

OSCILLATORY REGULARITY IN THE ENERGY SPECTRUM OF TRAPS IN ORDERED MEDIA. I. EXPERIMENTAL METHODS AND RESULTS (REVIEW)

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Abstract. The article presents the results of the author's research into the energy spectra of traps in over 30 ordered materials - including metal oxide crystals, halide perovskites, alkali halide crystals, and specific types of polymers - using an improved fractional thermoluminescence (FTL) method. The trap energies exhibit oscillatory regularities described by $E = \hbar\omega_{TL}(n+1/2)$, where, in most cases, ω_{TL} coincides with the frequencies of the Raman spectrum lines. Depending on the crystal structure, we observed one to five oscillatory series. The oscillator regularities in trap energies are attributed to the polaron nature of the charge carriers. We propose a polaron model of traps in inorganic crystals and a one-dimensional (1D) trap model for organic linear conjugated polymers. Part I describes thermoluminescence methods for investigating trap energy spectra, presents the experimental results, and formulates the polaron trap model.

Keywords: thermoluminescence, Raman scattering, polaron, oscillatory regularity

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1. Introduction.

The article describes the results of the author's 30 years of experimental studies on the energy spectra of traps in various inorganic crystals and linear conjugated polymers. The main research method is fractional thermoluminescence (FTL).

In total, more than three dozen substances were studied and divided into three categories based on their thermoluminescent properties. The first category (Ct1) includes metal oxide crystals (hereinafter MOs) and alkali halide perovskites of the CsCdCl₃ type. The second category (Ct2) includes alkali halide crystals (AHs). The third category (Ct3) includes two organic linear conjugated polymers (LCPs): σ -conjugated poly(di-n-hexylsilane) (PDHS) and π -conjugated methyl-substituted ladder-type poly(p-phenylene) (MeLPPP).

The main conclusion that follows from these studies is the presence of an oscillatory regularity in the energy spectrum of traps. We observe this regularity in all substances we studied under moderate defect content, i.e., in the absence of hopping inter-impurity conductivity. In addition, the substances must have a sufficiently wide bandgap. That is, the oscillatory regularity was reliably observed in crystals with sufficiently wide bandgaps and a moderate amount of impurities.

In MOs, depending on the complexity of the crystal structure, from one to five oscillatory series with energies $E = \hbar\omega_{TL}(n+1/2)$, ($n=1,2,3,\dots$) were observed. Each series corresponds to a certain value of the energy quantum $\hbar\omega_{TL}$. Another important result is that

in most cases the frequency ω_{TL} of these series coincides with the frequency of fully symmetric stretching modes in the Raman spectrum of the studied compound. In other cases, oscillatory series arise from second-order Raman modes, local vibrational modes, and modes forbidden in first-order Raman scattering.

The cubic structure of AHs, according to the selection rules, does not have vibrational modes active in the first-order Raman spectra. Despite this, the trap energies in these crystals also show oscillatory regularity (a single series) with frequencies corresponding to local H -center vibrations. In PDHS, four oscillatory series of trap energies were observed, each corresponding to a specific silicon-backbone conformation. In MeLPPP, a single oscillatory series is observed.

The article uses experimental results both previously published and recently obtained in MeLPPP. Simultaneous analysis of properties across various compounds allowed us to derive several new generalizations for both individual material groups and the set as a whole. As a result, we proposed a consistent TL mechanism for all three compound types studied. In addition, we clarified the concept of the frequency factor and explained the reasons for linear TL kinetics in the studied compounds.

Despite a diligent and extensive search, we found no other reports in the available literature on oscillatory regularity in trap energies. Only one paper reported four traps with equidistant energies in AlN:O [1]. We have published most of our results on this topic, but we consider it necessary to provide a wider range of researchers interested in crystal spectroscopy with an overview of research on this non-trivial regularity.

Among the substances studied, we also examined those with somewhat ambiguous oscillatory regularity, as their energy spectra became practically continuous. We observed this in crystals with high impurity concentrations (YSZ (ZrO_2 stabilized with Y_2O_3), ruby (Al_2O_3 with a high concentration of chromium)), as well as in nano- and microcrystalline compounds A_2B_6 (CdS, CdSe), nanosized YSZ powders, and others. In some cases, the oscillatory regularity was “washed out” because $\hbar\omega_{TL}$ was very small. In such cases, the fractional emission method was not very effective, and other methods were used to determine the activation energies. We will only briefly discuss these studies further, since this article emphasizes the interesting observation of oscillatory regularity in activation energy values.

2. Methods and materials

2.1. Determination of thermal activation energies of traps by the improved FTL method

Thermoluminescence (TL) is a main method for studying the energy and kinetic parameters of traps in crystals. The method's advantages include high sensitivity, accuracy, and clear results, as well as the relatively low cost of the required equipment. The essence of the TL method is to study the intensity of recombination phosphorescence of a sample previously irradiated with ionizing radiation during its heating at a constant rate $\beta = dT/dt = \text{const}$. The trap activation energy E_a is determined using various TL-peak parameters: its half-width, the temperature at the peak maximum (T_m), the dependence of this temperature on the heating rate, etc. Almost all of these methods (more than 20 [2-4]) require knowledge of TL kinetics, which itself requires preliminary analysis. In addition, most apply only to weakly overlapping TL peaks.

We used the initial slope method [3,4], which does not require knowledge of the process kinetics. In addition, we found that in the studied compounds repeated carrier capture by traps can be neglected; i.e., thermoluminescence generally follows linear kinetics. In this case, the TL intensity is proportional to the concentration of filled traps m (i.e., the light sum) and the probability of thermal release of the charge from the trap. For TL as a quasi-equilibrium process, the carrier-release probability is proportional to the Boltzmann factor $\exp(-E/kT)$, where E is the energy of the excited level from which the charge leaves the trap. That is, in the presence of traps of the same type, the TL intensity is described by the formula

$$I = -\frac{dm}{dt} = s_0 m \exp\left(-\frac{E}{kT}\right), \quad (1)$$

where the proportionality coefficient s_0 is called the frequency factor. Both of the above-mentioned coefficients in Eq. (1) describe the relaxation process regardless of the properties of the material under study. s_0 includes the specific properties of the substance. With increasing temperature, the concentration of filled traps decreases, while the exponential coefficient, on the contrary, increases, so the dependence $I(T)$ has the form of a curve with a maximum, as in Fig. 1. It can be seen that when a small part of the filled traps is emptied ($\delta m/m \sim 1-3\%$), the TL intensity is actually independent of m . That is, under such conditions, we can assume that $I = I_0 \exp(-E/kT)$, where $I_0 = s_0 m \approx \text{const}$. The trap activation energy is determined from the slope of this dependence, plotted as $\ln(I)$ versus $1/T$: $E = -k(\Delta(\ln I)/\Delta(1/T))$. Using a larger section of the TL-curve underestimates E because it violates the criterion $m \approx \text{const}$.

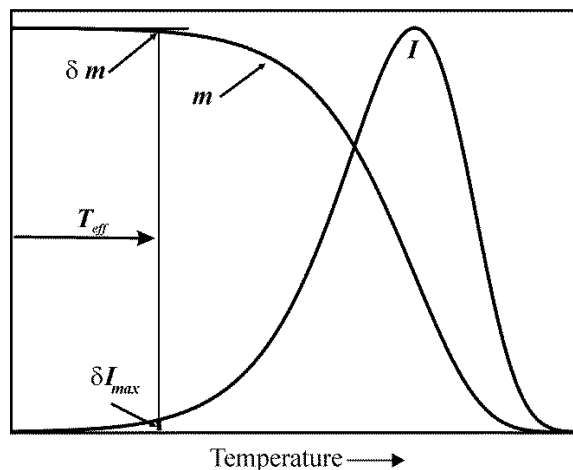


Fig. 1. TL-curve (I) and change in light sum m depending on temperature.

To improve result accuracy, fractional glowing is used, a further development of the initial slope method. The sample was excited by ionizing radiation at a low temperature, if possible, to saturation. The intensity channel sensitivity was set as high as possible so that the maximum intensity of the fraction, $\delta I_{\max}$, did not exceed 1-3% of the peak intensity of the investigated TL peak. For fraction thermoluminescence (FTL), dust-like heating is traditionally used because of its simplicity [5]. Here, short-term, rapid temperature oscillations are superimposed on a slow linear temperature increase. Another option involves stepwise heating-cooling [6]. With such modulation, the initial and final temperatures and corresponding intensities of the next fraction exceed those of the previous fraction. As a result, the number of fractions is limited because the intensity recording

channel overflows. This circumstance is schematically reproduced in the upper part of Fig. 2. In reality, it is possible to obtain no more than 20-30 fractions in the 100 K temperature range, which significantly limits the accuracy of energy determination and the method's resolution.

