SOLID MATTER

OSCILLATORY RULE IN THE ENERGY SPECTRUM OF TRAPS IN KCl AND NaI CRYSTALS

A.F. GUMENYUK, S.YU. KUTOVYI, O.P. STANOVYI,
V.G. PASHCHENKO, S.V. TOMYLKO

PACS 78.60.K
©2009

Taras Shevchenko National University of Kyiv
(2, Academician Glushkov Prosp., Kyiv 03127; e-mail: lns@univ.kiev.ua)

The thermoluminescence (TL) method is used for the investigation of the energy spectrum of traps in KCl and NaI crystals in the temperature range 80–500 K. It is shown that the thermal activation energies of traps in KCl and NaI form one oscillatory series $E_n = \hbar\omega n$ with vibrational quantum energies of 0.121 eV (979 cm^{-1}) in KCl and 0.061 eV (492 cm^{-1}) in NaI. In this case, the quantum number n assumes half-integer and integer values. Based on the generalized data on the investigated alkali-halide crystals (AHC), we confirmed the earlier proposed model of TL in AHCs. It is assumed that, in addition to the nonradiative H-F recombination, there exists the two-stage recombination of H-centers at anion vacancies resulting in the radiative recombination of a hole at an F-center. The energy of a quantum in the oscillatory rule corresponds to a local vibrational mode of an X_2^- halide molecule.

1. Introduction

Investigating the energy spectrum of traps in a number of crystals (about 15) with ion-covalent bonds, we discovered [1–11] that the thermal activation energy of traps is described by the harmonic oscillator formula $E_n = \hbar\omega_{\mathrm{TL}}(n + 1/2)$, where the quantum energy $\hbar\omega_{\mathrm{TL}}$ assumes values characteristic of lattice vibrations (0.01–0.18 eV, i.e. $\sim 100 - 1500$ cm^{-1}). We observed from one to five oscillatory series, each of which is characterized by its vibrational quantum energy $\hbar\omega_{\mathrm{TL}}$. Except for alkali halide crystals (AHC), the majority of the values of $\hbar\omega_{\mathrm{TL}}$ coincide with the energies of high-frequency lines of the basic first-order Raman scattering (RS) spectrum $\hbar\omega_{\mathrm{RS}}$, whereas the other values of $\hbar\omega_{\mathrm{TL}}$ correspond to the energies of lines not predicted by the group-theoretical analysis (second-order RS lines, local vibrational modes, lines forbidden by RS selection rules). No correspondence is found between $\hbar\omega_{\mathrm{TL}}$ and $\hbar\omega_{\mathrm{RS}}$ for crystals with simple lattices – NaCl and LiF AHCs. The obtained results gave grounds to state that the oscillatory rule reflects some general regularity rather than represents a unique peculiarity of certain crystal compounds. A polaron model of traps and TL process was proposed in [10].

In cubic AHCs, there are no vibrational modes active in RS, though the oscillatory rule for the trap energies with the vibrational quantum energies $\hbar\omega_{\mathrm{NaCl}} = 0.112$ eV and $\hbar\omega_{\mathrm{LiF}} = 0.162$ eV is also observed in the investigated NaCl and LiF crystals. These values exceed the energy of the only optical vibrational mode in these crystals by several times. We did not find any manifestations of the indicated frequencies in other phenomena, though we indicate the correlation between these frequencies and the masses of halogen atoms: $\hbar\omega_{\mathrm{NaCl}}/\hbar\omega_{\mathrm{LiF}} = 1.44$ and $\sqrt{m_{\mathrm{Cl}}/m_F} = 1.37$. This fact stimulated our searches for the oscillatory rule and the corresponding correlation in other AHCs. For the further studies, we chose KCl crystals, where we expected to find a vibrational frequency close to $\hbar\omega_{\mathrm{NaCl}}$, as well as NaI, whose vibrational frequency was predicted to be lower than that in NaCl by a factor of ~ 2. The work describes the results of these experiments and the generalizing conclusions concerning the TL mechanisms in AHCs.

2. Experimental Technique

The investigations were performed in the temperature range 80–500 K. The heating rate was $0.2 \pm 5\%$ K/s. The linear increase of the temperature and the data registration were controlled by a computer program. Samples 0.2–0.5 mm in thickness and 4–8 mm in transverse size were located in a vacuum cryostat and excited by

X-radiation (BSV-2, W, 30 kV, 10 mA) through a beryllium window 0.5 mm in thickness.

The samples were cut off from KCl crystals both specially undoped and Eu-doped. In the doped crystals, the TL peaks appeared to be rather intense and split, which allowed us to investigate the energy spectrum of traps using the fractional technique described in our previous works. KCl:Mg,Ca crystals appeared to be inappropriate for studying TL with the help of the fractional technique, because the corresponding peaks were substantially broadened due to the considerable concentration of impurities $10^{17} - 10^{18}$ cm^{-3}, and the trap energies were no more discrete. Some results were obtained for undoped KCl crystals both synthetic and natural. They are less accurate as compared to those obtained for KCl:Eu crystals, as our samples of undoped KCl manifested much weaker TL than doped crystals.

