Raman scattering, polaron, oscillatory regularity

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1. Introduction

The review describes the study of a number of (more than 30) materials of different types (metal oxide crystals, halide perovskites, alkali halide crystals, and polymers of certain types) using the improved method of fractional thermoluminescence (FTL). The activation energies of traps show oscillatory regularities, $E = \hbar\omega_{\text{TL}}(n+1/2)$, in which most values of ω_{TL} coincide with the frequencies of the Raman spectrum lines. These regularities are observed in all studied substances provided that they contain a moderate amount of defects. Part I of the review [1] describes the applied thermoluminescence methods and presents experimental results. It shows that oscillatory regularities in trap energies arise from the polaron nature of the charge carriers; the polaron trap model was formulated. Part II of the review describes the thermoluminescence (TL) mechanisms corresponding to the proposed model in different types of materials studied. The reasons for activation energies that are integer or half-integer multiples of ω_{TL} are discussed. The influence of an important parameter – the frequency factor – on the TL processes is described.

2. Ion-hole mechanism of TL in alkali halide crystals

The structure of alkali halide crystals (AHs) does not allow first-order Raman scattering. They also lack relatively isolated ion groups similar to quasimolecular complexes (QMC) in metal oxide crystals (MOs). We also note that the absence of non-equivalent anionic and cationic sites

explains why AHs show only single oscillatory series. At the same time, oscillatory sequences in both types of crystals indicate a common mechanism for thermal release of excess carriers. In a MO crystal, a hole is released at the temperature at which complete compensation of polarization distortion occurs, with the participation of symmetric stretching vibrations. In relation to AHs, this means that in an excited AH crystal, all populated traps of a given salt must contain some structural ionic component, which ensures the existence of one and the same symmetric local vibrational mode. For this, the component must contain two identical ions symmetrically located relative to the nodes of the crystal lattice. Because such structural elements are absent in the initial state of the AH crystal, the excitation process must be accompanied by an ionic rearrangement. Thus, the fact of the existence of an oscillatory pattern in the trap energies in the AH crystal directly implies the ionic nature of its TL.

Two such objects are known in AHs: V_K -centers (Kenzig centers) and H -centers [2-4]. The V_K - center arises from the formation of a covalent bond between the nodal ion X^- and the neighboring nodal atom of the halogen X , which has lost an electron. In fact, it is a molecular ion X_2^- , oriented along the close-packed halogen sequence $\langle 110 \rangle$. That is, the relaxed hole in AHs has a two-center localization. In terms of the charge sign, the V_K - center is equivalent to a band hole in covalent crystals. At low temperatures, the V_K - center can be localized near various defects and even self-localize due to distortion caused by the convergence of the components of the X_2^- - molecule under the action of a covalent bond.

In a first approximation, the H -center can also be treated as an X_2^- - molecule. However, unlike the V_K - center, one of its initial components is an extranodal halogen atom knocked out of the site during excitation. The molecule is centered on the anionic site, and its axis is directed towards the cation cavities in the form of tetrahedra, i.e., along $\langle 111 \rangle$. This is the so-called dumbbell form of the H -center.

Both objects are symmetrically arranged on the halide sequence and can form fully symmetric vibrational stretching modes. It is necessary to determine which of these mechanisms applies in AHs. In the first, TL is assumed to arise from the release of V_K - centers, i.e., holes from various defects, followed by their recombination at electronic recombination centers (RCs). The second is the ionic mechanism, where TL results from the decay of H -centers, i.e., the release of anionic interstitials. To determine which mechanism applies, we compare the frequencies of various vibrational processes in AHs, as shown in Table 1.

Column 3 contains the experimentally found TL frequencies. They are 3-5 times higher than the limiting LO frequencies listed in column 4 [4,5]; i.e., the TL frequencies belong to local oscillations. The calculated V_K - frequencies are in column 5 [6]. They are also several times (4-5) smaller than the corresponding TL frequencies. V_K - frequencies can also be determined experimentally by studying Raman scattering in pre-excited samples. In LiF, this frequency, $\omega=437 \text{ cm}^{-1}$ [7], is close to the calculated $\omega=449 \text{ cm}^{-1}$. A characteristic feature of the V_K - lines is their relatively fast decay (15-25 s) under laser irradiation. Comparing the data in columns 2 and 3, we see that the TL frequencies decrease with increasing mass of the halogen atom M_{an} , while in NaCl and KCl, they are quite close. Column 6 presents the results of calculations of the force constants η taking into account only the mass of the corresponding anion, i.e. $=M_{an}\omega_{TL}^2$. They are quite close to each other, with an average value $=2066 \text{ kg/s}^2 \pm 5\%$. Some discrepancy is even expected, since the influence of the cation

Table 1. Comparison of halogen atomic masses and frequencies in AHs: 2) halogen atomic masses (M_{an}); 3) experimental TL frequencies (ω_{TL}); 4) LO cutoff frequencies (ω_{LO}); 5) V_K -frequencies (ω_{V_K}); 6) force constants (η).

AH	M_{an} , at.un.	ω_{TL} , cm^{-1}	ω_{LO} , cm^{-1}	ω_{V_K} , cm^{-1}	η , kg/s^2
LiF	19.0	1307	669	449	2127
KCl	35.5	976	210	248	2216
NaCl	35.5	904	274	257	1901
KBr	79.9	629	160	147	2072
NaI	126.9	492	169	104	2013

subsystem is not taken into account. However, the closeness of these values is explained by the fact that the properties of related substances are compared. For compounds with the same anions but different cations, this difference is quite significant: $\eta_{\text{NaCl}} / \eta_{\text{KCl}} = 1.16$, due to the larger size of the potassium ion and, accordingly, a greater degree of compression of the H -center. For compounds with the same cations and different anions, this difference is significantly smaller: $\eta_{\text{KCl}} / \eta_{\text{KBr}} = 1.07$ and $\eta_{\text{NaI}} / \eta_{\text{NaCl}} = 1.06$. Given that $\eta \approx \text{const}$, we obtain $\omega_{TL} \sim 1 / \sqrt{M_{an}}$, confirming that the TL frequencies in AHs are associated with local vibrations of the H -centers. The significantly higher frequency of these vibrations than that of V_K -centers is due to the extranodal status of both components of the H -center. This significantly compresses the H -center, i.e., increases η .

We did not find TL from V_K -centers above 80 K, since all the energies fit into oscillatory H -sequences. Because V_K -center frequencies are small, TL curves from V_K -centers can be found only below 80 K. Many AH crystals have been studied in the low-temperature range (8–60 K) [8–10], but detailed results on the trap energy spectrum in this range are unknown. Therefore, the connection between these low-temperature traps and V_K -centers remains open.

The main radiation defect in AHs is the F -center, i.e., a halogen vacancy plus an electron localized on it due to the positive cationic environment, as well as the complementary H -center. Together with the ionic environment, it is a source of symmetric local stretching vibrations. At the same time, the H -center component in the form of an off-site atom is the excess carrier that is localized during excitation and released during TL. H -centers have fairly high mobility, so to fix them in space, certain violations of the lattice's translational symmetry are required; that is, certain structural defects are required. In addition to F -centers, a certain number of halogen vacancies are present, which is important for further analysis.

Alvarez Rivas and co-workers proposed and repeatedly confirmed the ionic mechanism of TL in AHs [11–14]. It was assumed that the energy released during H - F recombination is realized in the radiative electronic transition of the excited F -center. However, this raises the problem of substantiating the efficiency of converting phonons (i.e., thermal energy) released during ion relaxation into electronic energy, which has lower entropy. As calculations [15] showed, the radiative efficiency of H - F recombination was extremely low.

In [16], the authors proposed a more plausible two-stage mechanism for radiative recombination during TL. In the first stage, the vacated H -center on the anion vacancy undergoes non-radiative recombination according to the reaction



where i_a^0 denotes the interstitial halogen atom (component of the H -center), v_a is the anion vacancy (ionized F -center). The reaction products are the nodal anion X^- and the hole e^+ in the form of a V_K -center. The other part of the halide interstitials, often the main one, non-radiatively recombines on the F -centers



where $v_a e^-$ denotes the F -center.

In the second stage, the hole created in the reaction (1) recombines radiatively on the F -center by the reaction



These two consecutive reactions (1) and (3) emit a quantum of light and “heal” one F -center. The concentration of halogen vacancies remains unchanged. In addition to the main F -band, the TL emission spectrum may show additional bands due to hole recombination on metal impurity ions: $Me^{(n-1)+} + e^+ \rightarrow Me^{n+} + \hbar\omega_{Me}$.

