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Oscillator regularity of trap activation energies in NaCl crystals

A.F. Gumenjuk, S.Yu. Kutovyi and V.A. Kurilova
Department of Physics, Kyiv Taras Shevchenko University,
6, Academician Glushkov prosp., Kyiv-22, 252022, Ukraine
E-mail: expdept@expphys.ups.kiev.ua

Abstract. The energy spectra of traps in NaCl crystals were studied in detail by the method of thermoluminescence. Crystals of NaCl were undoped but treated thermally in different ways. The activation energies of traps form a single oscillator series, $E_n = \hbar\omega_{TL}(n+1/2)$, $\hbar\omega_{TL}$=903 cm^{-1}. Contrary to the other previously studied crystals having the complicated lattices, in Raman spectra of NaCl the corresponding line $\hbar\omega_{Ram} = \hbar\omega_{TL}$ was not found. It is assumed that the oscillator regularity is governed by the polaron nature of traps. The trap activation energy is determined by a vibration level from which a transition of a charge carrier to an excited luminescence center becomes possible and depends on a distance between these centers.

Keywords: NaCl crystal, thermoluminescence, activation energy, polaron.

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1. Introduction

In works [1–6] we reported that as a result of careful investigation by the thermoluminescence (TL) methods of the trap energy spectra in complex oxide and halide crystals the oscillator regularity of the thermal activation trap energy had been found:

$$E_n = \hbar\omega_{TL}(n+1/2), \quad (1)$$

The energy of the vibration quantum $\hbar\omega_{TL}$ is typical for lattice vibrations (100 – 1500 cm^{-1}).

In different crystals from one to five series were observed. Each series is characterized by the definite value of the vibration quantum $\hbar\omega_{TL}$. It was found that an appropriate Raman line corresponds to each $\hbar\omega_{TL}$. Discrepancy between $\hbar\omega_{TL}$ and $\hbar\omega_{Ram}$ is 0.1–3%. Most of $\hbar\omega_{TL}$ correspond to the high-frequency lines of the first-order Raman spectra, others correspond to the second-order Raman lines or to the weak Raman lines caused by impurities (local modes) or by symmetry violations (IR-modes).

We have offered a trap model based on our experimental data. According to the model, a filled trap is a small polaron – either a self-trapped one or polaron stabilized by the field of the intrinsic or impurity defects. Undoubted reason for that is the availability of the oscillator regularity (1), which points to the decisive role of the charge carrier interactions with lattice vibrations in the trap states formation. The recombination in a TL-process was described as a result of the transition of a charge carrier (activated by interaction with a definite type of phonons) from the excited trap vibration level to the nearly excited state of a luminescence center. The thermal activation energy is determined by the vibration level closest to the point of geometrical intersection of the trap and luminescence center potential curves. This mechanism gives an opportunity to explain the availability of the series (1): since the luminescence centers and traps can be situated at different distances, different vibration levels responsible for the transition of a charge correspond to them, thus to different activation energies of the traps formed by a single type of defect. The model can explain without any additional conditions the first-order kinetics of the thermoluminescence. Besides that, in the framework of the model, great numbers of traps in investigated crystals is naturally explained: e.g., the series with $\hbar\omega_{TL}$=250 cm^{-1} in $CsCdCl_3$ includes 27 different values of the activation energy (32 of them have been found all in all), in $Y_3Al_5O_{12}$ 27 traps have been found. Such great quantities of the TL curves is impossible to explain judiciously on the assumption that one defect must correspond to one trap of a definite kind.

The purpose of this paper is to describe TL-investigations of the trap energy spectra in undoped NaCl crys-

tals. In contrast to the above-mentioned crystals NaCl have a simple lattice and therefore is interesting for the quest of the oscillator regularities in it, specifically from the viewpoint of the generalization of the shortly described trap model. The results of the searching for the regularity are presented here.

2. Experimental details and data handling

The TL-experiments were carried out in the temperature range between 80 and 600 K. The heating rate of 0.15 K/sec was kept unchanged by the computing program. The data were also registrated and processed with a computer. X-rays irradiated specimens of sizes around $0.5\times10\times10$ mm^3 placed in a vacuum cryostat through a 0.25 mm thick berillium window at 80 K. Both as grown and thermally treated (quenched and tempered in air or in vacuum at 610 K) specimens were used. The relative impurity content of specimens was obtained by the mass-spectrometer method. It turns out that the oxygen complexes are the dominant impurity in crystals being studied.

Typical TL-curves are plotted in Fig. 1. Positions of the TL peaks are given in the next to last column of Table. The trap activation energies were determined by the fractional curve glowing method (a variant of the initial rise method), which was tested by us for many crystals [1-6]. It consists in registration at high sensitivity of the recording channel of initial TL-curve portions of the singly-excited specimen by slow heating and following fast cooling back to the initial temperature. The cycles of heating – cooling were repeated up to the total glowing of one or several near TL peaks. For certain intense peaks it could be possible to obtain more than a hundred of initial portions of the TL-peak. It gives opportunity to determine the trap activation energy with accuracy in 1–3 meV, and it is much more exactly than by any other of single stage methods.