As another material, we used dosimetric NaI:Tl crystals both without preliminary thermal treatments and those annealed under various conditions (variation of the anneal temperature and duration with the following fast cooling). The change of the anneal parameters was used to increase the intensity of individual maxima of the heat-treated samples, which improved the sensitivity of fractional experiments.

The experimental procedures and the technique of data treatment were considered in our previous works [5–8] in detail.

3. Experimental Results

3.1. KCl

General description of TL curves

Figure 1 shows the TL curves of some investigated samples without preliminary thermal treatment both undoped (a) and Eu-doped (b).

The TL curve of the undoped sample includes four intense bands with maxima at 206, 255, 359, and 443 K. The TL curves were decomposed into elementary contours. For the sake of agreement with the experimental curves, each contour was chosen in the form corresponding to the linear and quadratic kinetics [12]. It turns out (Fig. 1,a) that the 206-K peak is elementary, whereas the 255-K one consists of three components. Moreover, the intensity of the principal component (254 K) considerably exceeds that of two high-temperature satellites at 269 and 284 K. The 359-K peak includes an intense peak at 358 K and four relatively weak ones at 314, 342, 370, and 387 K. The peak at 443 K is elementary. All the indicated peaks glow according to the linear kinetics. In addition, the temperatures of their maxima practically do not depend on the irradiation dose, which also testifies to the linear kinetics of the process.

A more pronounced overlapping observed for the peaks at higher temperatures (caused by the proportional increase of their width) considerably complicates the procedure of fractional glowing of individual peaks. Therefore, the accuracy of determination of their activation energies significantly worsens, as the program used for the calculation of activation energies based on initial slopes of TL curves describes the glowing of a fraction with the help of only one exponent that must fit into a straight line in the graph $ln(I/n) = f(1/T)$ with a minimal deviation. This fact explains the increasing spread of the trap activation energies in the case of more high-temperature peaks – if a peak is compound, then the calculation results in a relatively larger spread of the activation energies at a shelf (as compared to a simple peak) even in the case of the domination of one of the components. However, due to the fact that the lateral peaks in KCl are of considerably lower intensity, we still used such a way of calculation of the energies.

The TL curves of the other samples of undoped KCl include a band of low-temperature TL peaks in addition to the described ones (the general maximum at 153 K), while the peaks at 314, 387, and 443 K are more pronounced and have a higher intensity (inset in Fig. 1,a).

The decomposition of the TL curve of doped KCl:Eu into elementary contours (Fig. 1,b) demonstrates that it consists of a compound peak at 114 K, two simple ones at 138 and 184 K, as well as bands at 220–270 K and 320–420 K. Moreover, the peaks at 114, 138, and 184 K can be considered elementary (the low-temperature 95-K component is negligibly weak), the band at 220–270 K consists of three simple peaks (226, 241, and 268 K) of approximately equal intensities, while the intense band at 320–420 K consists of four components (357, 372, 384, and 395 K), where the most intense peak is the 357-K one (the same way as in undoped KCl). The glowing kinetics of these peaks is also linear.

In order to obtain information on the nature (intrinsic or impurity) of traps, we investigated thermoluminescence of undoped KCl and KCl:Eu depending on the X-ray irradiation dose in the range 1–180 min at the nitrogen temperature. It turns out that the light sum stored in each peak linearly increases with excitation time in the whole investigated time interval. The only exclusion is the peak at ∼ 268 K, whose intensity saturates after the 120-min irradiation both in doped and in undoped KCl, so this peak is not related to Eu impurity.
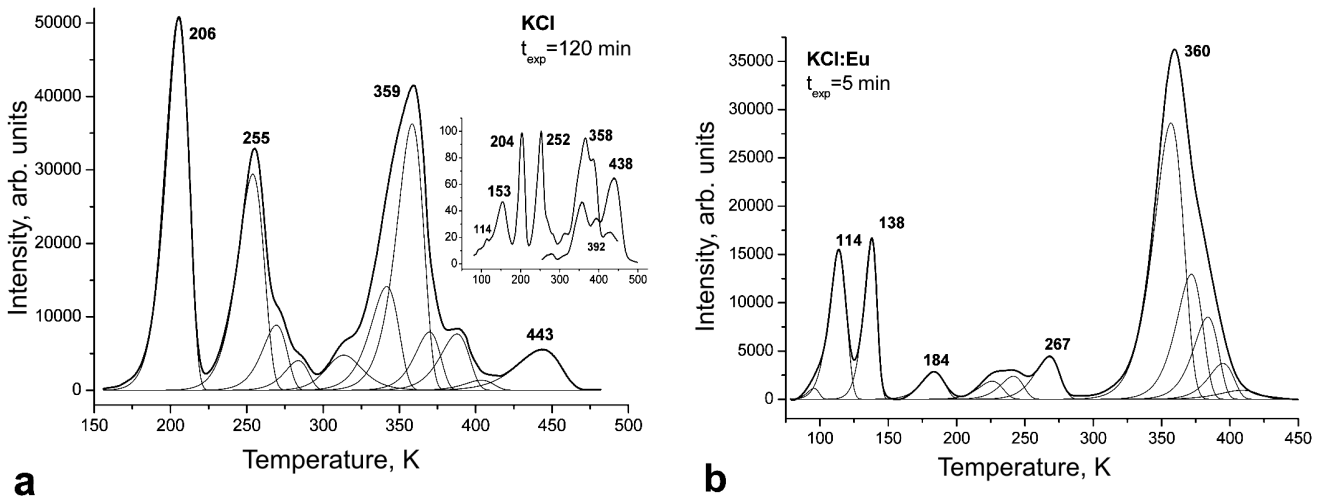
Fig. 1. TL curves of KCl (*a*) and KCl:Eu (*b*) crystals and their decomposition into elementary contours

