

Polaron Model of Traps and their Activation Energies in KBr Crystals

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The activation energy spectrum of traps in KBr crystals has been studied by the thermoluminescence (TL) methods in the temperature range of 80-450 K. The energies of thermal activation of traps in KBr were found to form an oscillator-like series $E = \hbar\omega_n$, with the vibrational quantum energy 0.078 eV (629 cm^{-1}). Using the generalization of the data on other investigated alkali halides crystals the early-proposed model of the TL in alkali halides based upon two-stage recombination of the H -centers was confirmed. The energy of the quantum in oscillator regularity corresponds to the local vibration mode of the halide molecule X_2^- .

Keywords: Thermoluminescence, Traps, Energy spectrum, Alkali halide crystals.

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1. INTRODUCTION

Polarons form in many wide-band gap materials as a result of charge carrier localization due to strong electron-phonon interaction. Their formation, transport and relaxation [1-4] are crucial to understanding important electron transport processes occurring in scintillation detectors, electrochemical devices such as batteries and fuel cells [5].

Investigating the energy spectrum of traps in a number of crystals with ion-covalent bonds, we discovered [6-9 and references there in] that the thermal activation energy of traps is described by the harmonic oscillator formula $E_n = \hbar\omega_{TL}(n+1/2)$, where the quantum energy $\hbar\omega_{TL}$ assumes values characteristic of lattice vibrations (0.01-0.18 eV, i.e. ~ 100 -1500 cm^{-1}). We observed from one to five oscillatory series, each of which is characterized by its vibrational quantum energy $\hbar\omega_{TL}$. The majority of the values of $\hbar\omega_{TL}$ coincide with the energies of high-frequency lines of the basic first-order Raman scattering spectrum $\hbar\omega_{TL}$, whereas the other values correspond to the energies of the second-order RS lines, local vibrational modes, lines forbidden in Raman spectra. The obtained results gave grounds to state that the oscillatory rule reflects some general regularity. A polaron model of traps and TL process was proposed in [6].

In alkali halide crystals (AHC) with cubic lattice there are no vibrational modes active in RS, though the oscillatory rule for the trap energies with the vibrational quantum energies $\hbar\omega_{NaCl} = 0.112 \text{ eV}$, $\hbar\omega_{LiF} = 0.162 \text{ eV}$, $\hbar\omega_{KCl} = 0.121 \text{ eV}$ and $\hbar\omega_{NaI} = 0.061 \text{ eV}$ is also observed in the investigated NaCl, LiF, KCl and NaI crystals. These values exceed the energy of the only optical vibrational mode in these

crystals by several times. The correlation between these frequencies and the masses of halogen atoms was indicated for all these crystals, for example, $\hbar\omega_{LiF}/\hbar\omega_{NaCl} = 1.44$ and $\sqrt{m_{Cl}/m_F} = 1.37$. Because we consider the proposed model suitable for all AHC, it is important to analyze the trap energy spectrum and to test the model with another AHC - KBr. Thus, in the paper the results of the TL-experiments for KBr are presented, the model of TL in the AHC is briefly described, and general conclusions about the mechanisms of TL at AHC are made.

2. EXPERIMENTAL TECHNIQUE

The investigations were performed in the temperature range of 80-500 K. The heating rate was $0.2 \pm 5\% \text{ K/s}$. The linear increase of the temperature and the data registration were controlled by a computer program. Samples $\sim 0.5 \text{ mm}$ in thickness and 4-8 mm in lateral size were placed 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 excitation time was varied from 1 min to 30 min.

Here crystals of undoped KBr, and KBr:Ba were investigated. The TL peaks in KBr have appeared to be rather intense and split, which allowed using the fractional technique and did not require the crystal annealing for healing of intrinsic defects.