We used a different temperature modulation mode: after each partial heating and recording of a fraction, the sample was quickly cooled by intensive blowing of the coolant (to reduce the light sum consumption) to a temperature at which the afterglow disappeared, or its intensity reached a value that did not decrease with further cooling. The recording of each fraction continued until the intensity reached a program-set value. For intense TL peaks, we used the full intensity-channel scale (Fig. 2 below).

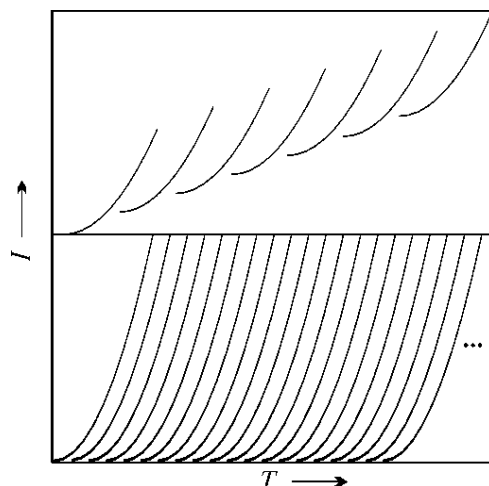


Fig. 2. Schematic representation of fractional TL curves. Top: dust-like heating; bottom: the temperature-cycling method we used. Only parts of the areas with increasing temperature are reproduced.

Unlike classical temperature cycling [5,6], our method is not limited by the ADC bit size, since each fraction starts at the minimum intensity. The number of fractions depends only on the intensity channel sensitivity. In many cases, this sensitivity could be increased (with an acceptable signal-to-noise ratio) by 2-3 orders of magnitude compared to the sensitivity required to record the investigated TL peak. This allowed, in favorable cases, obtaining 100 or more fractions in the temperature range $\Delta T \sim 100$ K (the record was 230 fractions).

Because the intensity channel is highly sensitive, dark-current drift occupied a significant portion of the intensity scale. Therefore, unlike the classical version of FTL [5,6], where data are recorded as a continuous stream, we accounted for this drift by measuring the zero-signal level at the beginning and end of each fraction. We monitored FTL sections with decreasing temperature to achieve a constant minimum intensity. After completing fraction registration, we programmatically reduced each point's intensity to the corresponding linearly interpolated zero-level value, then wrote the data to a text file as a separate record.

The proposed FTL technology made it possible to establish that, for low-temperature peaks in AHS and LCPs, after registering the next fraction and subsequent cooling, a background afterglow (AG) is observed, whose intensity slowly decreases from fraction to fraction. The slight decrease in AG allowed it to be removed during calculations by reducing the intensity of all points in the fraction by the same value until the dependence $\ln(I)=f(1/T)$ was maximally straightened. If the rate of change of this background noticeably affected the

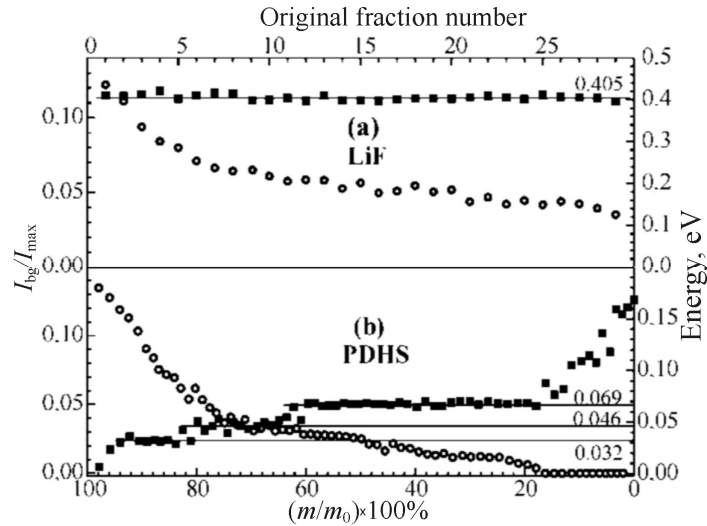


Fig. 3. Dependence of fractional energies (squares) and relative background magnitude (circles); (a): on the fractional ordinal number for the TL peak at 120 K in LiF; (b): on the remainder of filled traps in PDHS.

results, we kept the sample for a set time before starting the next fraction to reduce background intensity and its influence on the results. We also decreased the registration time for a separate fraction.

Fig. 3(a) shows the results of calculating the first 30 fractions of the TL peak at 120 K in LiF. The background rejection procedure provides a distinct horizontal shelf at $E=0.405$ eV ($=2.5 \times 0.162$ eV). Fig. 3(b) shows a similar dependence for PDHS. It can be seen that the background disappears within the shelf at $E=0.069$ eV around 30 K (TL fraction no. 22). In LiF, the background disappears after the trap is emptied at $E=0.32$ eV, i.e., after $T \approx 150$ K. For NaCl, the corresponding figures are $E=0.45$ eV and $T=160$ K.

The effect of taking into account the background on the value of the fractional energy is illustrated in Fig. 4. In part (a), where the background is not removed, the dependence $\ln(I)=f(1/T)$ clearly differs from the straight line. The graph in part (b) was obtained after removing the background to the value corresponding to the minimum of the root-mean-square deviation (RMSD) of the experimental points from the straight line $\ln(I)=\ln(I_0)-E_c/(kT)$.

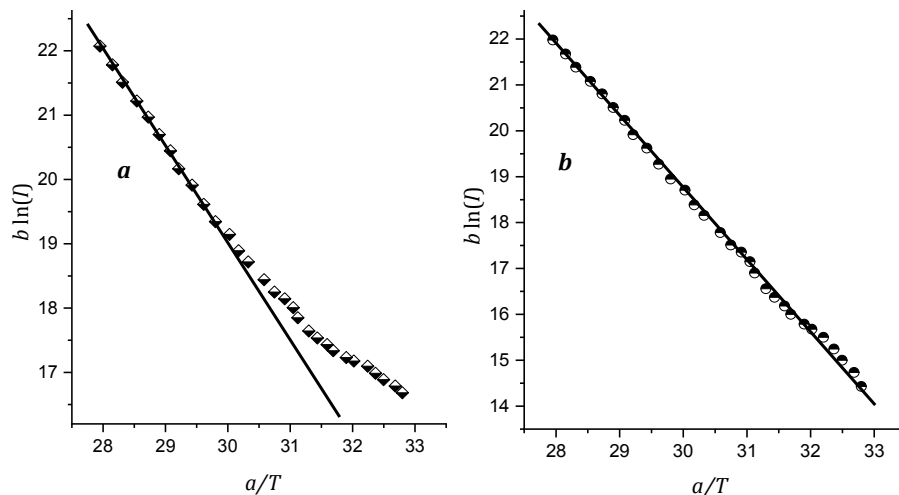


Fig. 4. Typical plot of $\ln(I)$ versus $1/T$: (a) with background; (b) after background removal.

The value of $\ln(I_0)$ was determined by averaging over all points of the fraction, i.e.

$$\ln(I_0) = \frac{\sum_{i=1}^n [\ln(I_i) + E_{fr} / (kT_i)]}{n}, \quad (2)$$

where E_{fr} was determined by averaging the energies E_i calculated for all consecutive pairs of experimental points, i.e.

$$E_i = -k [\ln(I_{i+1}) - \ln(I_i)] / [1/T_{i+1} - 1/T_i],$$

and

$$E_{fr} = \sum_{i=1}^{n-1} E_i / (n-1).$$

Although the initial background value was only 4% of the fraction's maximum intensity, the energy after background subtraction increased by 30%, and the error decreased by one order of magnitude.

In the final cycles of the TL peak illumination, the condition $m=\text{const}$ within the fraction is not fulfilled. In these cases, when calculating the energy, we represent the data as $\ln(I/m)=f(1/T)$. In the ideal case, as shown in (1), this dependence should be linear over the entire temperature range where the TL peak exists. This allows us to obtain correct energy values for the fractions corresponding to the final stages of trap emptying. In real cases, the studied TL peak often overlaps with the next peak. The increase in the intensity of the high-temperature peak with temperature violates the linear dependence $\ln(I/m)=f(1/T)$. In such cases, the residual light sum m was represented as the sum of two terms: $m = m_1 + m_2$, where m_1 is the area under the fraction from a given point to the end of the fraction and is calculated programmatically. During one fraction, a small part of the light sum is displayed. The remaining light sum, i.e., m_2 , is implemented in the following fractions. The operator's task is to select the desired value of m_2 until the $\ln(I/m)=f(1/T)$ dependence is reached for the majority of the fraction. After such a procedure, the "infected" high-temperature part of the fraction becomes clearly visible and can be removed from the calculation.