The linear dependence on the irradiation dose, i.e. the constant rate of storage of the light sum testifies to the fact that the trap population practically is not changed with increasing the time of X-ray irradiation. Such a dependence can be explained taking into account the local nature of X-ray excitation. A high-energy electron generates free electrons and holes as well as interstitial ions and vacancies with a considerable concentration of $10^{18} - 10^{20}$ cm^{-3} in a small region of the crystal. An optical excitation source of the same electric power has a much larger photon flux density (by 3–4 orders of magnitude). Each absorbed optical photon can release only one charge, whereas a photoelectron liberated by an X-ray quantum generates a substantial number of excitations located in a small volume. In addition, due to the inessential absorption coefficient of X-radiation in a substance consisting of light elements (~ 10 cm^{-1}), excitation regions occupy the whole sample, while optical radiation from the fundamental region (> 100 cm^{-1}) excites only a thin (~ 0.01 cm) surface layer. As a result, every following X-ray quantum is mainly absorbed in the unexcited region of the sample, and one will observe a proportional dependence of the light sum on the excitation time until excitation regions start to overlap. It is worth noting that, in $Y_3Al_5O_{12}$ crystals under similar excitation conditions, one observes a sublinear dose dependence after the 20-minute excitation [13]. However, X-ray bremsstrahlung does not generate radiation defects in this crystal. In this case, processes of charge exchange of defects are determined by electrons and holes. Due to their considerable mobility, they form much larger excitation regions than those in alkali halides, as the dominant role in the

latter is played by radiationally created vacancies and interstices with much smaller mobilities. Due to this fact, the overlapping of excitation regions in KCl can be neglected even after the three-hour irradiation.

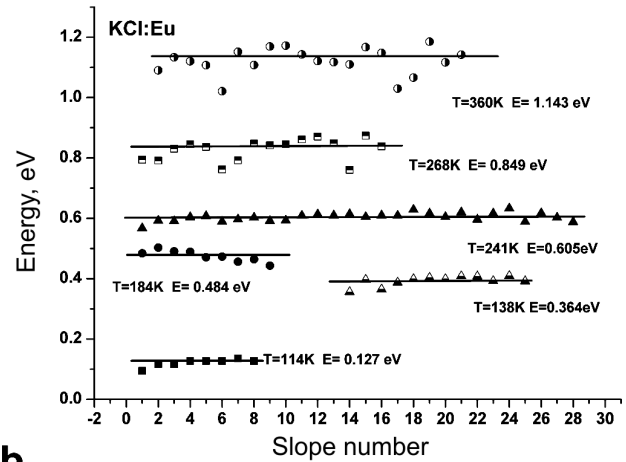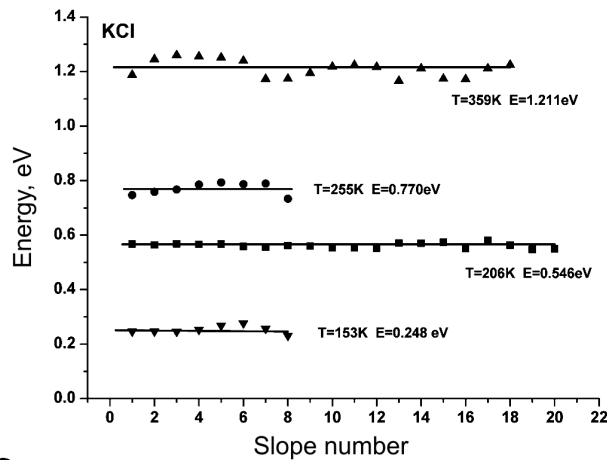*Fractional glowing. Oscillatory rule for trap energies*

Experimental E_{exp} and calculated E_{clc} activation energies, maximum temperatures T_m, and frequency factors p_0 are given in Table 1.