Thus, both non-radiative H - F and radiative F - e^+ recombination involve F -centers. The EPR method reliably records the emergence of free holes upon heating an excited sample.

The probability of a radiative process in the presence of radiative and non-radiative recombination channels can be given as

$$W_{\text{radiat}} = \frac{\sigma_v N_v}{\sigma_v N_v + \sigma_F N_F}. \quad (4)$$

where σ_v is the cross section for the capture of an off-node halogen atom by an anion vacancy; N_v is the concentration of these vacancies; σ_F, N_F are the cross section for the non-radiative recombination of an off-node halogen atom on the F -centers and their concentration, respectively. This may explain why many studies maintained the exclusively hole nature of traps in AHs [17-19]. During excitation, the surrounding positive charge of the anion vacancy ensures effective recombination with anion interstitials and electrons. Therefore, as the irradiation dose increases, the concentration of anion vacancies quickly saturates and becomes insignificant compared with the monotonically increasing concentration of created F -centers. In addition to the dynamic component, halogen vacancies also exist in equilibrium due to the crystal's non-stoichiometric nature (excess of the metal component) and form Schottky defects.

From Eq. (4) it is seen that an increase in the concentration of F -centers relative to the concentration of anion vacancies leads to a decrease in the radiative yield. Therefore, at high irradiation doses, low-temperature TL peaks are absent because almost all thermally released H -centers recombine nonradiatively on F -centers according to reaction (2). During TL, the concentration of F -centers decreases, while the concentration of anion vacancies remains unchanged. At higher temperatures, the probability of radiative transitions (3) increases, so the intensity of subsequent TL peaks becomes sufficient for reliable registration. For small irradiation doses, the concentration of F -centers remains insignificant, while the concentration of anion vacancies approaches saturation, making it possible to register low-temperature TL peaks as well. Modern ideas about H -centers allow them to exist in two different forms. The localized form (or dumbbell) is described above. A delocalized structure (or crowdion) arises when an excess halogen atom is placed directly in the halogen row. That is, a gap of n halogen nodes has n valence electrons and $n+1$ halogen atoms. If n is sufficiently large, the ions in the crowdion sit close to the

nodes of the unperturbed lattice. Therefore, the mobility of the H - center in the crowdion form is much higher than in the localized form. It can be assumed that the released H - center moves to the recombination center as a crowdion, while the captured H - center relaxes into a molecular configuration, X_2^- . The energy required to transform the H - center from a localized to a delocalized form is probably a significant part of the trap activation energy, or equal to it.

The H - center does not carry excess charge, since it forms when an off-site neutral halogen atom attaches to the site anion. The polarization, important in explaining TL with electron or hole carriers, is in this case a secondary effect caused by inhomogeneous displacement of the surrounding ions in different coordination spheres. Therefore, the H - center should be treated not as a polaron, but rather as a local mechanical compression caused by short-range repulsion forces of the electron shells of the contacting ions.

3. Properties of 1D traps

In this section, based on experimental facts from σ -conjugated poly(di-n-hexylsilane) (PDHS) and confirmed in π -conjugated methyl-substituted ladder-type poly(p-phenylene) (MeLPPP), we consider the properties of one-dimensional traps in these conjugated polymers. The polysilane molecule is a linear chain whose backbone consists of silicon atoms connected by paired (vicinal) bonds. The length of the sp^3 hybrid orbitals of the silicon atom is much longer than that of the carbon atom, so orbitals on the same Si atom overlap significantly (geminal bond). These two types of bonds form a continuous overlap of orbitals along the silicon backbone, causing electronic delocalization (i.e., σ -conjugation). This manifests when σ -electrons are excited, creating delocalized holes in the valence band.

The angle Si-Si-Si between bonds in polysilanes is close to tetrahedral ($\sim 110^\circ$). In substituted polysilanes, hydrocarbon groups (hexyl in the case of PDHS) are attached to the lateral Si bonds instead of hydrogen atoms. Unlike conventional 3D crystals, where traps are point defects, in polysilanes and other linear conjugated polymolecules, the traps are linear defects, namely polymer chain segments of different lengths [20-23]. Within the segment, the Si-Si bonds have a regular mutual orientation. Conformational defects separate the segments; they violate this regularity, i.e., the translational symmetry of the silicon backbone [23-26]. At low temperatures, a hole can move only within one segment, since intersegment conformational defects form potential barriers [20,25,26]. In works [27-29], it is assumed that the hole interacts strongly with ions along the segment, i.e., forms a polaron.

The phenomenon of thermoluminescence requires localization of both types of excited carriers, electrons and holes, on their defects. As noted, holes are localized within the segments, and each segment is a potential valley in the ridge. A hole's localization within the segment is caused by a potential barrier at both boundaries. That is, the intersegment defect creates a positive effective charge, whose field repels the hole into the depth of the segment. The potential profile for an electron, as a particle with the opposite charge, is obtained by mirroring the hole profile. Therefore, the profile of the valence-band top mirrors the profile of the conduction-band bottom, and the appearance of the conduction-band bottom profile implies that non-equilibrium electrons must be localized between the segments [30]. The excited electron is in a narrow potential well, separated from the neighboring well by a wide barrier (strong localization). Such an electron acts as a recombination center. In contrast, the hole is located in a wide valley, separated from the next valley by a narrow barrier (delocalization in the segment). Therefore, the tunneling probability for holes is significantly

higher than for electrons. Indeed, in PDHS only hole photoconductivity is observed [20,29,31], indicating a much greater degree of electron localization than hole localization. Thus, because of the conjugation of the silicon backbone and its polysegment structure, PDHS, like other piecewise conjugated polymers, is a self-activated phosphorus.

Several factors determine the depth of the potential well in which a localized hole resides. First, it is necessary to consider the fundamental difference in carrier-movement and localization mechanisms between conventional 3D crystals and linear conjugated polymolecules (LCPs). In a conventional crystal, excess charge movement is confined to a small 3D region because it is attracted to the electric charge of a point trap. In a linear polysilane molecule, σ -conjugation determines one-dimensional charge movement along the polymer chain. A hole localizes within a segment because of repulsive forces from the end barriers. The segment length is not regulated and affects the depth. Indeed, because of the tendency toward polymerization, a longer molecular chain should correspond to lower electronic energy. The quantification of this dependence is based on the uncertainty relation

$$\Delta p L \geq \hbar, \quad (5)$$

where the coordinate uncertainty corresponds to the segment length L , and Δp is the momentum uncertainty. Taking into account the one-dimensionality of the motion, the uncertainty in the kinetic energy, ΔE , is equal to:

$$\Delta E = \frac{\hbar^2}{2\mu a^2 n^2}, \quad (6)$$

where $L=na$, a is the length of the vicinal Si-Si bond, n is the number of Si atoms in the segment, and μ is the particle mass. Formula (6) describes the quantum-size effect that underlies nanophysics. This additional kinetic energy is significant for short segments and decreases to zero as segment length increases. That is, as the segment length increases, the potential valley depth for the hole decreases. The height of the intersegment barrier also depends on the type of the bordering conformations. If the non-equilibrium electron is localized near the segment where the non-equilibrium hole is located, its field significantly reduces the hole's activation energy.

In Fig. 1, graph 1 shows the TL curve of the PDHS film. At first glance, the absence of fine structure in the glow curve indicates a continuous or quasi-continuous trap energy spectrum. However, the shelves in graph 2 indicate that PDHS has a discrete sequence of trap energies. In addition, elementary TL curves 3 and 4, calculated from data from two neighboring shelves, do not overlap.

These facts can be reconciled only if, in PDHS, a discrete spectrum of traps is accompanied by a dispersive frequency factor. That is, in the temperature range where traps with the same energy empty, the glow curve is a superposition of elementary curves of the type $I(T)=s_0 m \exp(-E/kT)$, with the same energy E but different frequency factors s_0 . The formula for calculating s_0 can be obtained by analyzing the function $I(T)$ at the extremum, namely:

$$s_0 = \frac{E\beta}{kT_m^2} \exp\left(\frac{E}{kT_m}\right), \quad (7)$$

where T_m is the temperature at the maximum of the TL curve and $\beta = dT / dt = \text{const}$.