The curves with complex contours were decomposed into elementary components, for each the activation energy, the frequency factor and temperature of a maximum were determined as approximation parameters of experimental curves by analytic ones. The shape of each contour for agreement with the experimental curves was selected in according to the equations of a linear or quadratic TL kinetics [10]:

$$I(T) = -\frac{dn}{dt} = n_0 p_0 \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{p_0}{\beta} \left(\int_{T_0}^T \exp\left(-\frac{E}{kT}\right) dT\right)\right]$$

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$$I(T) = -\frac{dn}{dt} = n_0 p_0 \exp\left(-\frac{E}{kT}\right) \left[1 + \frac{p_0}{\beta} \left(\int_{T_0}^T \exp\left(-\frac{E}{kT}\right) dT \right) \right]^{-2}$$

where E (eV) is the activation energy of traps, n_0 (m^{-3}) is the initial light-sum (which is proportional to the peak area); β (K/s) is the heating rate (specified in the experiment); p_0 (s^{-1}) is the frequency factor; T (K) is the sample temperature; and k is Boltzmann constant. The approximation parameters are n_0 , p_0 and E . The selection of the kinetics type (the shape of the curve, which describes the elementary peak) was held both in terms of getting the exact decomposition that reproduces experimental curves and with additional experiments (the observation position changes when changing the maximum peak intensity, i.e. the dose dependence). This gave definite conclusions about the kinetics type.

3. EXPERIMENTAL RESULTS

The experimental TL curves for KBr samples were simple in terms of the provisions of the existing maximums peaks (Fig.1). With decomposition, all peaks that form the TL curve can observe visually. Hence, a reliable comparison of the peaks obtained from decomposition with peaks observed on the experimental curve can be one of the criteria data reliability and the uniqueness of the performed decomposition. From decomposition, it was determined that the kinetics of all TL peaks was linear. In addition, the temperature positions of the peaks are almost independent on the initial light-sum that also indicates the linear kinetics.

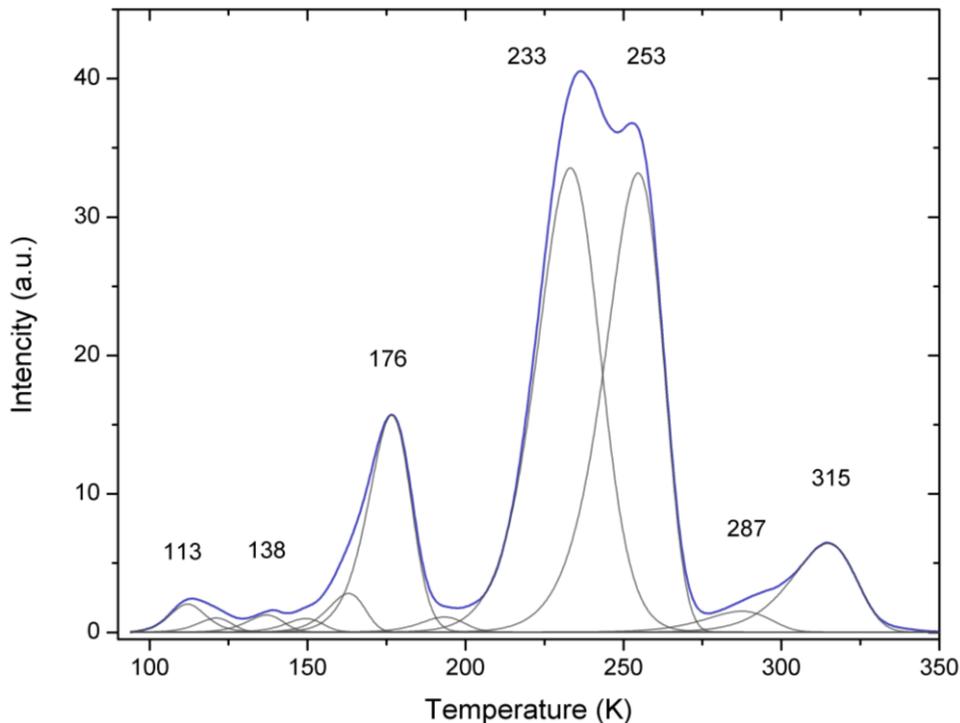


Fig. 1 – TL curve of undoped KBr crystal and its decomposition into elementary contours

In Fig.1, the TL curve of undoped KBr excited at 80 K is shown. In the low-temperature region the low-intensity band at ~ 113 K, consisting of at least two peaks (112, 121 K) and the peak with maximum at 138 K are observed. The band with a maximum at 176 K has intense peak at 176 K and two weak low- and high-temperature satellites with maxima at 158 K and 190 K, respectively. At temperatures, 233 K and 253 K there are two peaks of about equal intensity, which account for the main part light-sum (the value proportional to the number of carriers that are localized in traps after X-ray excitation). Some differences between the experimental curve and the result of decomposition are probably due to inaccurate execution of conditions for realization of the linear TL-kinetics, i.e. the requirement that the concentration of luminescence