It is worth noting that the literature data on trap energies in KCl are very ambiguous (see, e.g., [14, 15]).
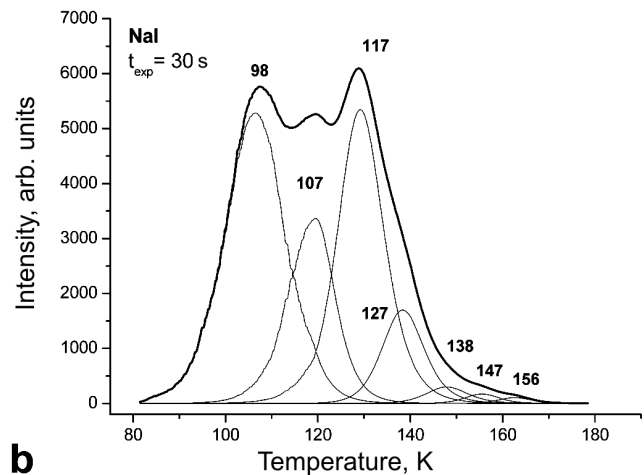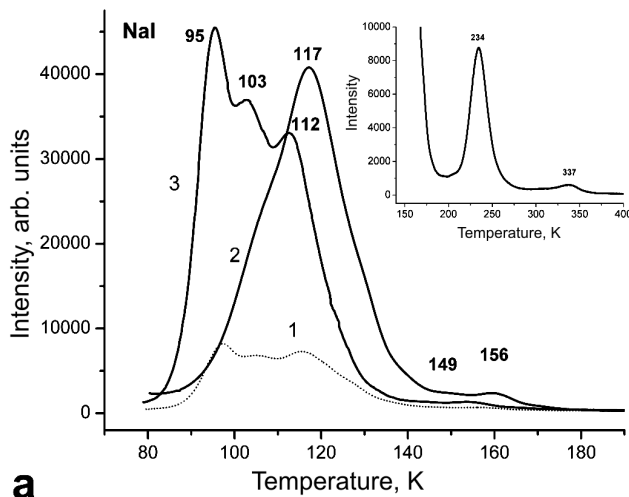
In addition to Table 1, we adduce some results of calculating the energies based on the fractional data in

T a b l e 1. KCl: n is the quantum number; E_{exp} are the experimental energies; E_{clc} are the energies calculated according to the formula $E_n = \hbar\omega n$, $\hbar\omega = 0.121$ eV; T_m is the temperature of the TL peak; p_0 is the frequency factor

n	E_{clc}	E_{exp}	p_0	T_m
1	0.121	0.127 ± 0.004	1.1×10^4	114
2	0.242	0.248 ± 0.005	2.0×10^7	153
3	0.363	0.364 ± 0.013	6.6×10^{11}	138
4	0.484	0.484 ± 0.006	3.9×10^{11}	184
		0.475 ± 0.006	2.7×10^{11}	226
4.5	0.545	0.546 ± 0.002	5.2×10^{11}	206
5	0.605	0.605 ± 0.002	5.9×10^{10}	241
6	0.726	–	–	–
6.5	0.786	0.770 ± 0.007	1.7×10^{13}	255
7	0.847	0.849 ± 0.004	1.6×10^{14}	268
...				
9.5	1.149	1.143 ± 0.014	4.4×10^{14}	360
10	1.210	1.211 ± 0.007	2.5×10^{15}	359

Fig. 2. Fractional deexcitation of KCl (*a*) and KCl:Eu (*b*)

Fig. 3. TL curves of low-temperature NaI:Tl peaks at different excitation times (*1* – 40 *s*, *2* – 300 *s*, hardened, *3* – 300 *s*, annealed) and high-temperature ones (inset)(*a*); decomposition of the NaI:Tl TL curve into elementary contours (30-second excitation) (*b*)

Fig. 2,*a* (undoped KCl) and 2,*b* (KCl:Eu), where the activation energies are presented depending on the serial number of the fractional curves. The activation energies $E_{\exp}$ were determined from the shelves of these dependences. In order to make perception easier, the serial numbers of the slopes for some shelves were increased by several unities (~ 10). The error of determination of the energy was estimated as the root-mean-square deviation of the fractional energies at the shelf. The registration of all peaks is accompanied by the background glow, whose intensity decreases with increasing the number of the fractional curves and disappears for the last of them; this background was eliminated with the help of the procedure described in detail in [7–9].

As one can see from the table, all experimental energies are in good agreement with the generalized oscilla-

tory formula $E_n = \hbar\omega n$, i.e. for integer and half-integer values of n (column E_{clc} of the table), the quantum energy $\hbar\omega = 0.121 \pm 0.004$ eV (979 cm^{-1}). The majority of trap energies in KCl are multiple of $\hbar\omega$, except for the peaks at 206 K (n=4.5), 255 K (n=6.5), and 360 K (n=9.5). The experiments on the fractional glowing for some low-intensity peaks did not provide reliable results and therefore were not included in Table 1.