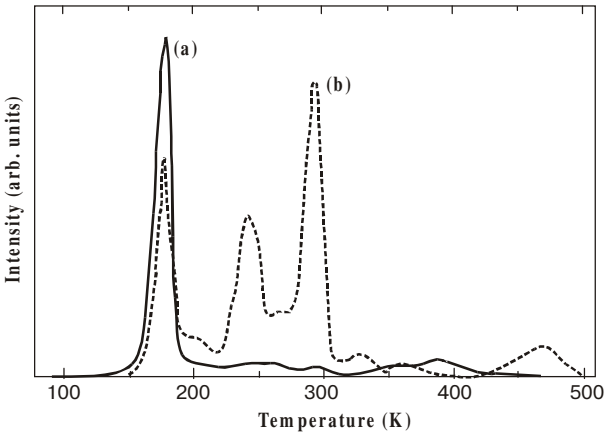

Fig. 1. Review thermoluminescence spectra of NaCl: (a) (full line) as-grown specimen; (b) (dotted line) quenched specimen.

Data handling was performed by the using of the special computer program. On the basis of the temperature dependence of the initial rise intensity $I=I_0\,exp(-E/kT)$ the parameters of a straight-line $\ln(I)=A-E/kT$ were found. Criteria for choosing an E value was a minimum of a root-mean square deviation of experimental and calculated (that is the straight-line points) values of $\ln(I)$.

Table. Activation energies (E_a, eV) determined in different ways: (a) from equation (1), (b) by fractional glowing method, (c) by total glow peak method $\hbar\omega_{TL}$ = 0.112 eV.

n	$E_a{}^a$	$E_a{}^b$	$E_a{}^c$	T_m	S
1	0.168	–	0.167±0.005	95.7	$1.9\cdot10^7$
2	0.280	–	–	–	–
3	0.392	–	0.393±0.005	162.5	$4.6\cdot10^{10}$
4	0.504	0.502±0.001	0.501±0.005	176.2	$6.4\cdot10^{12}$
	0.504	0.503±0.002	0.497±0.005	210.0	$2.4\cdot10^{10}$
5	0.616	0.616±0.001	0.615±0.005	241.0	$1.4\cdot10^{11}$
6	0.728	0.736±0.003	–	260.4	$2.1\cdot10^{12}$
7	0.841	–	–	–	–
8	0.953	0.951±0.003	0.978±0.010	292.3	$4.7\cdot10^{14}$
9	1.065	1.064±0.002	1.066±0.020	331.6	$3.8\cdot10^{14}$
10	1.177	1.178±0.002	–	390.5	$2.2\cdot10^{13}$
11	1.289	1.292±0.003	1.273±0.020	408.3	$1.4\cdot10^{13}$
	1.289	1.300±0.007	1.292±0.020	442.0	$3.4\cdot10^{12}$
12	1.401	1.408±0.003	1.397±0.020	474.0	–
13	1.513	1.514±0.002	–	450.0	–

The main procedures of the data handling programs were as follows:

Excluding a background. This procedure was very important for most of investigated crystals. Since the recording of fractional curves is carried out at the very increased amplification (~100 times comparatively to review TL-curves), the background increases correspondingly. The handling without regard for the background gives very understated (by ~0.05-0.1 eV) values of E_a.

Excluding low- and high-temperature points. The necessity of the procedures is caused by a small value of a signal/noise ratio for low-temperature points and violation of a constant lightsum (n_t) criteria at final stages of glowing.

Determination of the trap energies from the fractional glowing data. The data obtained from the initial rises were handled by another program which permit to gain the fractional energy dependency versus the ordinal number of the initial rise n. The activation energy was determined if the shelf in this dependency occurred. For intense peaks it could be possible to obtain more than a hundred of initial rises of the TL-peak. It gives opportunity at proper data handling to determine E_a with a high accuracy (down to 0.001 eV), that is much more exactly than that of any other method.

The example of work of the procedure of the background excluding for one of initial rises of the 176 K TL peak is given in Fig. 2. From the analysis of data it follows that: 1) the fractional curve glowing method under close data handling gives an opportunity to determine the trap activation energies with a high accuracy (e.g., RMS ~0.001 eV for the discussed 176 K TL peak); 2) the procedure of the background excluding is correct since as it is seen from Fig. 3 the energies determined from initial rises fall good within the shelf even though the

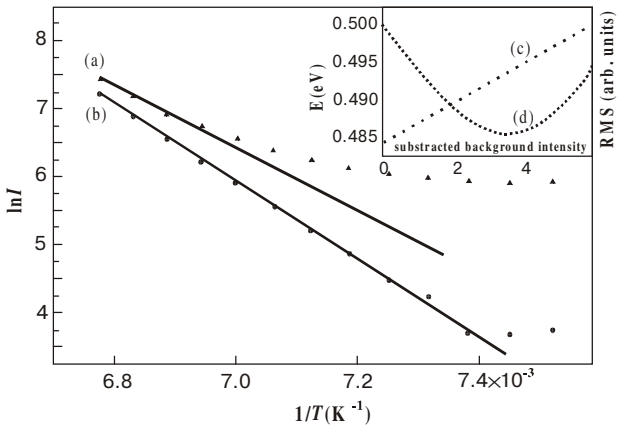

Fig. 2. An example of the background excluding for the 176 K TL peak: (a) (triangles) the initial $1/T$-dependence of $\ln I$ (with the background); (b) the same dependence after excluding of the background value which corresponds to the RMS minimum. On the insert: plots of the energy determined from the above dependence of $\ln I$ (c) and the RMS (d) versus the subtracted value of the background.