Elementary TL peaks sometimes overlap so much that the resulting glow curve appears as a single peak. The resulting TL peak is usually broader, which may raise questions about carrier recapture. In [7], we proposed a simple test to establish both the non-elementary nature of the TL peak and its kinetics. To do this, it is necessary to compare the graphical dependences of the position of the maximum of the TL curve on the area under it, changing this area in two ways: 1) changing the excitation time and 2) heating the sample previously excited under constant conditions to different temperatures with subsequent cooling to the initial temperature and subsequent registration of the residual light sum. For an elementary TL peak and a constant frequency factor, both methods of varying the light sum, regardless of the type of kinetics, give identical results. For linear kinetics, the maximum should not shift. For a complex peak, these dependences should differ. Indeed, if partial temperature purification reduces the number of trapped carriers, the preferential emptying of the low-temperature trap shifts the maximum of the residual TL curve to higher temperatures. When the excitation time is varied, the position of the maximum of the integral curve can shift in either direction (depending on the ratio of carrier-trapping cross-sections to trap concentrations), but the resulting dependence will always differ from the dependence obtained by the first method.

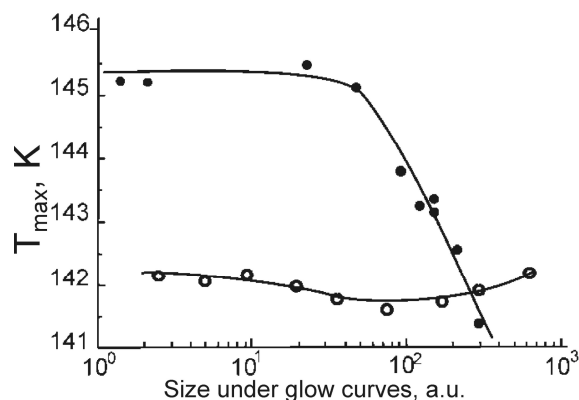


Fig. 5. Behavior of the 141 K peak in LiF as a function of excitation time (open circles) and partial purification at different temperatures (solid circles) [7].

The results of such studies for the TL peak at 141 K in LiF (see the TL curve in Fig. 9, part II) are shown in Fig. 5. The dependence of the temperature at the maximum of the glow curve on the area under the curve due to the variation of the excitation time is shown by empty circles. The corresponding dependence from partial heating is shown by solid circles. These data indicate that the 141 K peak results from the superposition of two closely spaced elementary peaks. The high-temperature peak maximum is at ~ 145 K. According to the FTL data, the low-temperature TL peak anneals in the 110–130 K interval. The constant position of the integral maximum across varying excitation times (142 ± 0.5 K) indicates linear kinetics for this TL peak.

Fig. 6 shows the results of the FTL study of the 141 K peak as a function of the fraction number. The circles indicate the results of a trial FTL taken at low sensitivity in the intensity-recording channel. The obtained sequence was anomalous: the fractional energies did not increase but instead decreased from 0.4 eV to ~ 0.35 eV. To clarify the trap-energy values, we repeated the FTL with 30-fold higher intensity-channel sensitivity. The corresponding fractional energies are shown in Fig. 6 as squares. After recording 50 fractions, we heated the sample to 145 K (without TL recording) and quickly cooled it to 80 K. Then, the remaining light sum was emptied in five cycles at 0.32 eV. The previous 50 fractional energies were placed on a shelf at 0.404 eV. If necessary, we plotted the calculated fractional energies against the fraction serial number (Fig. 6), the residual light sum (Fig. 3b), or the effective fraction temperature

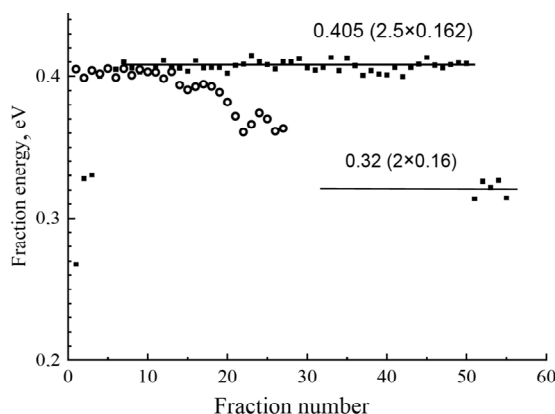


Fig. 6. FTL peak at 141 K in LiF. Fractional energies for the low-sensitivity intensity channel (circles) and the 30 $\times$ increased-sensitivity channel (squares).

T^* (Fig. 10, part II). T^* is the temperature of the last point of the fraction, or the true temperature of the maximum if it is present.

The improved FTL technique and in-depth data analysis, including the removal of background luminescence, the actual absence of the restriction under the condition $m \approx \text{const}$, as well as a significant number of identical fractional data, made it possible to obtain averaged values of trap energies with an accuracy of up to three significant figures. The presence of a shelf in the fractional data indicates a discrete trap energy, and several dozen identical data points significantly increase the reliability of the results. To process FTL data, we developed a program that, because of its narrow specialization, proved much more productive than standard packages. As a result, processing 100 fractions took no more than 2 hours. Other data processing procedures are described in [8]. The presence of several dozen points on the shelf significantly increases the reliability of the results. Actually, this is the advantage of the fractional method of determining the trap energy compared to any other single-shot method of determining the energy.

Figs. 3 and 6 show a "shelf" for one of the observed oscillatory dependencies (in LiF), clearly demonstrating a plateau in activation energy values determined from individual fractions. For example, to illustrate the accuracy of the, Table 1 presents activation energy data for NaCl. The difference between the experimentally determined activation energy values and those calculated using the formula $E_n = \hbar\omega(n+1/2)$ appears in the third, or sometimes the second, significant digit; that is, the discrepancy is on the order of a few meV. The uncertainty in determining the activation energy values also falls within a few meV. The same holds true for ZnWO_4 (Table 2, Section 3) and all other materials in which oscillatory dependencies were recorded. This indicates a very high level of accuracy in determining emission parameters from luminescence spectra. We achieved this accuracy for all materials with sufficiently wide bandgaps and moderate impurity levels; we provide detailed results, including uncertainty estimates, in the relevant publications. This accuracy is attributed not only to the experimental procedure itself but also to data processing performed using specialized software developed by the authors.

Table 1. Serial sets of trap energies in NaCl ([8] and new data); N is the quantum number, E_{exp} is the experimental energies, E_{clc} is the energies calculated by formula (5) using the averaged experimental values of $\hbar\omega_{\text{TL}}$ (0.112 eV – 904 cm^{-1}).

N	$E_{\text{clc}}, \text{eV}$	$E_{\text{exp}}, \text{eV}$	N	$E_{\text{clc}}, \text{eV}$	$E_{\text{exp}}, \text{eV}$
1.5	0.168	0.167 ± 0.005	9	1.009	-
2	0.224	0.212 ± 0.010	9.5	1.065	1.064 ± 0.002
2.5	0.280	-	10	1.121	1.120 ± 0.002
3	0.336	-	10.5	1.177	1.178 ± 0.002
3.5	0.392	0.393 ± 0.005	11	1.233	1.227 ± 0.005
4	0.448	0.450 ± 0.002	11.5	1.289	1.292 ± 0.003
4.5	0.504	0.502 ± 0.001	12	1.345	-
5	0.560	-	12.5	1.401	1.408 ± 0.003
5.5	0.616	0.616 ± 0.001	13	1.457	1.460 ± 0.002
6	0.672	-	13.5	1.513	1.514 ± 0.002
6.5	0.728	0.736 ± 0.003	14	1.569	-
7	0.784	-	14.5	1.624	-
7.5	0.841	-	15	1.682	-
8	0.897	0.880 ± 0.010	15.5	1.738	1.730 ± 0.005
8.5	0.953	0.951 ± 0.003			

Regarding the agreement between TL and Raman frequencies (see below, Table 3, Section 3) the difference of a few cm^{-1} between ω_{TL} and ω_{Ram} also represents a high degree of correspondence. This confirms the reliability of the results and, consequently, the existence of oscillatory dependencies in the trap activation energy spectrum.

Briefly about other methods we used to determine the activation energy.

1. In some cases, a slightly different method for obtaining, processing, and presenting the results was developed and used, involving analysis of the initial slope as a whole. Registration of fractional curves began with low-temperature points long before the start of the thermoluminescence band, and each subsequent fraction was measured until a certain temperature was reached, not until intensity dropped. Thus, each subsequent fractional curve had a lower intensity, but the criterion of light sum constancy was better fulfilled, and it was also possible to better separate close peaks - the peak clipping method was automatically used. The initial slope curves of high orders had a significantly lower intensity than those of the first orders, but the installation - namely, a 16-bit ADC - could provide high-intensity separation without the harmful effects of digitization noise. We processed the results using standard software packages. We approximated the initial slope curves with a function of the form $I = I_0 + A \exp(E/kT)$, minimizing the RMSD (Fig. 7a).