3.2. NaI

General description of TL curves

Figure 3,*a* presents TL curves in the temperature range 80–180 K for NaI:Tl crystal preirradiated by X-rays during 40 *s* (curve *1*) and 300 *s* (*2, 3*). The low-temperature

band is compound; one can distinguish at least seven close strongly overlapped peaks of different intensities. The inset in Fig. 3,a shows the TL curve for the region of higher temperatures. It contains two more compound low-intensity TL peaks with the maximum temperatures of 234 and 337 K.

The form of the TL curve changes depending on the excitation time. In general, the TL properties of NaI appeared to be very unstable in the sense of the reproducibility of low-temperature TL curves as compared to other studies of AHCs. Certain difficulties were also induced by the hygroscopicity of the crystal. A positive feature of this instability consists in the fact that each following experiment was actually performed with a sample that could be considered thermally treated. As it was shown in a number of our earlier investigations, a considerable range of n in the course of searches for the oscillatory rule in the absence of a set of samples grown under different conditions and doped by different impurities was provided due to different conditions of the thermal treatment. In addition, we used a dosimetric NaI:Tl material, where intense thermoluminescence was observed.

The decomposition of the TL curve into elementary contours (Fig. 3,b) demonstrates that the low-temperature band consists of seven peaks: four ones are rather intense (98, 107, 117, and 127 K), the other three peaks (138, 147, and 156 K) are weak. The form of all the peaks corresponds to the quadratic kinetics.

The investigation of the dose dependences (as well as the decomposition into contours) shows that, for annealed samples, an increase of the irradiation dose results, first of all, in the growth of the intensity of the

T a b l e 2. NaI: n is the quantum number; E_{exp} are the experimental energies; E_{clc} are the energies calculated according to the formula $E_n = \hbar\omega n$, $\hbar\omega = 0.061$ eV; T_m is the maximum temperature of the TL peak; p_0 is the frequency factor

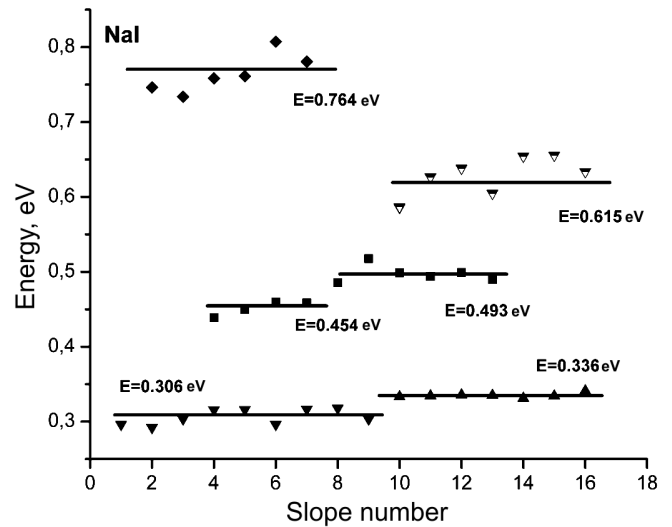| n	E_{clc}	E_{exp}	p_0		T_m
			eV	s^{-1}	T_m
4.5	0.276	0.284 ± 0.004	0.309	7.5×10^{13}	98
5	0.305	0.306 ± 0.003	0.273	6.6×10^{13}	107
5.5	0.336	0.336 ± 0.001	0.279	6.7×10^{13}	117
6	0.366	0.366 ± 0.005	0.598	1.4×10^{14}	127
...					
7.5	0.458	0.454 ± 0.006	0.432	1.0×10^{14}	147
8	0.488	0.493 ± 0.002	1.697	4.1×10^{14}	156
...					
10	0.610	0.615 ± 0.013	0.002	4.7×10^{11}	234
...					
12.5	0.763	0.764 ± 0.009	3.92	9.5×10^{14}	234

Fig. 4. Fractional glowing of NaI:Tl

first low-temperature peak ~ 98 K, whereas, for hardened ones – of the third 117-K peak (in this case, the intensity of the 98-K peak remains constant). Moreover, annealing or hardening appeared to be equivalent to slow cooling and settling of a sample ($\sim 10-12$ hours) or fast nitrogen cooling down to initial temperatures. As a result, two successive records of TL curves (obtained with a minimal pause) at the five-minute excitation gave very different forms of the curves (Fig. 3,a, curves *2, 3*), whereas the forms of those recorded with an interval of twenty-four hours were practically identical. With increasing the dose, the maxima of the peaks for annealed samples shift toward lower temperatures (down to 4 K), while such a shift for hardened ones is practically absent (< 1 K).

The quadratic kinetics is realized in the case of the recapture and at approximately equal concentrations of carriers at traps of a given kind and free luminescence centers (LC). This is possible in the presence of genetically related low-mobility pairs of traps and LCs.