From Eq. (7), the frequency factor decreases with temperature within one shelf. This change is usually quite significant. For example, the shelf $E=0.069$ eV begins at about 31 K, which

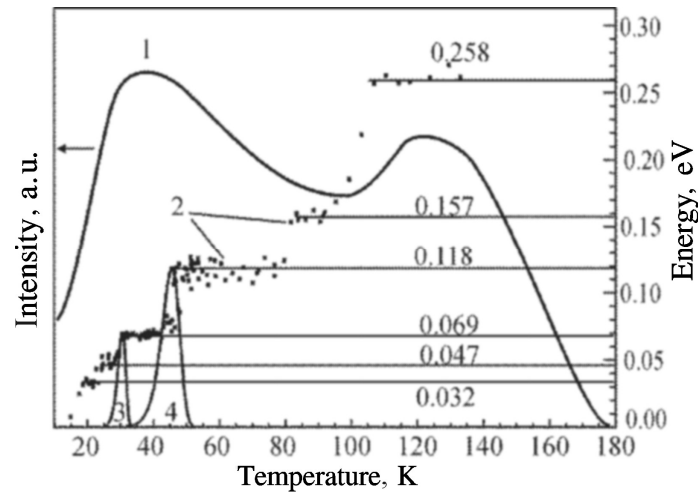


Fig. 1. Fractional TL of PDHS film [32]. (1) TL glow curve; (2) fractional energies depending on T_{eff} ; (3) calculated elementary TL curve for the shelf $E=0.069$ eV, where $T_m=31$ K corresponds to the beginning of the shelf; (4) the corresponding elementary curve for $E=0.118$ eV, $T_m = 47$ K.

according to (7) gives $(s_0)_{max}=1.7 \times 10^{11} \text{ s}^{-1}$. At the end of this shelf, we have $T_{max}=45$ K and $(s_0)_{min}=6.3 \times 10^6 \text{ s}^{-1}$, i.e. the frequency factor has decreased by almost 6 orders of magnitude.

Discrete energy-spectrum traps are also observed in MeLPPP, Fig. 12b (part I). At the same time, the TL curve does not show clearly defined maxima (Fig. 2), where curve 1 corresponds to the sample on which the fractional experiments were performed, as presented in Fig. 13 (part I).

The absence of clear maxima on the TL curves in the considered examples is not an obstacle for the fractional method, since the intensity of the fraction, the energy of which is on the shelf, is a superposition of exponential initial rises with the same exponent, i.e.

$$I = \sum_i \delta I_0^i \exp(-E/kT), \quad (8)$$

where $\delta I_0^i = \delta m_i s_0^i = \text{const}$ combines traps with the same values of the frequency factor. For the initial terms of the sum in Eq. (8), the condition $m=\text{const}$ may not be fulfilled, but their intensity is insignificant because the corresponding trap group empties in the previous fractions.

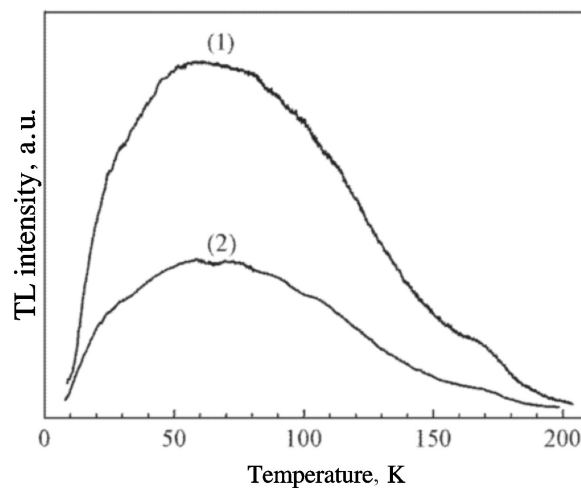


Fig. 2. TL curves of MeLPPP films. Substrates: sapphire (1), aluminum (2).

The main reason for the dispersion of the frequency factor in PDHS is the possibility of a very small increase in energy depending on the segment length. To estimate this, we calculate the relative change in kinetic energy (6) as a function of the number of links in the segment. We obtain $dE / \Delta E = -2dn / n$. If the segment length is 100 atoms, then when it increases by one atom ($dn=1$), the kinetic energy decreases by only 2%. That is, formally, we can assume that the frequency factor occupies a continuous spectrum of values.

So, in LCPs, traps are not point defects but segments, i.e., segments of chains of different lengths. Within each segment, the chain has translational symmetry. Transition regions lie between the segments and act as barriers to hole motion. Because the segments have arbitrary lengths, the frequency factor is highly dispersed, distorting the shape of the glow curve. Therefore, the energy characteristics of matter can only be studied by the differential method, i.e., FTL.

4. Polyconformity of PDHS molecules

In section 3.3 (part I), we noted that several oscillatory series in MO crystals arise from non-equivalent quasimolecular complexes with different internal vibrational frequencies. In PDHS, each of the four oscillatory series (Fig. 12 (part I)) corresponds to a specific conformation of the Si backbone [30]. The conformation type is given by the value of the dihedral (torsional) angle τ . Fig. 3 illustrates how to construct this angle: bond 1-2 lies in the 1-2-3 plane, bond 2-3 lies at the intersection of the planes, and bond 3-4 lies in the 2-3-4 plane.

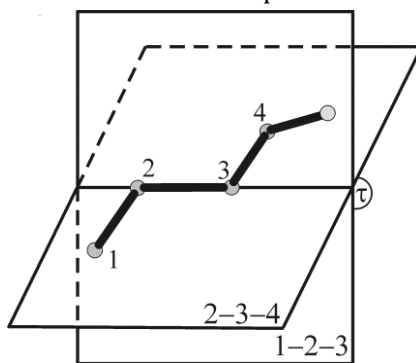


Fig. 3. Determination of the dihedral angle τ . The arc indicates which of the two adjacent dihedral angles to choose.

Along the straight line connecting neighboring silicon atoms, a vicinal bond acts, and between the orbitals of the same atom, a geminal bond acts. Considering only these bonds does not physically allow fixing certain values of the torsion angle along the silicon backbone. In earlier studies, experimental data on PDHS were interpreted under the assumption that the silicon backbone of a molecular chain at temperatures below the order-disorder phase transition point (42°C) forms a flat zigzag. The ordering of the silicon backbone is provided by intramolecular van der Waals repulsion between the side branches (hexyl in PDHS). In the solid state, you must also account for intermolecular interactions.

In [24], a classification of conformations was proposed based on the torsion angle. The A or *anti* (formerly *all-trans*) conformation is reserved for torsion angles that may differ from 180° by several degrees. T₊, T₋ or *transoid* (formerly 15/7 *helix*), $\tau \approx \pm 165^\circ$; D₊, D₋ or *deviant* (formerly 7/3 *helix*), $\tau \approx \pm 150^\circ$; O or *ortho* (formerly 4/1 *helix*), $\tau \approx \pm 90^\circ$; G or *trans gauche* (TG₊, TG₋), $\tau \approx \pm 60^\circ$; C or *cisoid*, $\tau \approx 40^\circ$. Except for the planar A conformation, all other

conformations are chiral and exist as enantiomorphic pairs. The subscripts + and – denote right- and left-handed torsional angles. The designations of chiral conformations as fractions are interpreted as follows: the numerator indicates the number of silicon atoms in the primitive cell of this conformation, and the denominator equals the number of complete turns of the Si chain within the cell. [30] shows the structure of certain silicon backbone conformations in PDHS.

In order to establish the existence of certain conformations of the silicon backbone, theoretical calculations of the potential energy $U(\tau)$ in isolated oligosilane molecules were carried out. It was found that the function $U(\tau)$ passes through several shallow and deep minima, each of which corresponds to a certain conformation [33-35]. It turned out that changing the length of the molecule, the addition of different types of side chains, and the presence of the polymer in the dissolved or solid state do not generate new types of conformations, but only slightly change the depth of the wells in $U(\tau)$, creating an advantage for one or another conformation. For example, the main conformation of the PDHS molecule, both isolated and in solution, is the 7/3 helix, while in the solid state the A trans conformation is more temperature-stable [35].

Fig. 4 shows the region 100-500 cm^{-1} of the Raman scattering spectrum, where the vibrational modes of the silicon backbone are located, as evidenced by the invariance of the values of these frequencies in samples enriched with the ^{13}C isotope [22].