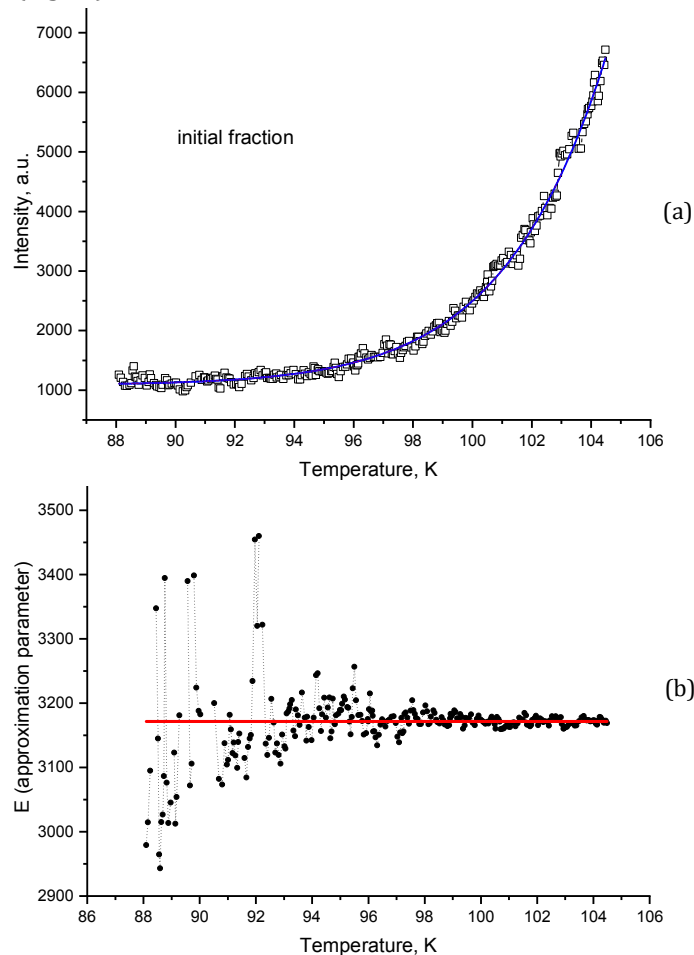


Fig. 7. Approximation of the initial slope curve during fractional glowing (a); the result of calculating the activation energy (b).

To verify the result, we compared the obtained trap activation energy (horizontal line in Fig. 7b) with the value calculated at each point on the experimental curve (Fig. 7b). As can be seen from the figure, at low-temperature points of the curve, a small signal/noise value leads to significant oscillation around the obtained activation energy value; however, these data contain information about the background, which is a physically important approximation parameter.

For a more correct presentation of the results, statistical processing of the results was used; namely, the energy spectrum was presented in the form of frequency histograms for energy values (Fig. 8). The error was estimated as the RMSD of the fractional energies on the shelf or the half-width of the “statistical” peak on the histogram. When comparing data from different methods, the activation-energy results agreed well; however, the modified method uses more data and therefore provides more data for statistical analysis, which is essential for these experiments. In addition, this method accounts for the background more accurately in the calculations.

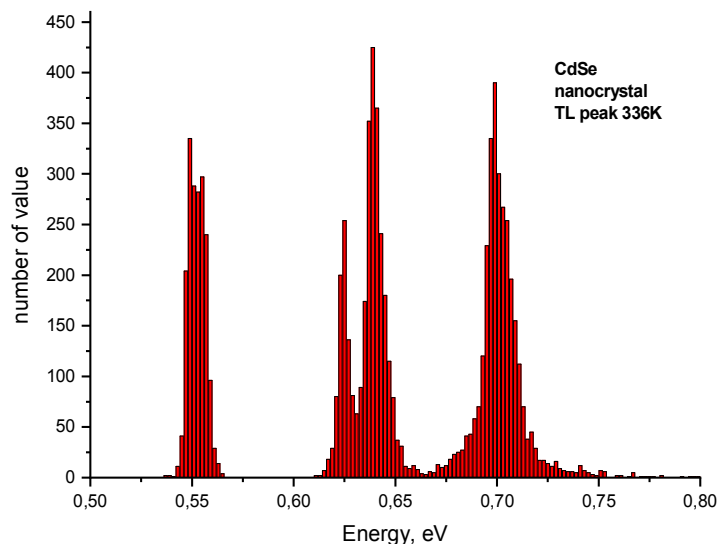


Fig. 8. Fractional glowing of the 336 K peak in nanocrystalline CdSe.

2. This method was used when the intensity of TL was insignificant, and the integral curve of TL was practically not divided into elementary peaks (Fig. 9). In this case, the most effective method was to determine the activation energy by the shape of the elementary curve of TL. For determination of activation energies of individual TL peaks by this method, as well as for comparative analysis, TL curves with complex contours were decomposed into elementary components using program *PeakFit* according to formulas (3), (4) for linear and quadratic kinetics, respectively [9]. For each peak, we determined the activation energy, frequency factor, and temperature of a maximum as approximation parameters of the experimental curves using analytical methods. We selected the shape of each contour to match the experimental curves, using linear or quadratic TL kinetics equations.

$$I(T) = -\frac{dm}{dt} = m_0 s_0 \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{s_0}{\beta} \left(\int_{T_0}^T \exp\left(-\frac{E}{kT}\right) dT\right)\right] \quad (3)$$

$$I(T) = -\frac{dm}{dt} = m_0 s_0 \exp\left(-\frac{E}{kT}\right) \left[1 + \frac{s_0}{\beta} \left(\int_{T_0}^T \exp\left(-\frac{E}{kT}\right) dT\right)\right]^{-2} \quad (4)$$

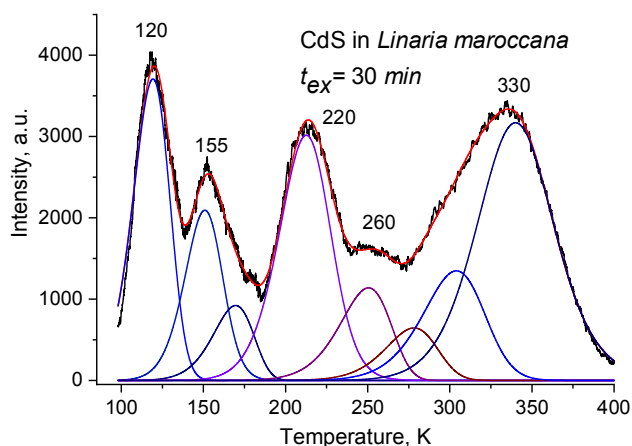


Fig. 9. Typical TL curve of nanocrystalline CdS grown by "green" synthesis [12]. The red curve represents the sum of the elementary peaks into which the experimental TL curve has been decomposed. The close agreement between this curve and the experimental one demonstrates the accuracy of the decomposition into elementary peaks.

Here, m_0 is the initial concentration of carriers on the traps (light sum), s_0 is the frequency factor, β is the heating rate, and E is the energy of thermal activation of the trap; m_0 , s_0 , and E are the parameters of the decomposition corresponding to the minimum RMSD of the analytical curve from the experimental one.

These methods were used by us for most of the micro- and nanostructures (CdS, CdSe, YSZ) and for CdS nanoparticles obtained by "green" synthesis, etc [10-13]).

Thus, one method or another could process practically all possible variants, and one could obtain sufficiently reliable results. Establishing oscillatory regularity clearly requires precise measurements. In our opinion, only the fractional TL method can provide the required accuracy because it can obtain a large amount of the same type of data and process it deeply.

2.2. Experimental details

Crystalline samples were polished plates with a thickness of <0.5 mm. Organic samples were films no thicker than $300\ \mu\text{m}$, deposited on metal or sapphire substrates by evaporation from toluene solutions. Samples grown in laboratory conditions were both nominally pure and doped with various metals. We used CdWO_4 and ZnWO_4 samples, both undoped and doped with Bi, Na, Ni, and Pb; yttrium-aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$, or YAG), both nominally pure and doped with Sm, Eu, and Cr; NaCl and NaCl:Bi; KCl and KCl:Eu; NaI and NaI: Tl; etc. We also used natural samples of NaCl and KCl. We also used heat-treated samples of alkali halides and PDHS (tempering and quenching). Such treatment often significantly increased individual low-intensity TL peaks, creating opportunities to conduct fractional experiments. In addition, we studied micro- and nano-sized samples (YSZ, ZnS:Cu, CdS, CdSe, etc.).

A chromel-copal thermocouple (80-600 K) and a silicon thermodiode (4-340 K) were used as temperature sensors. An ADUC834 board transmitted analog temperature and intensity signals to a PC. Data were recorded at 1-sec intervals. Because of the significant thermal inertia of both nitrogen and helium cryostats, feedback to stabilize the heating rate proved ineffective. Accordingly, the sample heating rate $\beta \approx 0.3$ K/s was set using the polynomial $U = U_0 + b_1T + b_2T^2$, where U is the analog voltage at the DAC output used to control heater power, and T is the temperature. The values of U_0 , b_1 , and b_2 were previously selected experimentally to maximize linearization of heating.