Fractional glowing

A considerable overlapping complicates the procedure of fractional glowing and therefore substantially worsens the accuracy of determination of the activation energy of each peak. In this case, a partial clipping is ineffective, but we applied it as it still gave some useful information. Some results of calculating the energies based on fractional data are presented in Fig. 4 depending on the serial number of the fractional curves. The values of E_{exp}, maximum temperatures T_m, and frequency factors

p_0 are given in Table 2. Due to the considerable overlapping of the low-temperature TL peaks, it appeared impossible to definitely correlate the activation energies with specific peaks from fractional experiments. That is why such a correlation was performed based on the correspondence of the frequency factor in the units of eV to the value of one of the found energies. These values must be close to each other. Our calculations demonstrated that such a correlation could be performed rather unambiguously – a variation of the activation energy by ~ 0.02 eV resulted in the change of the frequency factor by orders of magnitude. A substantial disagreement between the activation energy and the frequency factor was observed only for the high-temperature peak at 234 K (nonannealed sample).

The same way as in the case of KCl, the experimentally determined energies agree with the oscillatory formula (column E_{clc} of the table) for the quantum energy $\hbar\omega_{\mathrm{TL}} = 0.061$ eV (492 cm^{-1}). The totality of the low-temperature peaks is characterized by a collection of activation energies from 0.284 to 0.493 eV, and these energies fit the oscillatory rule with integer and half-integer n (n=4.5–8). The activation energy of the 234-K peak determined for the annealed sample is 0.615 ± 0.013 eV (n=10), for the nonannealed one – 0.764 ± 0.009 eV (n=12.5). The results of the fractional glowing of the 337-K peak appeared unreliable, that is why they are not included in the table.

4. Discussion of the Results

4.1. Polaron model

The earlier obtained results [1–11] allowed one to propose a model considering a filled trap as a polaron that is self-trapped or stabilized by the local field of an intrinsic defect or impurity. In all crystals not belonging to AHCs, the vibrational TL frequencies correspond to modes of the Raman scattering spectrum. In the case of AHCs including KCl and NaI, there appear the local vibrational modes that form one-series oscillatory rules. Unlike the materials we investigated earlier, where the trap energy in a series was described by the formula $E_n = \hbar\omega_{\mathrm{TL}}(n + 1/2)$, n=0,1,2..., the energies of series in AHCs are generally described by the formula $E_n = \hbar\omega_{\mathrm{TL}}n'$, where n' can assume both half-integer and integer values. For example, for traps glowing in NaCl in the temperature range 80–500 K, one observes a "classical" oscillatory rule excluding one trap, whose energy appeared to be multiple of the quantum number. In contrast, the energies of all traps in LiF in this

temperature region appear to be multiple of the corresponding quantum number except for one trap, whose energy is multiple of the half-integer quantum number. In KCl, the energies of eight traps are multiple of the vibrational quantum energy, whereas three of them correspond to its half-integer value (Table 1). NaI represents an intermediate variant: four trap energies are described by the formula for half-integer n and the same number – for integer one (Table 2).

The mechanism of existence of trap energies multiple of integer or half-integer values of the quantum number n was clarified in our previous work [10]. Here, we briefly state the basic points. The thermoactivation processes are accompanied by changes in the ion subsystem that consist in a shift of a polaron in the field of some defect – a stabilization center. Due to the considerable local polarization, this shift is realized by means of thermoactivation jumps. A polaron trap can be presented in the energy diagram as a parabolic potential well with equidistant vibrational levels. The depth of the potential well, i.e. the number of the vibrational level n, from which a charge is thermally released, is determined by the nature of the defect localizing the polaron. A thermally released polaron can reach a luminescence center in the following ways: a) according to the band mechanism realized in the case where polarons have a high mobility; in this case, the energy of thermal activation of a trap is determined by the energy level, from which a charge passes to the polaron band; b) if relaxed polarons are capable of self-trapping, then a thermally excited charge can tunnel to the neighboring equivalent position in the lattice on the assumption that there appears the corresponding configuration of the ionic surrounding caused by thermal motion; c) if a luminescence center is close to a trap, there appears a possibility of tunneling of the excited charge directly to the excited LC state. Thus, variant (a) determines the band mechanism of transfer of a charge thermally released from an LC, whereas the other two mechanisms are realized without participation of the band.

It is shown [10] that charges are thermally released from traps with the energy multiple $\hbar\omega$, if they tunnel to the equivalent neighboring crystalline surrounding without passing to a band state and reach an LC after several such jumps. They can also directly tunnel to the excited state of a recombination center if there is one in the neighborhood. If the trap energy is determined by a half-integer value of the quantum number, then the charge is released from the trap to the band with the following recombination at an arbitrarily located LC. Such a mechanism is realized in all the materials we investi-

gated that do not belong to AHCs; partially, it takes place in AHCs, where the both indicated mechanisms are realized. Moreover, they appear equivalent in NaI, as one can see from Table 2, where integer and half-integer values n alternate.