centers must be much higher than the concentration of unoccupied traps. Thus, at the beginning of the peak the number of the free traps is negligible, while in the final stage the concentration of its increases due to release charge carriers; the probability of recapture increase with it. In this sense, we could not be considered that the certain type kinetics is strictly implemented for a particular peak. It must be taking into account if the TL peak accounted for a significant part full light-sum. High-temperature region has two considerably overlapped peaks at temperatures of 287 K (weak) and 315 K. In the high-temperature range, the peaks overlapping increases with the increasing the peaks half-width, and it complicates determination of the activation energy by fractional glowing method because the dispersion of the energy values within a peak increases

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When excitation is performed at a high temperature (200-250 K), then the high-temperature peaks (eg., 380 K) begin to appear which are almost unobservable when excited at 80 K, and therefore in Fig.1 it is not shown.

3.1 Fractional Glowing. Oscillatory Rule for Trap Energies

The experimental E_{exp} and calculated E_{clc} by the equation $E_n = \hbar\omega_{\text{TL}} \cdot n'$, activation energies, maximum temperatures T_m , and frequency factors p_0 are given in Table 1. Besides Table 1, the results of calculation of activation energy by fractional glowing method are presented graphically in Fig. 2, as a statistical distribution (a) and the dependence on the serial number of the fractional curves (b).

As can be seen from Table 1 all the experimental energy values are in good agreement with the generalized oscillatory formula $E_n = \hbar\omega_{\text{TL}} \cdot n'$, where

$\hbar\omega_{\text{TL}} = 0.078 \pm 0.004$ eB (629 cm^{-1}), although for the high temperature peaks more differences in theoretical and experimental results are observed. This is because of the considerable TL peaks overlapping. In KBr all values of activation energy are proportional to the value $\hbar\omega_{\text{TL}}$, with integer coefficient of proportionality. For some low-intensity peaks, the fractional glow experiments did not give reliable results and therefore they are not included in Table 1.

Table 1 – Data on KBr: n' is the quantum number; E_{exp} are the experimental energies; E_{clc} are the energies calculated by the formula $E_n = \hbar\omega_{\text{TL}} \cdot n'$, $\hbar\omega_{\text{TL}} = 0.078$ eV; T_m is the temperature of the TL-peak maximum; p_0 is the frequency factor.

n'	E_{clc} , eV	E_{exp} , eV	p_0 , s^{-1}	T_m , K
3	0.234	0.237 ± 0.003	$2 \cdot 10^9$; $2.8 \cdot 10^8$	112; 121
...				
6	0.468	0.469 ± 0.003	$8.9 \cdot 10^{11}$	176
...				
8	0.624	0.623 ± 0.004	$7.7 \cdot 10^{11}$; $5.6 \cdot 10^{10}$	233; 253
...				
11	0.858	0.865 ± 0.004	$1.1 \cdot 10^{12}$	318

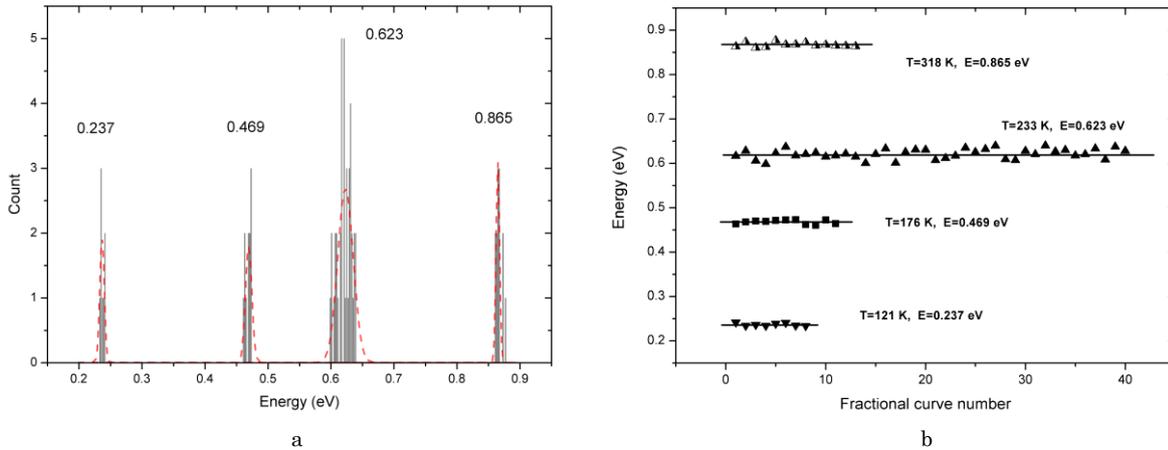


Fig. 2 – Fractional glowing of KBr: the statistical distribution of activation energies for the set of fractional curves (a); the dependence of the activation energies values on the serial number of the fractional curves (b)