To study TL in wide-gap inorganic crystals, as well as in micro- and nano-sized samples, an X-ray source (W, 30 kV, 20 mA) and a nitrogen cryostat (80-600 K) were used. We studied organic materials in a helium cryostat (6-300 K) and performed optical pumping with a high-pressure mercury lamp (500 W).

3. Experimental results

3.1. Experimental facts of the existence of oscillatory regularities in the energy spectrum of traps

Improved FTL technology and detailed mathematical processing of experimental data allowed us to reliably establish regular spacing in the trap energies of the materials we studied. This section describes these facts. The following section describes the facts of the coincidence of TL frequencies with the frequencies of vibrational modes - most often with the modes of symmetric vibrations (A_g) active in the first-order Raman spectra of the corresponding compounds.

The following sections provide a detailed analysis of these results and the proposed TL models. Fig. 10 shows examples of the existence of oscillatory regularities for trap energies in MO crystals

$$E = \hbar\omega_{TL} \left(n + \frac{1}{2} \right), \quad (5)$$

where E is the trap energy, $\hbar\omega_{TL}$ is the vibrational quantum energy, and $n = 1, 2, \dots$ is the vibrational quantum number.

In corundum Al_2O_3 (Fig. 10a), a single oscillatory series with a vibrational quantum energy of $\hbar\omega_{TL} = 0.079$ eV is observed [14]. Here and further, the quantum energies $\hbar\omega_{TL}$ are pointed out in the insets of the corresponding graphs. A single-series pattern is also found in $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ crystals with $\hbar\omega_{TL} = 0.031$ eV [15]; ZnSe with $\hbar\omega_{TL} = 0.026$ eV [16]; YAlO_3 with

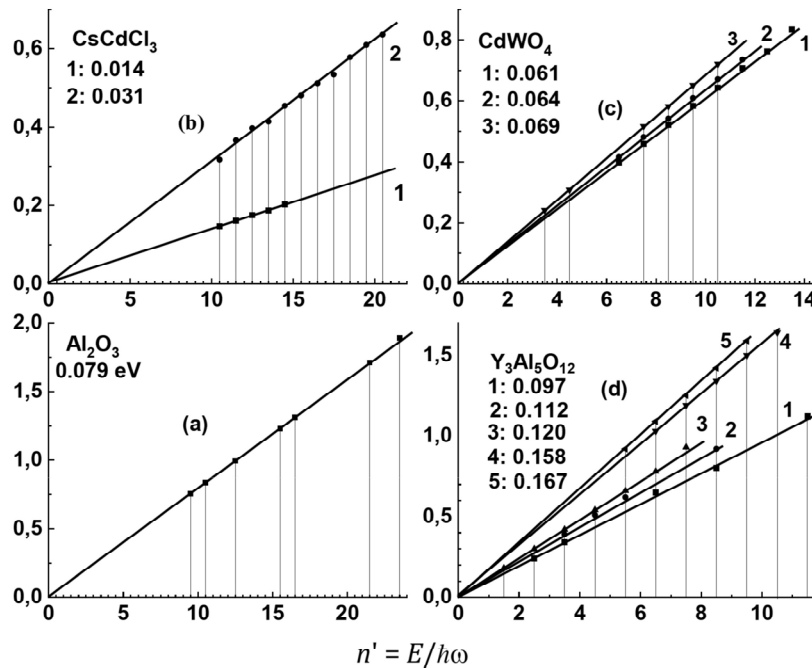


Fig. 10. Examples of oscillatory regularity in MO crystals. (a): Al_2O_3 ; (b): CsCdCl_3 ; (c): CdWO_4 ; (d): $\text{Y}_3\text{Al}_5\text{O}_{12}$. The straight lines correspond to the dependence $E = \hbar\omega_{TL}(n + 1/2)$; the points on them represent values of activation energy, and the vertical lines indicate the values of n - whether integer or half-integer.

$\hbar\omega_{TL}=0.130$ eV (unpublished results), and others. Two oscillatory series are found in CsCdCl_3 crystals (Fig. 10b) [17]. In CdWO_4 crystals [18] and in ZnWO_4 [19], there are three oscillatory series, Fig. 10c. The results for ZnWO_4 are given in Table 2 to demonstrate how closely the experimental results agree with those calculated by formula (5). Finally, the maximum number of series, namely five, is found in yttrium aluminum garnet (YAG) crystals (Fig. 10 d) [20].

Table 2. Serial sets of trap energies in ZnWO_4 [19]; n is the quantum number, E_{exp} is the experimental energies, E_{clc} is the energies calculated by formula (5) using the averaged experimental values of $\hbar\omega_{TL}$.

N	$\hbar\omega_1, \text{eV}$ 0.0683		$\hbar\omega_2, \text{eV}$ 0.0720		$\hbar\omega_3, \text{eV}$ 0.0778	
	E_{clc}	E_{exp}	E_{clc}	E_{exp}	E_{clc}	E_{exp}
3	0.239	–	0.252	–	0.272	0.270
4	0.307	0.305	0.324	–	0.350	0.355
5	0.375	0.377	0.396	0.394	0.426	0.428
6	0.443	0.441	0.467	0.469	0.506	0.507
7	0.512	0.507	0.539	–	0.584	0.583
8	0.580	0.583	0.611	–	0.661	–
9	0.648	0.646	0.683	–	0.739	0.738
10	0.716	0.713	0.755	0.752	0.817	0.810
11	0.784	0.791	0.827	–	0.894	–
12	0.853	0.860	0.899	–	0.972	–

A common property of these compounds is that each trap energy equals a half-integer multiple of $\hbar\omega$. The number of series tends to increase as the crystal structure becomes more complicated. Results for low-energy traps ($n=1,2$) are absent, since materials in this category were studied starting at the liquid-nitrogen temperature. The exception is the only trap in YAG with $E = 0.18$ eV ($1.5\hbar\omega$, series 2).

Fig. 11 shows the oscillatory regularities in the studied alkali halides [8,21-23]. In these cubic crystals, only single-series sequences occur. Unlike the crystals in the previous category, here the trap energies are multiples of both the half-integer number $\hbar\omega$ of quanta and their integer value. Therefore, in such cases, the trap energy will also be described by formula (5), but now n can take both integer and half-integer values.

In our KBr sample, all detected traps had energies that were integer multiples of the quanta. In other AHs we investigated, trap energies were multiples of both integer and half-integer numbers of corresponding quanta $\hbar\omega$: LiF – 8 integer values and 2 half-integers, KCl – 9 and 2, NaCl – 6 and 12, NaI – 4 and 4. Detailed data for NaCl (Table 1) are presented as an example.

In PDHS (Ct3), trap energies form four oscillatory series [25-27]. A feature of PDHS is that all series begin with energy values equal to the corresponding quantum $\hbar\omega_{TL}$, while the following energies are "half-integer" (Fig. 12a). Series 4 is represented only by its first member. It is impossible to confirm the existence of the next two energies in series 4, since the next two terms actually coincide with the energies that begin series 3 and 2 (0.0177 and 0.0175, 0.030 and 0.032 eV, respectively). Section 3, part II discusses the reason for the existence of several oscillatory series in the PDHS.

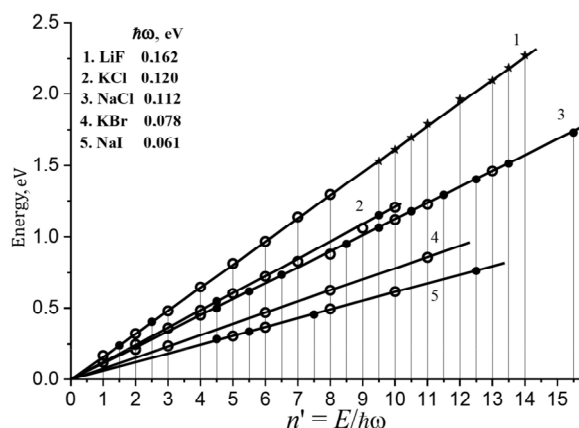


Fig. 11. Oscillatory energy sequences of traps in alkali halides. 1: LiF own data (filled circles) and work data [24] (open circles); 2: KCl; 3: NaCl (open circles represent later data); 4: KBr; 5: NaI. The straight lines correspond to the dependence $E = \hbar\omega n_L(n+1/2)$; the points and circles on them represent values of activation energy, and the vertical lines indicate the values of n - whether integer or half-integer.