4.2. Nature of TL-active traps

Models of the TL phenomenon in AHCs proposed by various authors reduce to three basic ones: electron, hole, and ion models. Their analysis carried out in our previous work [10] demonstrated that the only consistent mechanism is the ion one. In Introduction, we noted that, in LiF and NaCl, the vibrational quantum energies correlate with the atomic masses of halides. It turned out that such a correlation also exists for KCl and NaI (for LiF and KCl: $\hbar\omega_{\text{LiF}}/\hbar\omega_{\text{KCl}} = 1.34$, $\sqrt{m_{\text{Cl}}/m_F} = 1.37$; for KCl and NaI – 1.99 and 1.89; KCl and NaCl – 1.08 and 1.0; LiF and NaCl – 1.44 and 1.37; LiF and NaI – 2.66 and 2.59; NaCl and NaI – 1.84 and 1.89, correspondingly). A certain disagreement between the ratios of the TL frequencies and the inverse ratios of the roots of the atomic masses is natural, as the force constants of crystals must somewhat differ due to the difference in their anion components. Thus, TL frequencies in AHCs are related to vibrations of halide molecules; moreover, these molecules are present in each filled trap, as it is the only way to explain the existence of the oscillatory rule for trap energies. Such a molecule can be, first of all, presented by an H-center, i.e. an interstitial halide atom that, together with the nearest site halide ion, forms an X_2^- molecule centered at a halide site in [110] direction.

In [20], there were calculated the energies of migration of interstitial atoms and vacancies in AHCs. It was established that the minimal migration energy is characteristic of interstitial anion atoms – H-centers. For the investigated crystals, these values lie in the range 0.05–0.16 eV, correlate with the ionization energies of traps (our data), and determine the minimal trap energy, whose role is played by the self-trapped state of the H-center.

It is worth noting that a hole in the relaxed state also has a two-center localization in AHCs and can be considered as a single-charged halide molecule X_2^- (V_K-center). However, the calculations and experiment [21,22] demonstrate that the local frequencies related to the V_K-center in the investigated crystals are lower than the corresponding TL frequencies by a factor of 3–4. Thus, we have grounds to state that TL in AHCs is

caused by the release of H-centers from traps with their following recombination.

A thermally released H-center can recombine in two ways: at an F-center and at an anion vacancy. In the first case, there appears the nodal halide atom at a place of the F-center. In [15–18], it is assumed that the energy of H-F recombination is transformed into the energy of radiative electron transition. However, the radiative efficiency of H-F recombination is extremely low [19]. The model becomes logically completed if one allows for the recombination of H-centers at anion vacancies [10]. This reaction produces a hole and a nodal anion, which is followed by the radiative recombination of the hole (V_K-center) at the F-center and the formation of a halide vacancy. These two successive reactions result in the generation of a light quantum corresponding to the characteristic radiation band present in the TL emission spectrum of all traps and the healing of one F-center. In this case, the concentration of anion vacancies remains constant.

4.3

Thus, KCl and NaI have joined the list of crystalline materials with the oscillatory rule observed in the energy spectrum of traps. In KCl, the majority of the energies appeared to be multiple of an integer number of vibrational quanta $\hbar\omega_{\text{KCl}} = 0.121$ eV. Based on the estimates of the statistical sum for the oscillatory states, it was concluded that TL in KCl is mainly realized by means of the charge tunneling from excited vibrational states of traps to those of luminescence centers without transition to a band state. That is, the activation energy of traps appears to be multiple of an integer number of vibrational quanta. If a charge passes to a recombination center via a band, then the activation energy corresponds to a half-integer number of vibrational quanta (there exist three such values in KCl). In NaI, the value of the vibrational quantum $\hbar\omega_{\text{NaI}} = 0.061$ eV. TL is realized both by means of the charge tunneling from excited vibrational states of traps to those of luminescence centers without the transition to a band state and by means of the charge transition to a recombination center via a band. The both mechanisms of transition of a charge carrier from a trap to a luminescence center are equivalent and competitive.

In the earlier investigated materials, the vibrational quantum energies coincided with the energies of certain Raman scattering lines. But, in AHCs, these energies correspond to local vibrational modes. Based on the existence of the correlation between the values of $\hbar\omega$ in

LiF, NaCl, NaI, and KCl and the anion masses, these frequencies can be ascribed to a local vibrational mode of the X_2^- halide molecule (H-center).

5. Conclusions

The existence of the oscillatory rule in the energy spectrum of traps is caused by the polaron effect, and this regularity represents a universal property of crystals with the mainly ion-bond type. The parameters of this regularity can be established by means of precise measurements, whose required accuracy can be provided by the method of fractional TL due to the possibility of obtaining a considerable number of single-type data and their deep mathematical treatment.

– It is shown that, in KCl and NaI AHCs, the thermal activation energies of traps form one oscillatory series with the vibrational quantum energies $\hbar\omega = 0.121$ eV (979 cm^{-1}) in KCl and $\hbar\omega = 0.061$ eV (492 cm^{-1}) in NaI.