The spectrum contains a certain number of fairly narrow bands corresponding to vibrational modes of ordered regions of the silicon backbone in different conformations, as well as a background with intensity ≥ 0.2 of the band intensity that corresponds to contributions from disordered regions, which are conformational defects. A sufficiently strong background indicates that the conformational defect is not a violation of translational symmetry in only one silicon link; rather, it is a segment of the silicon backbone along which a gradual transition from one conformation to another occurs. Conformational defects are closely analogous to domain walls in ferromagnets (or ferroelectrics), which separate domains with different orientations. Within the domain wall, magnetic moments gradually transition between the orientations of neighboring domains. Like the domain wall, the disordered segment of the silicon backbone has higher energy than the ordered segment. As a result, the hole is localized by potential barriers at both ends of the segment.

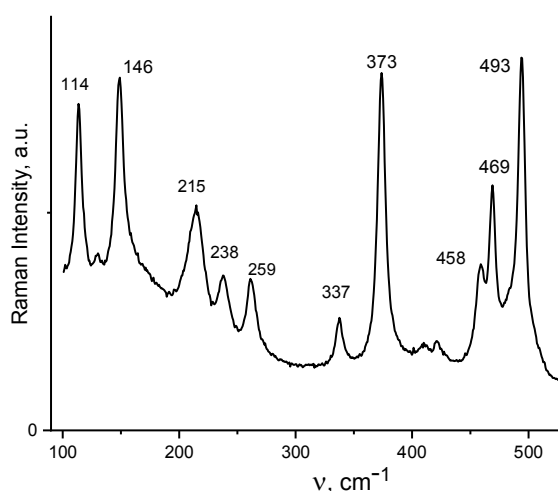


Fig. 4. Raman spectrum of PDHS powder at 20°C.

The unit cell of the A-trans conformation contains two silicon atoms and belongs to the D_{2h} point group. The primitive A-trans cell contains only one silicon atom; therefore, this conformation should be assigned the highest frequency of fully symmetrical vibrations. For the D_{2h} group, there are two Raman-active modes: 373 cm^{-1} (0.0462 eV) and 458 cm^{-1} of the A_g and B_{2g} symmetries, respectively [22]. Thus, TL series 1 belongs to the A-trans conformation, $\omega = 373\text{ cm}^{-1}$.

The number of Raman lines in the region $100\text{--}500\text{ cm}^{-1}$ exceeds the value predicted for the A-trans conformation; therefore the molecules of this polymer should have a polymorphic structure in the form of segments of the silicon backbone of different conformations, which alternate along the chain. This conclusion follows from the experimental observation of several oscillatory TL series, each corresponding to its own A_g vibrational mode of the Si backbone. Because van der Waals forces are weak, the angle between adjacent bonds, i.e., the strength of the Si-Si interaction, does not depend on the conformation type [36]. Therefore, for an arbitrary conformation, we have $\omega^2 = \eta / (nM_{\text{Si}})$, where $\eta = \text{const}$, n is the number of silicon atoms in the primitive cell for this conformation, and M_{Si} is its mass.

Series 2 is generated by an energy quantum $\hbar\omega_2 = 0.032\text{ eV}$ (258 cm^{-1}); Raman frequency 259 cm^{-1} (Fig. 4). It should correspond to the A_g mode of the Si backbone in another conformation. The ratio of the squared frequencies for series 1 and 2 $(\hbar\omega_1/\hbar\omega_2)^2 = M_2/M_1 = 2.08 \approx 2$ corresponds to the vibration of mass M_2 , which equals the mass of two Si atoms. This condition is met by the trans gauche conformation ($AG+AG-$), whose primitive cell includes two silicon atoms. The torsion angle for this ladder conformation is approximately equal to half the Si-Si-Si bond angle ($\tau \approx 55^\circ$) [33,34,37].

For series 3, we have $\hbar\omega_3 = 0.0175\text{ eV}$ (141 cm^{-1}). In the Raman spectrum, the corresponding line is 146 cm^{-1} , Fig. 4. Data on the symmetry of this line are absent in the available literature, and our measurements were carried out on unoriented samples. However, based on the results of the analysis of the two previous conformations, we assume that this mode is also fully symmetric. Based on the ratio between the energies of TL quanta: $(0.0462/0.0175)^2 = 6.97$, this vibrational mode should correspond to the compatible vibrations of heavy clusters of seven silicon atoms each. This condition is met by the deviant ($7/3$ helix) conformation, whose primitive cell contains exactly seven silicon atoms [20,33,34]. The bonds between silicon atoms form a broken helical line around the segment axis. Within the cell, Si-Si bonds perform three full rotations, so the torsion angle is $\tau = 360 \times 3/7 = 154^\circ$.

Finally, for the only member of series 4, the analogous ratio is: $(0.0462/0.0118)^2 = 15.3$, i.e. $M_4/M_1 \approx 15$, so the cluster contains 15 silicon atoms. This is a transoidal conformation, or $15/7$ helix; $\tau = 360 \times 7/15 = 168^\circ$. This conformation in PDHS, like the previous ones, follows from quantum-chemical calculations and is also experimentally confirmed by X-ray diffraction data [38-41].

Fig. 5 shows the results of calculating trap energies from fractional experiments for three PDHS samples, including all energies found for series 3 and 4. In addition, separate shelves show energies belonging to series 1 and 2.

The correspondence between the Raman frequencies of the silicon backbone and its conformational types is confirmed by data for methyl-substituted polysilane:

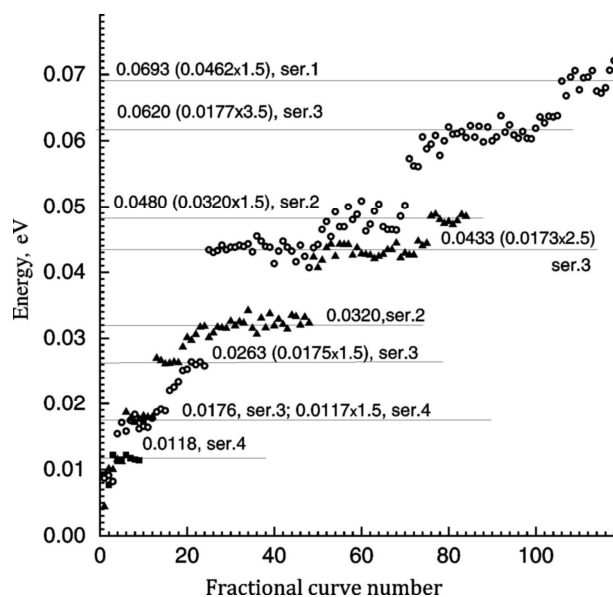


Fig. 5. Dependence of the trap energies in PDHS on the fraction number in the low-temperature region (5-60 K). The films were kept in the dark for over a year. Circles, triangles, and squares correspond to different film samples.

poly(di-n-methylsilane), or PDMS. In the Si backbone vibration region, four lines are observed at 140, 188, 268, and 373 cm^{-1} , with the last two identified as A_g modes [42]. Three frequencies, 140, 268, and 373 cm^{-1} , actually coincide with the frequencies that create the corresponding series 3, 2, 1 in PDHS. For the fourth frequency, $\omega = 188 \text{ cm}^{-1}$, the ratio $(373/188)^2 = 4$ determines the vibration frequency of clusters of four Si atoms. This condition corresponds to a helical conformation known as ortho, O (4/1 helix), $\tau=90^\circ$. Thus, in the PDMS sample used in [42], four conformations coexist: T, D, O, A.

At temperatures above the phase-transition temperature (42°C in PDHS), the side chains melt, which in turn causes conformational disordering of the silicon backbone. Because of intense thermal motion, random conformations appear and disappear chaotically in individual parts of the backbone. Subsequent rapid cooling to $T < 42^\circ\text{C}$ freezes this high-temperature polyconformal structure, which slowly relaxes over time to a state corresponding to the existing temperature. Indeed, after heating PDHS films to 100-125°C and rapidly cooling them to 20°C, the broad absorption band $\lambda_{\text{max}} = 375 \text{ nm}$, attributed to $\sigma\text{-}\sigma^*$ transitions in the ordered structure, is replaced by three narrower bands at 358, 374, and 385 nm [43,44]. PDHS solutions also showed a complex UV absorption spectrum after rapid freezing [44]. Similar transformations of UV absorption spectra after the indicated heat treatments were also observed in other polysilanes symmetrically and asymmetrically substituted with other alkyl or phenyl groups [45,46].