4. DISCUSSION OF THE RESULTS

Unlike the investigated earlier materials, where the trap energies in oscillatory series were described by the formula $\hbar\omega_{\text{TL}}(n+1/2)$, $n = 0, 1, 2, \dots$, the energies of series in AHCs are described by the general formula $E_n = \hbar\omega_{\text{TL}} \cdot n'$, where n' can be both half-integer and integer (or, in other words, with or without 1/2 in a formula). For example, for traps glowing in NaCl in the temperature range of 80-500 K, a “classical” oscillatory rule was observed excluding only trap, whose energy appeared to be multiple of integer value of the $\hbar\omega_{\text{TL}}$. In LiF and KBr for traps glowing in this temperature region the energies of all traps, in contrast, are multiples

of integer values of the $\hbar\omega_{\text{TL}}$ (i.e., the formula without 1/2), except for one trap in LiF, whose energy is multiple of the half-integer number $\hbar\omega_{\text{TL}}$. In KCl the energies of eight traps are multiple of integer values of $\hbar\omega_{\text{TL}}$, and three of them correspond to its half-integer value. NaI is an intermediate variant: four energies of traps are described by the formula with 1/2 and four without 1/2 (see Table 2).

Table 2 presents the values of the vibrational quantum energies $\hbar\omega_{\text{TL}}$ and the values of quantum numbers for KBr and other AHC investigated in our previous works. In the introduction, it was noted that for early investigated AHC there is a correlation between energies of vibrational quantum and the atomic masses of

halides. It was found that this correlation exists for KBr too (see Table 3). It is seen that the ratio of TL-frequencies with inverse relation of the square roots of atomic masses are slightly different, but some divergence of these values are natural, because power constants that determine the frequency of oscillation H-center should be different for various crystals due to different anionic component.

Table 2 – The comparison table for various AHC: $\hbar\omega_{TL}$ is the vibrational quantum energies; n' is the quantum number in $E_n = \hbar\omega_{TL} \cdot n'$

	$\hbar\omega_{TL}$, eB	n'
LiF	0.162	1.5, 2, 2.5, 3, 5, 6, 7, 8
NaCl	0.112	1.5, 3.5, 4.5, 5.5, 6.5, 7.5, 9.5, 10, 11.5, 12.5, 13.5
NaI	0.061	4.5, 5, 5.5, 6, 7.5, 8, 10, 12.5
KCl	0.121	1, 2, 3, 4, 4.5, 5, 6, 6.5, 7, 9.5, 10
KBr	0.078	3, 6, 8, 11

Table 3 – The correlation ratios of the vibrational quantum energies and the masses of anions

n'	$\hbar\omega_2/\hbar\omega_1 : \sqrt{m_1/m_2}$			
	LiF	NaCl	NaI	KCl
LiF				
NaCl	1.44:1.37			
NaI	2.66:2.58	1.84:1.89		
KCl	1.34:1.37	0.93:1.00	0.50:0.53	
KBr	2.08:2.05	1.44:1.50	0.78:0.79	1.55:1.50

4.1 Nature of Traps in AHCs

The earlier obtained results [6-9] allowed one to propose a model considering a filled trap as a polaron that is a self-trapped or stabilized by the local field of an intrinsic defect or impurity. The argument in favor of the polaron model is equidistant thermal energy levels of traps. This indicates the elastic character of interaction, which can be provided only by the crystal lattice. Thus, in all early investigated crystals the binding of a charge with lattice vibrations realizes, i.e. a polaron state. In all crystals not belonging to AHCs, the vibrational TL frequencies correspond to modes of the Raman spectrum. In AHCs there appear the local vibrational modes that form one-series oscillatory rules.