– The generalization of data concerning the investigated alkali-halide crystals NaCl, LiF, KCl, and NaI allowed us to confirm the earlier proposed model of TL in AHCs. In particular, it is assumed that, in addition to the non-radiative H-F recombination, there exists the two-stage recombination of H-centers at anion vacancies resulting in the radiative recombination of a hole at an F-center.

– The found oscillatory rule in the energy spectrum of traps in KCl and NaI has confirmed the conclusion that this regularity is caused by the polaron effect and is universal for crystals with the mainly ion-bond type.

1. I.S. Gorban', A.F. Gumenyuk, and V.A. Omel'yanenko, Ukr. Fiz. Zh. **33**, 529 (1988).

2. G.P. Blinnikov, V.N. Golonzhka, and A.F. Gumenyuk, Opt. Spektr. **69**, 1054 (1990).

3. I.S. Gorban', A.F. Gumenyuk, V.Ya. Degoda, and S.Yu. Kutovoi, Opt. Spektr. **75**, 47 (1993).

4. I.S. Gorban', A.F. Gumenyuk, and S.Yu. Kutovyi, Ukr. Fiz. Zh. **40**, 73 (1995).

5. A.F. Gumenyuk, S.Yu. Kutovyi, and O.B. Okhrimenko, Ukr. Fiz. Zh. **42**, 870 (1997).

6. A.F. Gumenjuk, S.Yu. Kutovyi, and M.O. Grebenovish, Funct. Mater. **9**, 314 (2002).

7. A.F. Gumenyuk and S.Yu. Kutovyi, Ukr. Fiz. Zh. **45**, 1093 (2000).

8. A.F. Gumenjuk and S.Yu. Kutovyi, Centr. Europ. J. Phys. **1**, 307 (2003).

9. A.F. Gumenyuk and S.Yu. Kutovyi, Ukr. Fiz. Zh. **50**, 345 (2005).

10. A.F. Gumenyuk and S.Yu. Kutovyi, Ukr. Fiz. Zh. **50**, 1125 (2005).

11. A.F. Gumenjuk and S.Yu. Kutovyi, Funct. Mater. **13**, 173 (2006).

12. C. Furetta, *Handbook of Thermoluminescense* (World Scientific, Singapore, 2003).

13. I.S. Gorban', A.F. Gumenyuk, V.Ya. Degoda, and T.O. Kuchakova, Ukr. Fiz. Zh. **31**, 370 (1985).

14. A. Halperin, A.A. Braner, A. Ben-Zvi, and N. Kristianpoller, Phys. Rev. **11**, 416 (1960).

15. S.A. Garcia, Ph.D. thesis, Universidad de Sonora, 2005.

16. V. Ausin and J.L. Alwarec Rivas, J. Phys. D: Appl. Phys. **5**, 82 (1972).

17. M.J. de Castro and J.L. Alvarec Rivas, J. Phys. C: Solid State Phys. **11**, 257 (1980).

18. F. Sagastibelza and J.L. Alvarec Rivas, J. Phys. D: Appl. Phys. **14**, 1873 (1981).

19. N. Itoh, A.M. Stoneham, and A.H. Harker, J. Phys. C: Solid State Phys. **10**, 4197 (1977).

20. D.K. Rowell and M.J.L. Sangster, J. Phys. C: Solid State Phys. **14**, 2909 (1981).

21. E. Goowaerts and D. Shoemaker, Phys. Stat. Sol. (b) **88**, 615 (1978).

22. J.H. Harding, J. Phys. C: Solid St. Phys. **13**, 3505 (1980).

ОСЦИЛЯТОРНА ЗАКОНОМІРНІСТЬ
В ЕНЕРГЕТИЧНОМУ СПЕКТРІ ЦЕНТРІВ
ПРИЛИПАННЯ КРИСТАЛІВ KCl ТА NaI

А.Ф. Гуменюк, С.Ю. Кутовий,
О.П. Становий, В.Г. Пащенко, С.В. Томилко

Р е з ю м е

Методом термолюмінесценції (ТЛ) досліджено енергетичний спектр центрів прилипання (ЦП) в кристалах KCl та NaI в діапазоні 80–500 К. Показано, що в KCl та NaI енергії термічної активації ЦП утворюють по одній осциляторній серії $E_n = \hbar\omega n$ з енергіями коливальних квантів 0,121 еВ (979 см$^{-1}$) в KCl та 0,061 еВ (492 см$^{-1}$) в NaI. При цьому квантове число n набуває як напівцілих, так і цілих значень. На підставі узагальнення даних по дослідженим лужно-галоїдним кристалам підтверджено запропоновану раніше модель ТЛ в ЛГК. Припускається, що крім безвипромінювальної H–F рекомбінації, існує двостадійна рекомбінація H-центрів на аніонних вакансіях, в результаті якої дірка рекомбінує випромінювально на F-центрі. Енергія кванта в осциляторній залежності відповідає локальній коливальній моді молекули галоїду X_2^-.