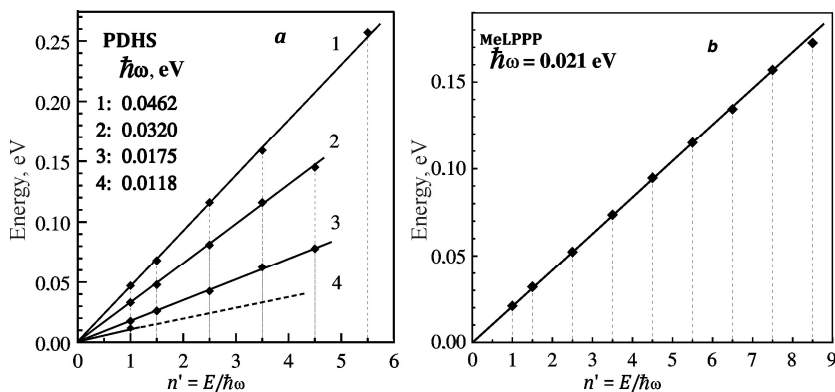


Fig. 12. Serial sets in the energy spectrum of PDHS traps (a) and MeLPPP (b). The straight lines correspond to the dependence $E = \hbar\omega n_L(n+1/2)$; the points on them represent values of activation energy, and the vertical lines indicate the values of n - whether integer or half-integer.

A similar, but single-series oscillatory sequence of trap energies was found in MeLPPP with a quantum energy $\hbar\omega = 0.021$ eV (169 cm^{-1}), Fig. 12b. These data are published for the first time. Fig. 13 shows the dependence of fractional energies on the fractional serial number for the MeLPPP sample as a film deposited on a sapphire substrate.

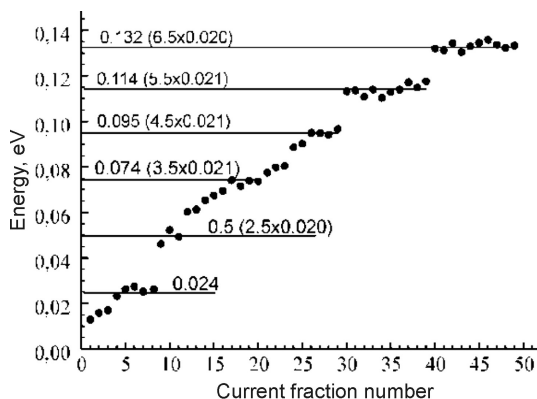


Fig. 13. Dependence of fractional energies on the ordinal number of fractions for the MeLPPP sample.

In light of these results, the question arose: what is generally known about the existence of oscillatory regularity in trap energies? Extensive literature searches allowed us to find more than ten examples of this regularity in other materials. Only one of these works [1] noted four equidistant traps in AlN:O films, with an interval ΔE of 0.06 eV between their energies. Part of the results of these searches are reproduced in Fig. 14 (ZnS: Cu [28]; AlN:O [1]; anthracene+carbazole [29]; PbSO₄ [30], microcline [31], CaS [32]), as well as in Fig. 11 in LiF (empty circles, [24]).

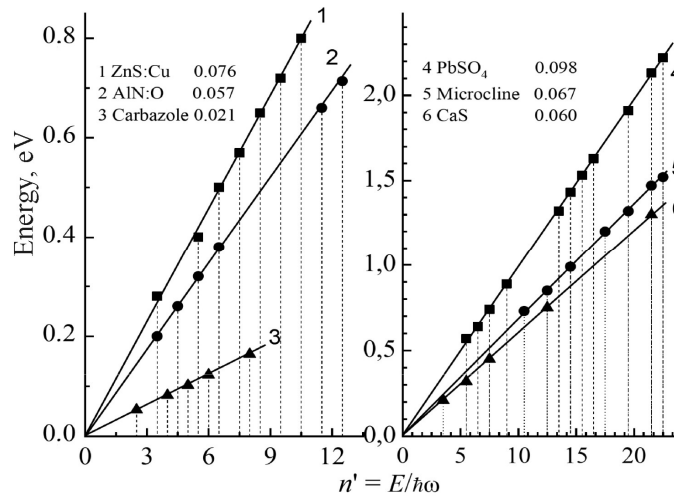


Fig. 14. Oscillatory regularities found by us in the published data: (1) ZnS:Cu; (2) AlN:O; (3) anthracene+carbazole; (4) PbSO₄; (5) microcline; (6) CaS. The straight lines correspond to the dependence $E = \hbar\omega_{TL}(n+1/2)$, the points on them represent values of activation energy, and the vertical lines indicate the values of n .

As mentioned, in some cases the spectrum of activation energies became practically continuous; the oscillatory dependence was ambiguous or did not manifest at all. This was observed in crystals with a high concentration of impurities, for example, in YSZ (ZrO₂ stabilized with Y₂O₃, Fig. 15 [13]), ZnS: Cu [11], and others. Such cases are not considered in this article, and in relation to them, despite the good correspondence of the activation

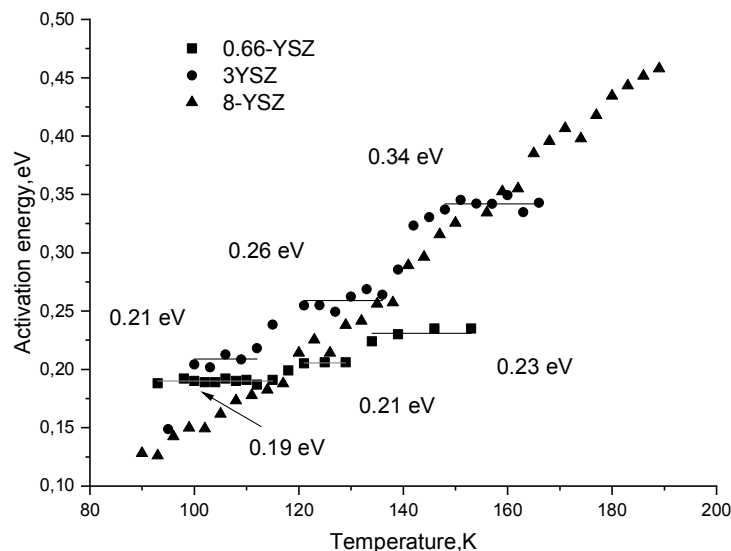


Fig. 15. Activation energies of traps in YSZ, determined by the partial illumination method, at different Y₂O₃ concentrations.

energies to the oscillatory regularity, it is better to speak about the consistency of the obtained data of the TL model developed based on the study of other crystals, including the consistency of the statement about the presence of oscillatory dependence as a universal property of crystals with a predominantly ionic type of bonding.

3.2. Correspondence between TL and Raman frequencies

The release occurs via phonon participation; an oscillatory regularity in the trap energy spectrum indicates this; each TL series corresponds to a specific optical vibrational mode.

These TL frequencies mostly coincide with symmetric stretching vibrational modes (A_g), which appear in the Raman scattering spectrum. In Ct1 crystals, they lie in the high-frequency region of the spectrum. In other cases, the oscillatory series arise from second-order Raman scattering, local vibrational modes, and modes forbidden in the first-order Raman spectra. Table 3 illustrates these correspondences.

High TL frequencies result from a significant contribution of the covalent bond between the central polyvalent metal ion and the surrounding non-metal ions (oxygen or halogen). These quasimolecular complexes (QMC) form tetrahedral MeX_4 or octahedral MeX_6 configurations (Me – metal, X – oxidant). The existence of several oscillatory trap series indicates a corresponding number of energetically non-equivalent quasimolecular complexes in the crystal, some of which may be somewhat distorted. Identical QMC can combine in different ways to form more complex structures. For example, in $CsCdCl_3$, two types of chains built from $CdCl_6$ octahedra correspond to two oscillatory trap series. One type forms when octahedra connect at vertices, while in the other type, every two adjacent octahedra share faces. The lower frequency of 113 cm^{-1} is associated with the latter.

Another manifestation of non-equivalent QMCs is YAG, whose unit cell contains 8 formula units. Because of the different lengths of individual M–X bonds and the asymmetry

Table 3. Illustration of the correspondence between TL frequencies (ω_{TL}) and Raman frequencies ω_{Ram} in Ct1 crystals. [8,14,15,18-20,33].

	$\omega_{TL}, \text{cm}^{-1}$	$\omega_{Ram}, \text{cm}^{-1}$
$Ba_2NaNb_5O_{15}$	249	252
Al_2O_3	642	645
$CsCdCl_3$	113	115
	250	248
$ZnWO_4$	551	545
	581	578
	629	633 ^a
$CdWO_4$	494	495 ^b
	516	514
	554	546
$Y_3Al_5O_{12}$	782	786
	901	912
	968	982
	1274	1309 ^c
	1347	1392 ^c

^aOnly in $ZnWO_4:Ni$.

^bObserved in doped crystals, presumably an IR-active mode.