Conformational lability may explain the absence of the 97 cm^{-1} frequency in the Raman spectrum (Fig. 4) because the freshly prepared PDHS lacked the transoid conformation (15/7 helix). This conformation developed in films stored for more than one year after manufacture; see Fig. 5.

Observing PDHS polyconformity in fluorescence spectra is complicated because excitons before recombination have time to migrate from their formation site to lower-energy sites, i.e., to longer segments (higher conjugation) and/or to segments with a low-energy conformation of the silicon backbone. Therefore, to observe the fluorescence spectra of each individual conformation,

it is necessary to exclude the migration of excitation along the polymorphic chain, for example, by introducing linear molecules into a porous material.

Because changes in the Si chain's conformation fracture the molecular axis, the chain can enter a straight, narrow pore only as a single segment with a specific conformation.

Fluorescence studies [47,48] of a composite based on the mesoporous silicate SBA-15 (stable mesoporous silica with average pore diameter 10 nm) with PDHS molecules introduced into these pores showed that instead of a broad structureless fluorescence band with a maximum of 365 nm, characteristic of films, three narrower bands with maxima at 337, 355 and 369 nm appear, Fig. 6. The splitting of the exciton fluorescence band indicates that PDHS molecules are introduced as single segments of three different conformations.

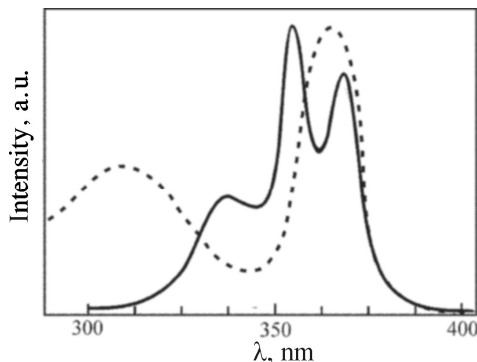


Fig. 6. Fine structure of the photoluminescence spectrum of the SBA-15:PDHS composite (solid curve) [47]. For comparison, the PDHS film spectrum (dashed line) is shown. The short-wave band with a maximum of 300-310 nm corresponds to the disordered regions of the PDHS molecules. $T=18^{\circ}\text{C}$.

TL characteristics similar to PDHS also appear in MeLPPP: the first energy of the series is $E_1=\hbar\omega_{\text{MeL}}=0.021\text{ eV}$, and the following energies correspond to half-integer values of this quantum (Fig. 13 (part I)). The building blocks of the MeLPPP molecule are a six-membered phenyl ring and a five-membered pyrrole ring that alternate periodically (Fig. 16, part I). The backbone chain includes segments of different lengths separated by conformational defects. One possible mechanism for these defects is a change in the pyrrole ring position from *trans* to *cis*. Cross-links give the MeLPPP backbone the necessary rigidity; therefore, unlike PDHS, only one conformation is possible, which explains the single oscillatory series in MeLPPP.

The study of TL mechanisms described in the previous chapters allowed us to establish the nature of the low-temperature background afterglow in AHs and LCP, and its absence in MO crystals. First, in FTL experiments, the background level is significantly higher than during TL-curve registration under identical conditions. Second, this background weakens with temperature and eventually disappears. In PDHS, the background is absent after $T=30\text{ K}$, and in AHs after $T=170\text{-}180\text{ K}$. The thermal-activation nature of this background excludes a tunneling origin. After the current fraction is completed, the subsequent rapid and deep cooling of the sample leaves some released carriers without time to recombine, so they are temporarily localized on shallow traps or self-localize. This is facilitated by the low mobility of interstitial halogen atoms in AHs. In LCPs, one must also account for low hole mobility in the disordered intersegment environment, as well as the one-dimensional nature of diffusion. The release of these temporarily frozen carriers in the next fraction contributes to the background. The absence of background afterglow in MO crystals is explained by the relatively high hole mobility.

Thus, in PDHS, four oscillatory trap sequences were found, each corresponding to a specific conformation of the silicon backbone. We determined these conformations using the formula $\omega^2 = \eta / (nM)$, where n is the number of Si atoms that enter the primitive cell of this conformation, and M is the mass of the atom. It was established that the background afterglow during FTL is due to the too-low carrier mobility in AHs and LCPs.

5. Thermoluminescent properties of the MCM-41: PDHS composite

Because porous materials can separate individual conformations, the energy spectrum of traps in composites may be simpler than in films. To test this assumption, FTL studies were conducted in the MCM-41:PDHS composite (MCM-41, a mesoporous material with a hierarchical structure) [30]. Polymer molecules were introduced into pores with a diameter of 2.8 nm from a toluene solution. The small pore diameter limited the number of conformer types that could be introduced.

Fig. 7 presents the results. Graph 1 shows the intensity of the composite's TL curve. For comparison, curve 2 depicts the TL from the PDHS film. The composite's TL curve is significantly narrower than the film's, which qualitatively confirms the above assumption. At the same time, it is significantly wider than the calculated elementary curve for 0.032 eV (curve 3). The triangles depict fractional energies, most of which fit on the shelf at 0.031 eV. The energy quantum $\hbar\omega = 0.032$ eV generates series 2, indicating the introduction of *trans gauche* conformers into the pores.

Curve 4 represents the dependence of $I(T)$ for the last fraction. From the last fraction, using the initial-slope method, we obtained $E = 0.041$ eV. This value is undoubtedly underestimated, since the criterion $m = \text{const}$ is not fulfilled here. In this regard, we used the procedure $\ln(I/m) = f(1/T)$. During the energy calculation, we had to perform complex manipulations, alternately changing the background and m in one direction or the other. In addition, high-temperature points "infected" with the shoulder $T_m \sim 45$ K, caused by contributions from unwashed PDHS tails on the substrate surface, were discarded. The obtained value, $E = 0.047$ eV, coincides with the quantum energy of 0.0462 eV, which

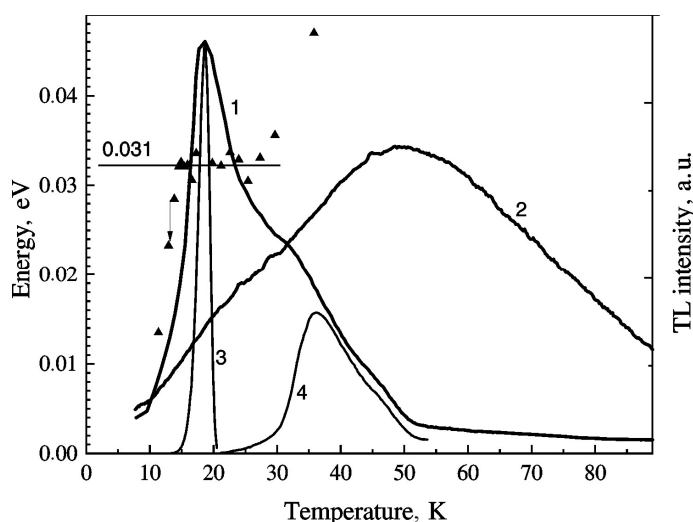


Fig. 7. TL of the composite MCM-41:PDHS. 1: integral TL curve; 2: integral TL curve of the film; 3: elementary TL curve calculated for $E=0.032$ eV; 4: last fraction; triangles indicate the values of fractional energies; the arrow indicates the temperature value of 13.1 K with energy 0.023 eV (see section 7).

generates series 1. This indicates that A trans conformers also enter the pores. The content of molecules in the A trans conformation, estimated from the area under the fractions, does not exceed 20% of the trans gauche conformation in this sample.

The work [49] builds on ideas about the influence of molecular vibrations on the thermoluminescence of polymers, particularly on the formation of an important parameter: activation energy.

6. "Integer" and "half-integer" trap energies

The oscillatory regularity was first discovered in YAG [50]. Five oscillatory trap series were found in this crystal. The energies of all traps in YAG and other MO crystals turned out to be equal to half an integer multiple of the corresponding vibrational quanta. This initial result seemed quite natural, since for a quasi-stationary process, which is TL, the thermal activation energy of a trap is equal to the energy of the excited vibrational level N , located above the barrier, i.e. $E_N = \hbar\omega(N + 1/2)$. However, studies of alkali halides and then linear conjugated polymers revealed that, despite the general subordination to oscillatory regularity, the trap energies in them correspond not only to half-integer ($N = n + 1/2$) but also to integer ($N = n$) values of the vibrational quanta. In AHs, these energies show no regular alternation (Fig. 11, part I), whereas in PDHS polymers and MeLPPP, the "integer" energy starts each oscillatory sequence (Fig. 12, part I). The prevalence of this phenomenon in all studied AHs and LCPs, and the absence of traps with "integer" energies in MO crystals, indicate that this phenomenon is not related to the nature of the carriers in the traps. After all, in polymers and in MOs the charge carriers are holes, while in AHs the released carriers are off-site halogen atoms.