Based on the estimates of the statistical sum for the oscillatory states it was defined [6] that the activation energy multiple of integer or half-integer value depend on the mechanisms moving of a charge carrier to the recombination center. A thermally released polaron can reach a luminescence center in different ways: (i) 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; (ii) 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; (iii) if a luminescence center is close to a trap,

there appears a possibility of tunneling of the excited charge directly to the excited state of a luminescence center (LC). Thus, variant (iii) 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. The activation energy is multiple of half-integer value n' in the case of mechanism (i), while the mechanisms (ii) or (iii) cause the integer n' .

Models of the TL phenomenon in AHCs proposed by various authors reduce to three basic ones: electron, hole, and ion models. The analysis [6] demonstrated that the only consistent mechanism is the ion one. Correlation between the values of $\hbar\omega_{TL}$ and the anion masses suggests that TL frequencies in AHCs are related to vibrations of halide molecules. Such a molecule can be 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 $\langle 110 \rangle$ direction and bound to two neighboring halogen atoms.

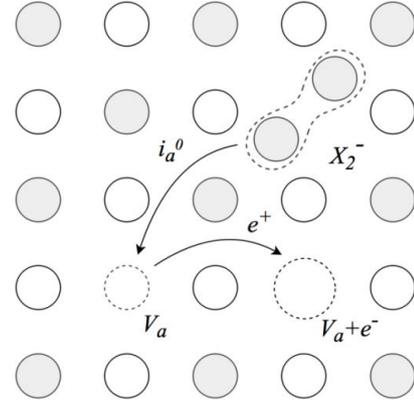


Fig. 3 – Two stage *H-F* recombination: i_a^0 is the haloid interstitial atom, V_a is the anion vacancy, X_2^- is the nodal anion and $V_a + e^-$ is the *F*-center.

Noticed that hole in the relaxed V_K -center also can be considered as a single-charged halide molecule X_2^- , however, the local frequencies related to the V_K -center in the investigated crystals are 3-4 times less than the corresponding TL frequencies [11].

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. It can be 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. The model is completed and self-consistent if one allows for the recombination of *H*-centers at anion vacancies. This reaction produces a hole and a nodal anion, which is followed by the radiative recombination of the hole at the *F*-center and the formation of a halide vacancy (see Fig.3). 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 [6]. In this case, the concentration of anion va-

cancies remains constant.

5. CONCLUSIONS

It is shown that the activation energy of traps in KBr crystal form the oscillatory series with the value of vibrational quantum $\hbar\omega_{TL} = 0.078$ eV (629 cm⁻¹).

The generalization of data concerning the investigated alkali halide crystals has confirmed early-proposed model of TL in AHCs based on the process of thermal excitation and two-stage relaxation of H-

centers.

The main conclusion is that the existence of the oscillatory rule in the energy spectrum of traps is caused by the polaron effect, and this rule is universal property of crystals with mainly ion-bond type. To establish parameters of this rule the precision measurements are necessary. The required accuracy can be provided by the method of fractional glowing due to the possibility of obtaining a considerable number of single-type data and their deep mathematical treatment.

REFERENCES

1. A. Lushchik, *Nucl. Instrum. Meth. B* **166**, 529 (2000).
2. H. Fujiwara, T. Suzuki, K. Tanimura, *J. Phys.: Condens. Matter* **9**, 923 (1997).
3. L. Shluger, K. Tanimura, *Phys. Rev. B* **61**, 5392 (2000).
4. K. Tanimura, W.P. Hess, *Phys. Rev. B* **69**, 155102 (2004).
5. T. Maxisch, F. Zhou, G. Ceder, *Phys. Rev. B* **73**, 104301 (2006).
6. A.F. Gumenyuk, S.Yu. Kutovyi, *Ukr. J. Phys.* **50**, 1125 (2005).
7. A.F. Gumenyuk, S.Yu. Kutovyi, O.P. Stanovyi, *Ukr. J. Phys.* **45**, 1000 (2009).
8. A.F. Gumenjuk, S.Yu. Kutovyi, *Funct. Mater.* **13**, 173 (2006).
9. A.F. Gumenjuk, S.Yu. Kutovyi, *Centr. Europ. J. Phys.* **1**, 307 (2003).
10. C. Furetta, *Handbook of Thermoluminescence* (Singapore: World Scientific Publishing: 2003).
11. D.B. Sirdeshmukh, L. Sirdeshmukh, K.G. Subhadra, *Alkali Halides: A Handbook of physical properties* **49**, Springer Science & Business Media (2013).