^cSecond-order modes, observed in YAG:Cr.

of their orientations, this structure contains four slightly distorted AlO_4 tetrahedra, six AlO_6 octahedra, and six YO_8 dodecahedra. In YAG, both undoped and with various metal impurities (Nd, Cr, Sm, etc.), the energies of 27 traps have been determined, which are distributed between five oscillatory series, Fig. 10d. The TL bands of series 1-3 are located in the low-temperature region of 80-370 K, the frequencies of the first two series (782 cm^{-1} , 901 cm^{-1}) have corresponding lines in the first-order Raman spectrum, in the region of the location of the vibrational modes of AlO_4 and AlO_6 complexes [20,34]. For the other three frequencies (968 , 1274 , 1347 cm^{-1}) the corresponding Raman modes are most likely second-order modes (they are characterized by the corresponding temperature behavior [20]). The TL series at 968 cm^{-1} has characteristics similar to the first two low-temperature series. The other two TL series are high-temperature (420–700 K), they have a low intensity compared to the low-temperature peaks of series 1–3, and they are present only in YAG:Cr samples with a fairly significant Cr concentration ($\sim 1\%$) [20]. These series are associated with oscillations of $\text{CrO}_4/\text{CrO}_6$ complexes, as evidenced by the disappearance of high-temperature TL after purifying the YAG:Cr crystal by zone melting. The larger mass and size of Cr^{3+} atoms compared to Al^{3+} atoms, as well as the change in the magnitude of the force constant, η can affect the vibration frequency (something similar happens in the case of H -centers in AHs, see section 2, part II). This can also violate selection rules for the possible manifestation of local modes associated with impurities and second-order lines (see, e.g., [35]). We note that we indicate the modes registered by us (1309 , 1392 cm^{-1}), although it is possible to select combinations closer to ω_{TL} , e.g., 1273 and 1336 cm^{-1} - however, the corresponding bands were not registered by us in the Raman spectra.

A similar situation occurs in the case of ZnWO_4 , where the TL series 3 (628 cm^{-1}) exists only in Ni-doped samples. The corresponding Raman line at 630 cm^{-1} appeared as a low-intensity maximum in a freshly grown Ni-doped sample [19]. After cutting the sample, this line could not be detected, indicating a higher concentration of Ni^{3+} on the surface of the grown boule than in its volume. In CdWO_4 , the first-order Raman line expected for TL series 1 was not observed. This series can be attributed to an IR mode that appeared in the Raman spectrum because impurities violated the selection rules. Thus, in the MO crystal, an impurity replacing the central QMC atom can generate a low-intensity TL series, and the corresponding Raman line may not be detected.

In cubic AH crystals, no active Raman modes appear in the first-order spectra (their activity is in the IR spectra). Only the second-order spectrum can be observed. Thus, in NaCl, the highest second-order band occurs at 540 cm^{-1} [36], almost half the TL frequency of 903 cm^{-1} . The only IR-active mode has an even lower frequency, $\omega_{\text{IR}}=162\text{ cm}^{-1}$. A similar situation occurs in other studied AHs (see Table 1, part II). Despite this, the trap energies in AHs also show oscillatory regularities (a single series throughout). That is, the release of non-equilibrium carriers here occurs with the participation of some local vibrational modes. These problems are analyzed in detail in Section 2, part II.

Table 4. Comparison of TL and Raman frequencies for PDHS [27].

Series	1	2	3	4
$\hbar\omega_{\text{TL}}, \text{ cm}^{-1}$	372.6	258	141	97
$\hbar\omega_{\text{Ram}}, \text{ cm}^{-1}$	373.0	259	146	111

In the case of PDHS, the frequencies that generate oscillatory series 1, 2, and 3 coincide with the frequencies of the first-order Raman A_g modes (Table 4). For series 4 ($\omega = 97 \text{ cm}^{-1}$), we did not identify a corresponding Raman frequency. In work [37], a 111 cm^{-1} Raman mode is reported, which probably corresponds to $\omega_{TL} = 97 \text{ cm}^{-1}$. The four oscillatory series in PDHS are associated with the polyconformal structure of molecular chains. We consider this problem in Section 4, part II.

A similar pattern in the distribution of trap energies is observed in MeLPPP (Fig. 13); however, in the Raman spectrum of MeLPPP, the line with a frequency of 169 cm^{-1} is not found. On the other hand, the same frequency (166 cm^{-1}) forms an oscillatory series in carbazole-doped anthracene (Fig. 14). This correspondence is not accidental, since both compounds contain diphenyl-pyrrole groups (Fig. 16). That is, the frequency of 169 cm^{-1} may be an internal vibrational mode of this group.

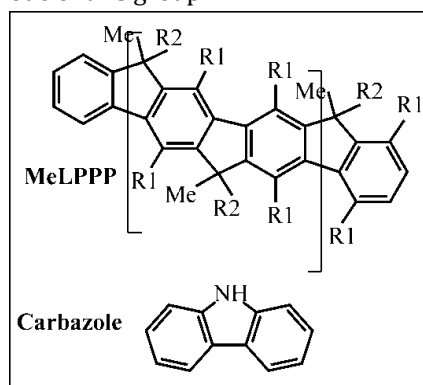


Fig. 16. Structural formulas of MeLPPP and carbazole. Me – methyl group; R₁, R₂ – other hydrogen substituents. The unit cell of MeLPPP is highlighted in square brackets.

3.3. Polaron model of traps

Due to the existence of oscillatory regularities in MO and AH crystals, there was a need to find out what new properties of traps need to be taken into account and what traditional ideas about the structure of traps should be discarded in order to confirm experimental facts with an adequate model.

1. In ionic (AHs) and ion-covalent (perovskites, MOs) crystals, the relaxed excess charge is in a polaron state due to the polarization of the nearest ionic environment. Finite particle motion discretizes its energy spectrum. The energy-level distribution features are determined by the specific interaction mechanism between the excess charge and the surrounding environment. The equidistant energy levels indicate the elastic nature of this interaction, that is, ionic polarization of the lattice. Therefore, the existence of an oscillatory regularity in the energy spectrum of traps can indicate that the charge carriers are localized as polarons.

2. Most often, fully symmetric stretching vibrations (A_g) turned out to be relevant during the thermal release of carriers. This feature arises because the ion displacements are symmetric in both the vibrational mode and the polarization distortion. Polarization distortion is a static displacement of oppositely charged ions toward/away from an excess point charge. The relevant vibrational mode is fully symmetric stretching “breathing” vibrations, i.e., comprehensive compression-extension between the ions of the substance. In Ct1 crystals, QMCs provide these vibrational modes. If, during one half of the oscillation period, the distortion increases because the directions of static and dynamic ion

displacements coincide, then during the next half it is partially compensated. With increasing temperature, the oscillation amplitude increases so much that ions periodically pass through the equilibrium positions characteristic of an unperturbed lattice. Since it is distortion that is the cause of charge localization, its absence means that the excess carrier has the opportunity to leave the trap.

3. The existence of oscillatory series associated with the crystal's eigenvibrational modes $\omega_{TL} = \omega_{Ram}$ indicates that the relaxed trap charge perturbs a region that does not exceed its own size, QMC. The small-radius polaron is best suited to this.

4. It is usually assumed that each new trap should correspond to a different intrinsic or impurity defect or a combination of them. The traditional idea of trap structure does not lead to oscillatory regularity, since each new structural feature in the crystal has an oscillation frequency different from the previous ones. The adequate task is to create a situation where the traps have different depths but the same oscillation frequency. In addition, it is necessary to ensure that the TL and Raman frequencies coincide.

5. The last requirement is satisfied if the light sum is stored by ionizing regular elements of the crystal structure, i.e., QMCs. The knocked-out electron localizes on a positively charged deep recombination center (RC), for example, a vacancy in a non-metallic component. The hole loses mobility because the ionized QMC (QMC⁺) relaxes. The absence of one electron changes the force constant in QMC⁺, which in turn changes the oscillation frequency. As a result, the resonant tunneling mechanism along the QMC chain disappears. The difference in the electrical parameters of QMC⁺ and the neighboring QMC means that only a thermally activated electronic transition is possible between them. The vibrational level from which the electron is released (recovering the relaxed hole) lies near the geometric intersection point of the QMC and QMC⁺ configuration curves. After the electron transitions to QMC⁺, the force constant is restored in the latter, i.e., $\omega_{QMC} = \omega_{Ram}$. This transition triggers the alternating movement of electrons towards the trap. In band theory, instead of considering this relay motion of many electrons, we consider the drift motion of a single fictitious positive charge, i.e., a hole, towards RC. The process is completed by the radiative recombination of the hole with the RC electron.

For TL, traps in the form of ionized QMCs are necessary, while the Raman spectrum is recorded without prior QMC ionization. Since QMC ionization changes the force constant, under favorable conditions an additional Raman line can be observed, caused by scattering on QMC⁺. To do this, you must first store light in the sample. This line has a negligible intensity, since it corresponds to scattering only on QMC⁺. In addition, it will decay quite quickly under the influence of the excitation laser radiation.