The lack of connection between the existence of "integer" traps and the carrier type indicated that the problem is statistical and related to the normalization of the Boltzmann probability [16,30]. This norm generally has two components. The first of them corresponds to the total probability of all vibrational states of the trap. The second component corresponds to the total probability of the carrier being somewhere between the trap and the recombination centers (RC). That is, the existence of "integer" and "half-integer" traps arises from differences in how released carriers are delivered to the RC.

For a one-dimensional oscillator, there is no degeneracy, so the probability of the n -th level being populated is

$$w_n = \frac{1}{S} \exp\left(-\frac{E_n}{kT}\right), \quad (9)$$

where $E_n = \hbar\omega_{TL}(n + 1/2)$ and S is the norm. We express S as the sum of terms of type (9) for $n=0$ to $n=N$, where N is the vibrational level from which the carrier is released. We obtain the sum of terms of the geometric progression:

$$S_{osc} = \exp\left(-\frac{\hbar}{2kT}\right) \frac{1 - \exp\left[-\frac{\hbar(N+1)}{kT}\right]}{1 - \exp\left[-\frac{\hbar}{kT}\right]}. \quad (10)$$

Based on the estimate [49], $E/kT_m \sim 25$, we have $\exp(-E/kT_m) \sim 10^{-11}$, i.e. with high accuracy

$$S = \exp\left(-\frac{\hbar}{2kT}\right) \quad (11)$$

From Eq. (11), the "integer" energy results from summing only the vibrational component belonging to the trap. An additional condition that the trap has an "integer" activation energy can be obtained from the fact that there is no band component in the parameter S . The absence of this component in the parameter S indicates that the distance between the trap and the RC is so small that their configuration curves intersect, and the carrier transition occurs by direct tunneling to the RC. That is, in this case, it is sufficient to consider only the trap's oscillatory states.

At the same time, this pair must be metastable, i.e., separated by a potential barrier. Therefore, the normalized Boltzmann probability Eq. (9) for "integer" energies has the form

$$w_N^{int} = \exp\left(-\frac{N\hbar}{kT}\right) \quad (12)$$

In LCPs, such a pair is a configuration in which the excess electron is located directly behind the segment where the hole is located. This placement ensures the receipt of "integer" energy. At the same time, the minimum trap energy is obtained, i.e. $E=\hbar\omega_{TL}$, as a result of the donor-acceptor interaction, or the hole is not localized at all. At low temperature, this configuration is metastable because the excess electron localizes on the side group due to carbon's greater electron affinity than silicon's. In AHs, close pairs of anion vacancy- H -center type arise from the presence of large aggregated defects and from the absence of an additional charge in the H -center.

For distant RC-trap pairs, the norm must be supplemented with the term S_{band} , which accounts for the carrier's band motion; i.e., $S = S_{osc} + S_{band}$. This radically affects the normalization result. Although it is impossible to estimate S_{band} exactly, it can be argued that, because of its significant statistical weight, the band component should exceed the oscillatory component, so the latter can be neglected. In principle, the band component can depend on temperature. However, based on the horizontal shelves in the fractional energy plot, this dependence is much weaker than the exponential one. Therefore, the corresponding probability has the form

$$w_N^{half-int} = \frac{1}{S} \exp\left[-\frac{(N+1/2)}{kT}\right], \quad (13)$$

where $S \approx S_{band}$. If the carriers are released from remote traps, their energies equal the half-integer value $\hbar\omega$.

For remote pairs in LCP, the excess electron is separated from the hole by one or more segments, and the hole must tunnel through one or more intersegment barriers before the act of recombination. Immediately after tunneling, the hole has a potential energy equivalent to the energy of the N -th oscillatory level. In the decreasing positive potential on the back side of the barrier, the hole gains significant speed quickly, so at this stage ionic polarization can be ignored, and the hole's motion can be treated as that of a hot Bloch particle in the free zone.

The results for the MCM-41:PDHS composite also support the proposed mechanism for the emergence of "integer" energies. Indeed, a chain in the form of a single segment with a specific conformation (*A-trans* and *trans gauche* being the most compact) can be introduced into a rectilinear pore of small diameter. The hole is delocalized along the segment, and the complementary electron is concentrated at the end of the segment (a strongly localized electron). Such a scheme provides the activation energy $E=\hbar\omega$. "Half-integer" energies in the composite do not appear because the introduced polysegment chains are absent.

In AHs, "integer" energies correspond to tunneling of an off-site halide atom from the trap to a nearby anion vacancy; i.e., the pair must be part of an aggregated defect. The formed hole can radiatively recombine with the *F*-center, which can be located both in the aggregate itself and outside it. This does not affect the trap energy, since the thermal dissociation of the *H*-center occurred earlier with a probability of $\exp(-N/kT)$. The value of $n' = N$ depends on both the nature of the defect included in the complex and the relative arrangement of the *H*-center and the anion vacancy. The non-point configuration of the aggregate allows these centers to localize in different places in the complex, preventing immediate recombination. In addition, the *H*-center does not introduce an additional electric charge, which contributes to the existence of "integer" energies for sufficiently large N (≥ 10).

So, traps with "integer" energies exist in the categories of AHs and LCPs. These categories differ profoundly in trap configurations, localization mechanisms, and carrier types. They share one common property: the ability to form metastable states between closely spaced complementary carriers. For such pairs, the normalization of the Boltzmann probability is limited to the vibrational states of the trap, which gives $S_{osc} = \exp(-\hbar\omega/2kT)$, providing trap energies that are multiples of the integer number $\hbar\omega_{TL}$ of quanta. This conclusion is reliably confirmed by the result obtained for the composite MCM-41:PDHS, in which the energies of both traps turned out to be "integer". In the studied MO crystals, traps with only "half-integer" energies were found because conditions for forming a barrier between the nearest components of the donor-acceptor pairs were absent.

7. Frequency factor

From a phenomenological point of view, the frequency factor s_0 is a parameter that transforms the proportional dependence of the TL intensity on the concentration of filled traps m and on the Boltzmann probability $\exp(-E/kT)$ into the equality $I = s_0 m \exp(-E/kT)$. In a given compound, s_0 can vary over a wide range: from less than 10^5 s^{-1} to 10^{16} s^{-1} . This range includes the frequencies of crystalline optical vibrational modes ($10^{12} \div 10^{14} \text{ s}^{-1}$); therefore, the frequency factor is usually interpreted as the frequency of attempts to release a carrier through an oscillatory process, and the TL intensity should be proportional to this frequency.

Randall and Wilkins developed the theoretical foundations of TL [51]. They introduced the concepts of a trap, a recombination center, and a frequency factor s_0 . They interpreted the trap as a potential well and s_0 as the product of the frequency of contact between a localized electron and the barrier wall and its transparency coefficient D ; it should be $10^{12} \div 10^{13} \text{ s}^{-1}$, corresponding to the range of optical vibrational frequencies in crystals.

Our studies of the energy spectrum of traps confirmed these hypotheses. In addition, we found that the most relevant modes during the release of excess carriers are symmetric valence vibrations (A_g modes), since the distortion caused by excess charge and the displacement of ions in the vibrational mode must have similar symmetry. The mechanism of thermal release of excess carriers consists in the periodic compensation of the ion distortion induced by the localization of non-equilibrium carriers by the action of these vibrations. Complete compensation occurs at a sufficient temperature (sufficient phonon density). At these moments ν , times per second ($\nu = \omega_{TL}/2\pi$), the ionic configuration favorable for carrier

release is recreated. Therefore, the frequency factor must include this frequency. In addition, s_0 must include the barrier transparency D , since the charge-release mechanism involves tunneling through the barrier; finally, s_0 must include the normalized Boltzmann probability.