6. The mechanism that can explain the existence of an oscillatory pattern, i.e., the formation of traps with different depths at a constant value of $\hbar\omega_{TL}$, is the donor-acceptor interaction. Because of the polaron effect, the electron and hole localize close to each other, forming donor-acceptor pairs with statistically different distances r_{da} between them. In the donor field, the trap depth decreases according to

$$E = E_{\infty} - \frac{e^2}{\epsilon r_{da}}, \quad (6)$$

where E_{∞} is the trap energy for infinitely distant donor-acceptor pairs. The next term describes the decrease in the trap depth in the donor field, where ϵ is the static dielectric constant of the substance. We have not found an alternative mechanism that could explain

the oscillatory regularities in trap energies in MO crystals. Therefore, we will carry out further analysis within the framework of the proposed model. Thus, to form an oscillatory regularity in the trap activation energies with a frequency $\omega_{TL}=\omega_{Ram}$ in MO crystals, it is not necessary to introduce special defects as traps. Any regular section of the crystal (here QMC) can become a filled trap if an electron is removed from it at a low temperature. Giant TL peaks are absent in this case, since the real light sum is limited not by the number of QMC in the crystal, but by a much smaller number of electronic RCs, i.e., lattice defects capable of localizing electrons. They can be vacancies of the non-metallic component. Impurities that replace the central metal ions in QMC create low-intensity TL series with local or pseudolocal frequencies, which can sometimes be observed in the Raman spectrum as weak peaks. Thus, the energy spectrum of traps always consists of one or more oscillatory series. A universal example is YAG, where 27 trap types are divided into five oscillatory series, with an average of five traps in each. Three intense low-temperature TL series are associated with hole self-localization on QMC AlO_4 and/or AlO_6 . In YAG:Cr, two additional low-intensity high-temperature series 4 and 5 are found. If each trap type is attributed to a unique defect, it would be unrealistic to propose 27 different impurity or intrinsic defects with sufficiently high concentrations to produce the observed number of TL peaks. We also note McKeever [3], who reported that introducing an impurity into the crystal either does not affect the TL at all or leads to the appearance of several new TL peaks at once.

7. The donor field ensures not only the existence of a set of traps belonging to the same oscillatory series. It also ensures that the released hole drifts toward the RC. Carriers do not re-localize to traps of the same type, since the trap is a self-localized hole that disappears as a defect after delocalization. The released hole does not actually undergo re-relaxation because the temperature is too high for this, i.e., the average phonon density is too high. Only a fluctuational decrease in this density can delay the hole on its way to the RC for a short time. Thus, the proposed model, without additional conditions, ensures linear TL kinetics in MO crystals. The correspondence between TL peaks and linear kinetics in ionic crystals has been repeatedly noted in the literature [3,4,38].

8. TL refers to quasi-stationary processes, since the rate of temperature change is much lower than the rate of phonon processes. This means that localized carriers populate the vibrational states of polaron wells according to the probability $w_n \sim \exp[(-\hbar\omega(n+\frac{1}{2}))/kT]$. That is, in each filled trap, one carrier is localized, with which n phonons are statistically associated at temperature T . The thermal activation energy of the trap is defined as the energy of the excited vibrational level $n_{max}=N$, from which carriers tunnel through a barrier reduced compared to the ground state, at a rate (amount of recombinations per second) sufficient for reliable registration of the TL signal. Therefore, the trap's thermal activation energy is $E = \hbar\omega(N+\frac{1}{2})$. This explains why, in MO crystals, the trap energies equal a half-integer number of $\hbar\omega_{TL}$ quanta (see more details in section 6, part II).

Unlike TL, transient processes (absorption, luminescence) depend on the transition energy, i.e., the difference between the energies of the initial and final states. Therefore, the thermal release of a carrier cannot be considered the result of an instantaneous transition from the trap ground state to the excited state via simultaneous absorption of the required number of phonons; i.e., TL can be considered a transient multi-phonon process. By this interpretation, the trap energy should equal an integer number of vibrational quanta. The TL

phenomenon involves a significant number of particles, so it is appropriate to interpret it from a thermodynamic point of view, rather than as events occurring in a single trap.

9. To further clarify the picture, let us consider thermal processes in an ensemble of quantum oscillators, which represents a set of m identical polaron traps. The kinetics of single-phonon processes of phonon absorption and emission due to the interaction of polarons with the thermostat-lattice is described by the system of equations

$$\begin{aligned}
 \frac{dm_0}{dt} &= f_{1,0}m_1 - f_{0,1}m_0 \\
 &\dots \\
 \frac{dm_n}{dt} &= f_{n-1,n}m_{n-1} - f_{n,n-1}m_n + f_{n+1,n}m_{n+1}, \\
 \frac{dm_{n+1}}{dt} &= f_{n,n+1}m_n - f_{n+1,n}m_{n+1} + f_{n+1,n+2}m_{n+2} \\
 &\dots \\
 \frac{dm_N}{dt} &= f_{N-1,N}m_{N-1} - f_{N,N-1}m_N - f_N m_N.
 \end{aligned} \tag{7}$$

Here, m_n determines the number of oscillators with energy $E_n = \hbar\omega(n+1/2)$. The proportionality coefficient $f_{n,n+1}$ describes the rate of the transition $n \rightarrow n+1$, i.e., the disappearance of one center with energy E_n due to phonon absorption. At the same time, the number of centers with energy E_{n+1} is incremented. Phonon emission by a center with energy E_n also reduces the number of centers of this type by one and, accordingly, increases the number of centers with lower energy E_{n-1} . The last equation, in addition to the exchange terms, contains the term $f_N m_N$, which describes charge release from the N -th oscillatory state due to tunneling through the barrier. Adding all Eq. (7) under the condition $f_{n,n+1} = f_{n+1,n}$, we obtain $I \sim dm/dt = -f_N m_N$. That is, the TL intensity is proportional to the number of traps excited to level N , from which the carrier can be released. For a quasi-equilibrium process, the probability of filling the N -th level is determined by the Boltzmann distribution

$$w_N = \frac{m_N}{m} = \frac{1}{A} \exp\left(-\frac{E_N}{kT}\right) \tag{8}$$

where A is the result of the probability normalization, $A = \sum_{n=0}^N w_n$. Substituting the expression for m_N from (8) into (7), we have

$$\frac{dm}{dt} = -\frac{f_N}{A} m \exp\left(-\frac{E_N}{kT}\right). \tag{9}$$

The resulting equation describes linear TL kinetics (1) with a frequency factor $s_0 = f_N/A$. As temperature increases, the population of excited oscillatory states initially increases according to the Boltzmann distribution. The equipment begins to record a useful signal as soon as the number of carriers released per unit time exceeds the intensity-recording channel's threshold sensitivity.

4. Conclusions

After electron removal and subsequent ionic relaxation of the QMC, the parameters of the newly formed well differ from those of non-ionized QMCs of the same type. As a result, the resonant mechanism of carrier transport in the periodic structure is lost; i.e., the hole becomes self-localized. Thus, the appearance of localized excess holes is not directly related

to impurities or intrinsic defects. These defects localize free electrons during excitation, preserving the corresponding part of the self-localized holes. The mechanism of thermal hole release consists in periodic compensation of distortion using symmetric stretching vibrations of the QMC. Excess carriers can be released at moments of complete compensation of distortion. The model is built on the quasi-stationarity of the TL process. That is, the trap activation energy is the energy of the vibrationally excited level N from which the carriers are released: $E_N = \hbar\omega(N+1/2)$. Oscillatory sequences arise from the influence of electric fields from remote negative charges.

We propose a model for the emergence of oscillatory dependence and an explanation of the TL mechanisms; both are largely qualitative. Overall, rigorous theoretical calculations are required to substantiate the proposed model and the mechanisms of its formation.

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Authors' contributions. A. Gumenyuk: Creating (with co-authors of published works) working equipment for TL research; obtaining scientific results; processing and analyzing them; and writing an article. S. Kutovyy: Maintaining scientific equipment in working condition; obtaining scientific results; processing and analyzing them; and writing an article.

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Анотація. Стаття містить результати авторських досліджень енергетичних спектрів пасток понад 30 впорядкованих матеріалів, зокрема кристалів оксидів металів, перовскітів-галогенідів, лужногалоїдних кристалів і полімерів певних типів. за допомогою вдосконаленого методу фракційної термолюмінесценції (ФТЛ). Енергії пасток демонструють коливальні закономірності, що описуються формулою $E = \hbar\omega_{\text{пл}}(n+1/2)$, де в більшості випадків значення $\omega_{\text{пл}}$ збігаються з частотами ліній раманівського спектру. Залежно від кристалічної структури спостерігалося від однієї до п'яти коливальних серій. Показано, що існування осциляторних закономірностей енергій пасток зумовлене поляронною природою носіїв заряду. Запропоновано поляронну модель пасток у неорганічних кристалах та одновимірну (1D) модель пасток для органічних лінійних спряжених полімерів. У частині I статті наведено детальний опис методів термолюмінесценції для дослідження енергетичних спектрів пасток, представлено експериментальні результати та сформульовано поляронну модель пасток.

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