The existence of oscillatory dependence of trap energies confirms this interpretation of the frequency factor. The carrier is released from some excited vibrational state $n=N$ by tunneling through the residual barrier. The transparency of an arbitrary barrier is described by the formula

$$D_N \cong D_0 \exp \left[-\frac{2}{\hbar} \int_{x_1}^{x_2} \sqrt{2M(E_N - U(x))} dx \right], \quad (14)$$

where E_N is the particle energy, M is its mass, U is the barrier height, and x_2-x_1 is the barrier width at the E_N level. As shown below, the carrier tunnels into an oscillatory state that becomes unbound after electronic relaxation.

As noted, in s_0 we must include the results of normalizing the Boltzmann probability. For close trap-RC pairs, i.e., when considering only oscillatory states, we have $S_{osc} = \exp(-\hbar\omega/2kT)$. This term is included in the main exponential dependence, which reduces the value of (half-integer) n' to the nearest integer value. For distant trap-RC pairs, it is necessary to take into account the probability of each band component, i.e., now $S = S_{osc} + S_{band}$, and $S_{band} \gg S_{osc}$. Therefore, the frequency factor for traps with "half-integer" energies is

$$s_0^{half-int} = \nu \frac{D}{S}. \quad (15)$$

The proportionality coefficient is omitted ($=1$) because all stages of carrier release from the trap and its transfer to CR are accounted for.

For "integer" energies, the S_{band} term is absent, i.e.

$$s_0^{int} = \nu D. \quad (16)$$

For a single barrier with $D_0 < 1$, there is always a non-zero probability that a particle is reflected by the inhomogeneity, even when the carrier energy exceeds the barrier height created by this inhomogeneity. Therefore, for "integer" energies, the condition must be fulfilled

$$\frac{s_0}{\nu} = D_0 < 1 \quad (17)$$

From Eq. (17), for traps with "integer" energies, we can estimate the barrier transparency after which the carrier becomes free.

Fig. 8, depending on $n' = E/\hbar\omega$, shows the s_0 values of the studied traps for four AHs. Dashed horizontal lines indicate the averaged frequency factors $\langle s_0 \rangle$ for "integer" energies. For this purpose, we used frequency factors starting from $n'=4$. Solid horizontal lines depict the oscillation frequencies of the H -centers. Fig. 8 also shows that for shallow traps ($N \leq 3$) the frequency factors for both types of energies are quite small, but they increase monotonically. This is due to the low transparency of the barriers, since the intersection points of the configuration curves lie on their initial gentle sections. In other words, the wave functions of trap states with small n' overlap slightly with the wave functions of the post-barrier states because of their short length. From the data in Fig. 8, we find that the barrier transparency D is 0.1 for KBr, 0.26 for KCl, 0.33 for LiF, and 0.85 for NaCl. These values are close to unity, so we can assume they correspond to the maximum barrier transparency, i.e., $D = D_0$ in these

cases. This means that the hole tunneling occurs above the barrier. Although this result is obvious for traps with "integer" energies, it holds for any trap, since the thermal-carrier release method should not depend on the trap's distance from the RC.

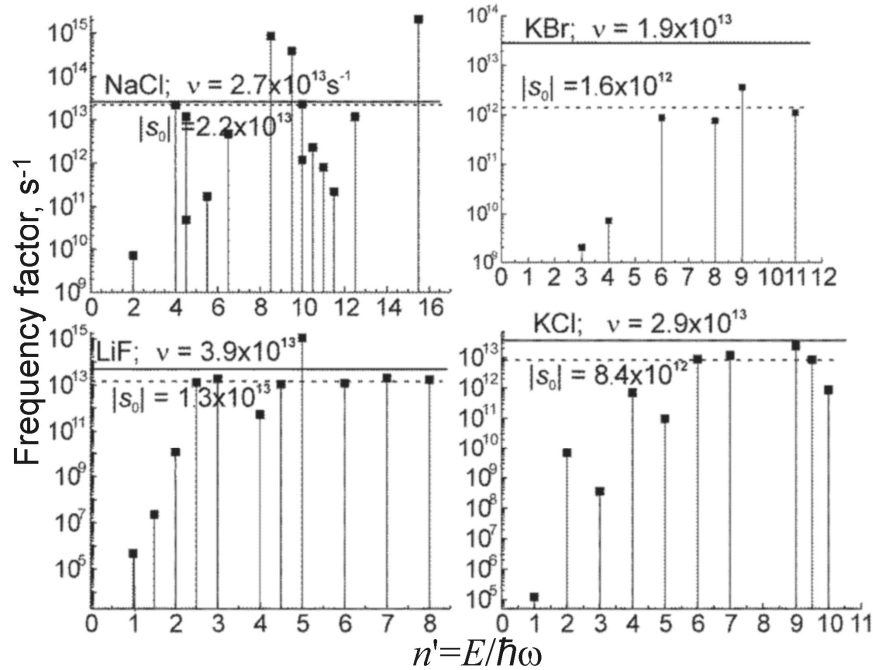


Fig. 8. Frequency factors of traps in AHs as functions of n' . Solid horizontal lines show the linear frequency $\nu = \omega/2\pi$; dashed horizontal lines show the averaged frequency-factor values $\langle s_0 \rangle$ for "integer" energies; vertical lines indicate the values of n (integer or half-integer).

In PDHS, each oscillatory series begins with "integer" energies, and the frequency factor for traps with the same energy varies over a wide range. We can estimate its maximum value, $s_0^{\max}$, by noting that the corresponding elementary peak corresponds to the effective temperature T^* at the beginning of the shelf of fractional energies. This value allows us to estimate the maximum barrier transparency D_0 for the "integer" energy. For testing, we selected the FTL results for the composite MCM-41:PDHS, where both traps have "integer" energies. In Fig. 7, the arrow indicates a temperature of 13.1 K (fraction No. 2) with an energy of 0.023 eV, intermediate between the energies of the quanta of series 3 ($\hbar\omega_3 = 0.0175$ eV) and series 2 ($\hbar\omega_2 = 0.032$ eV, $\nu_2 = 7.7 \times 10^{12} \text{ s}^{-1}$). Assuming that $T_m = 13.1$ K and $E = 0.032$ eV, we obtain from (7) that $s_0^{\max} = 1.3 \times 10^{12} \text{ s}^{-1}$. That is, the barrier transparency $D_0 = s_0^{\max} / \nu_2 = 0.17$. Therefore, condition (17) is also valid for phosphors with a dispersed frequency factor. This additional result gives grounds to assert the universality of the mechanism of thermal carrier release. Indeed, the transition of an excess carrier to an unbound state after the relaxation of the N -th vibrational state means the disappearance of the restoring force regardless of trap configuration.

The only exception to the condition $s_0/\nu < 1$ was observed for the trap in LiF, represented by the TL peak at 248 K with an energy of 0.81 eV, $n' = 5$, Fig. 9. For this peak, $s_0 = 9 \times 10^{14} \text{ s}^{-1}$, which is almost two orders of magnitude higher than the value $\langle s_0 \rangle$. For other "integer" TL peaks in LiF, the s_0 values are quite close to each other.

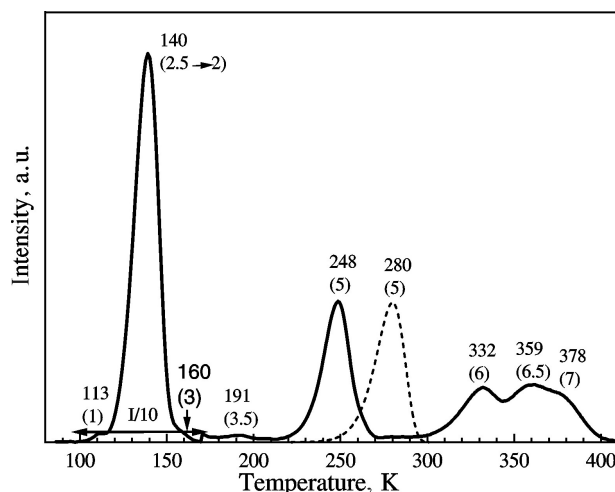


Fig. 9. Solid line: typical TL curve for LiF [15]; dashed line: calculated TL peak for $E=0.81$ eV, $\langle s_0 \rangle$. Numbers in parentheses indicate the value of n' .

A trap with parameters $E=0.81$ eV and $s_0=\langle s_0 \rangle$ should produce a TL peak with a maximum at 280 K (dashed curve in Fig. 9). Such a situation is possible if, in this case, the resonant tunneling mechanism is implemented due to the random coincidence of energy levels on opposite sides of the barrier.

Another type of anomaly associated with the frequency factor is observed in NaCl [52]. Fig. 10 shows a fragment of the TL curve of NaCl, where two well-separated TL peaks with maxima at 176 and 212 K arise from traps with the same energy of 0.5 eV ($n'=4.5$). The frequency factors of these peaks differ by more than two orders of magnitude: 6.4×10^{12} and $2.4 \times 10^{10} \text{ s}^{-1}$, respectively. An influx is observed on the low-temperature wing of the 176 K peak, which corresponds to a shelf with an energy of 0.45 eV ($n'=4$). The temperature at the maximum of this TL peak, $T_m \approx 156$ K, is estimated from the T^* value for the fraction at the transition region between the shelves (indicated by the arrow). For the estimated values of E and T_m , we obtain $s_0 = 2.2 \times 10^{13} \text{ s}^{-1}$. Also, the same energy $E=1.066$ eV, $n'=9.5$, with $s_0=7.2 \times 10^{14}$ and $1.6 \times 10^{12} \text{ s}^{-1}$, has two TL peaks with maxima at 329 and 389 K.

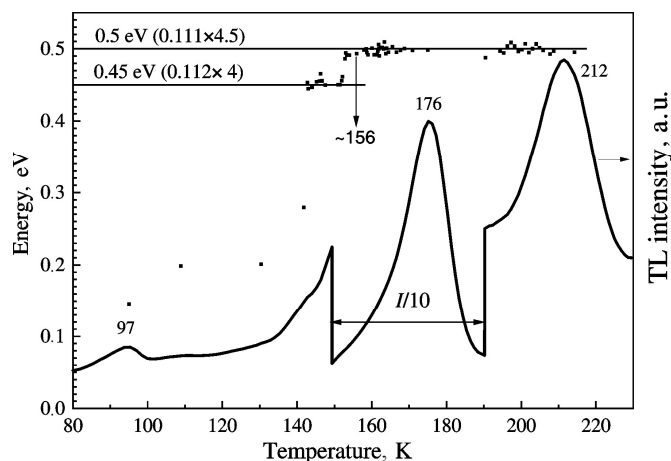


Fig. 10. Demonstration of different traps with the same energy in NaCl. The solid line is a fragment of the TL curve of NaCl; the squares are fractional energies as a function of T^* . $I/10$ denotes an intensity range reduced by a factor of 10.

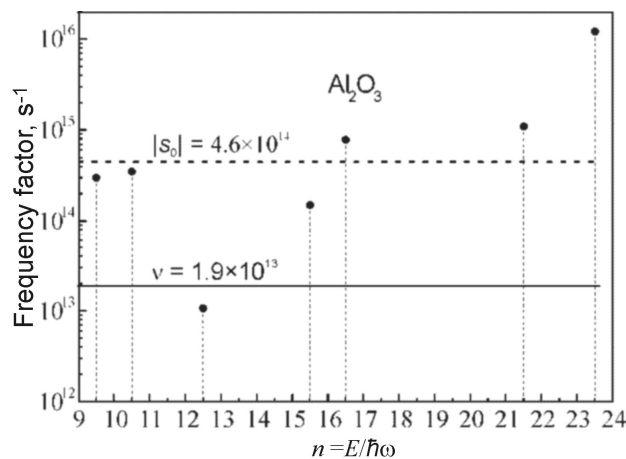


Fig. 11. The frequency factor values in Al_2O_3 . The vertical lines indicate the values of n .

For “half-integer” traps, the frequency factor depends on the ratio of two variables: D/S ; see (15). Since $S < 1$, the sum of Boltzmann exponents, s_0 , can be either less than or greater than ν . Therefore, in the previous case with NaCl, we could observe two cases in which two “half-integer” TL peaks ($n' = 4.5$ and 9.5 , Fig. 10) have the same energy but different frequency factors. Fig. 11 shows the value of s_0 for Al_2O_3 as a representative of Ct1. Here, all s_0 values, except one, exceed ν .

8. Conclusions

This review highlights two fundamental experimental facts in thermoluminescence:

1. The existence of an oscillatory pattern in the trap energy spectrum.
2. The close correspondence (with discrepancies typically not exceeding 0.1%) between the characteristic TL frequencies and the frequencies (in most cases) of fully symmetric stretching vibrational modes. In some cases, this correspondence is observed for the frequencies of second-order Raman scattering, local vibrational modes associated with metal impurity ions substituting the central atoms of quasi-molecular complexes, and modes forbidden in the first-order Raman spectra (the local vibrational modes of H -centers in alkali halide crystals).

In addition to these experimental observations, the combined analysis of the available experimental data allows several more general conclusions.

3. The oscillatory regularity in the trap energy spectrum is due to the existence of a strong electron-phonon interaction in materials with ionic and ion-covalent bonding. This interaction provides the elastic response of the crystal lattice to the presence of an excess charge carrier or interstitial ion.
4. The mechanism of non-equilibrium charge carrier release is based on the periodic compensation of the lattice distortion of the ion environment created by localized excess carriers. The distortion and the participating phonons must have the same symmetry; i.e., symmetric stretching vibrational modes play the dominant role.
5. The quasi-stationary nature of the TL process must be taken into account consistently in the analysis of thermoluminescence kinetics.

6. Despite the wide diversity of the physicochemical properties of the studied substances, the kinetics of the TL process is, as a rule, linear, although the physical mechanism responsible for this behavior differs among the three classes of materials considered. In metal oxide crystals, recapture is absent because the traps are self-localized. In alkali halides, the linear kinetics results from the low mobility of interstitial halogen atoms. In linear conjugated polymers, the process is linear

because of the low mobility of holes in disordered intersegment gaps and the essentially one-dimensional nature of charge transport.

Several important TL features are common to two material classes but absent in the third. For example, lattice distortion has a polarization origin in MOs and LCPs, whereas in AHs it results from the Pauli interaction associated with *H*-centers. In other cases, similar macroscopic properties arise from different microscopic mechanisms.

Although the TL glow curve in all three material classes results from radiative recombination of thermally released holes at electronic RCs, the defects acting as traps are fundamentally different. In MO crystals, hole-trapping centers may be absent in the unexcited crystal. They form during low-temperature excitation through ionization of the QMC, followed by structural relaxation. Likewise, AH crystals have no pre-existing trapping centers before excitation. They arise during excitation as *H*-centers, which then relax into the dumbbell configuration. These *H*-centers also serve as the source of the fully symmetric local vibrational modes. The first stage of the TL process is the thermally induced dissociation of the *H*-center, i.e., an ionic process. The next stage consists in the radiative recombination of the hole released at the first stage.

In LCPs, hole traps are not point defects but ordered conjugated segments of linear polymer chains, whose lengths may vary.

Given the common mechanism of charge-carrier release in thermoluminescence, thermally stimulated conductivity, isothermal decay, dark conductivity, and photoconductivity, the most relevant modes in all these phenomena should be fully symmetric stretching vibrational modes. Consequently, theoretical calculations of carrier mobility in ionic crystals and partially conjugated linear polymers should account for the interaction between polaronic charge carriers and these vibrational modes.

7. In general, oscillatory regularity in the energy spectrum of traps appears to be a rather universal property; it is reliably observed in materials with a sufficiently wide bandgap and a moderate impurity concentration. In narrow-gap crystals, as well as in micro- and nanostructured materials and chain polymers, it becomes less pronounced for several reasons.

Overall, systematic theoretical calculations are required to explain the proposed oscillatory model, the mechanisms of its formation, and its potential generalization to other types of materials.

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Анотація. В огляді описано дослідження ряду матеріалів різних типів удосконаленим методом фракційної термолюмінесценції. Показано, що енергії активації пасток утворюють коливальні закономірності $E = \hbar\omega_{TL}(n+1/2)$, в яких більшість значень ω_{TL} збігаються з частотами ліній спектру комбінаційного розсіювання. У частині I огляду описано застосовані методи термолюмінесценції (ТЛ), представлено експериментальні результати. Було сформульовано поляронну модель пасток. У частині II огляду описано механізми ТЛ, що відповідають запропонованій моделі в досліджуваних матеріалах різних типів. Обговорюються причини існування енергій активації, кратних цілим та напівцілим значенням $\hbar\omega_{TL}$. Описано вплив частотного фактора на процеси ТЛ.

Ключові слова: термолюмінесценція, комбінаційне розсіювання світла, полярон, коливальна регулярність