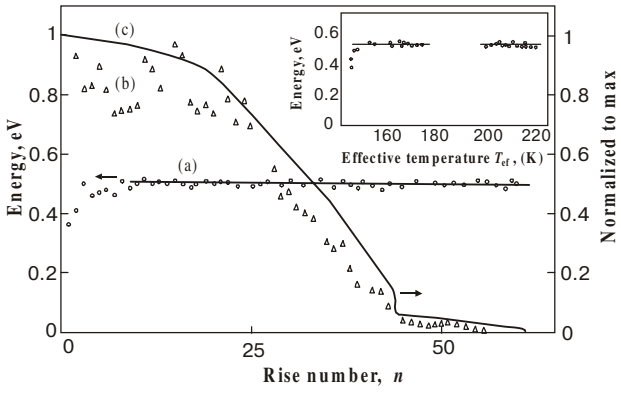

Fig. 3. Data on the fractional glowing of the 176 and 210 K TL peaks. n is ordinal number of the initial rise. The trap activation energy is determined from the shelf (line (a)) on the presented dependence; (b) (triangles) the relative value of the subtracted background; (c) (full) the rest of lightsum after each glowing cycle. On the insert: the similar to (a) dependence as a function of T_{ef}.

background considerably reduces (from an initial value ~0.15 of a maximum initial rise intensity I_s to about zero (~0.01 I_s) in final glow cycles). On the insert (Fig. 3) the similar to shown in Fig. 3 (a) dependence is presented, but as a function of T_{ef} (the latter was calculated for a maximum intensity of fractional curves (I = 2000.0). At this choice the temperature value T_{ef} for last rises were close to the temperature of the investigated TL peak maximum T_m). It consists of two shelves which are near equal in energies: E_1 = 0.502 eV and E_2 = 0.503 eV, one of them ends at T_{ef}=173 K, that is the 176 K TL peak corresponds to it, while the second shelf ends at 215 K. From Figure 1 it is seen that the latter value corresponds to the next low intensive peak at 210 K. The boundary between two peaks can be detected also on the fracture in the lightsum plot (see Figure 3 (c)). Thus, the analysis of the most intensive TL peak at 176 K revealed that in NaCl there are at least two TL peaks which are glowing at different temperatures but with the equal activation energies. Another pair of such TL peaks is regarded below. The trap activation energies determined by the fractional glowing method are given in the third column of Table.

The energies of certain intense TL peaks were also determined by a variant of the total glow peak method (with lightsum fitting), e.g. from slopes of a straight line (for the first order kinetics) $1/T$-dependence of $ln(I/n_t)$. It gives also good but less exact comparatively with the initial rise method results. This method even in the case of partially overlapped TL peaks with the properly corrected rest of lightsum can be successively used instead of the more cumbersome initial rise method.

The energy values calculated by this method for some TL peaks are given in the fourth column of the Table. In the next columns the values of temperature maxima T_m and pre-exponential factors for corresponding TL peaks are given. Truthworthy values of the energy for the high-

temperature (T>330 K) TL peaks can not be obtained by this method because of considerably overlapping peaks.

From the Table it is seen that the trap activation energies fit the oscillator regularity (1), as in the cases of all other crystals being investigated previously. One oscillator series has occurred with rather big value of $\hbar\omega_{TL}$ = = 0.1121 eV (903 cm^{-1}). In the second column of the Table energies calculated from (1) are given. For determination of the vibration quantum number the fractional glowing method data were used as the most exact, exclusing the TL peak with n = 1, for which the activation energy was determined by the total curve fitting method.

Some features specific to certain peaks should be noted.

The TL peak at 176 K is nonelementary in our specimens. There is the additional to dominant peak in the low temperature tail of it, as exemplified also by its considerable asymmetry: the ratio between the high-temperature and total halfwidths of the TL peak is only μ = 0.37 comparatively to the «standard» value μ = 0.42 for the first-order kinetics. This additional 163 K peak was separated from a total TL peak. The energy of it determined from the 1/T-dependence of ln(I/n_t) and averaged over five values received on variously treated specimens is 0.393±0.004 eV. From Fig. 3 one can see an influence of the additional TL peak at 163 K on the results of the main 176 K peak fractional glowing.

In Fig. 4 data on the 474 K TL peak fractional glowing are given. In Fig. 4 (a) the initial rise number dependence of the fractional energies without excluding of the background is presented. In Fig. 4 (b) and (c) the same dependencies after the background excluding are shown (versus the initial rise number and the effective temperature T_{ef}, respectively). In Fig. 4 (a) the monotonic decreasing of the fractional energies values from 1.47eV to 1.40eV is observed, whereas in Fig. 4(b) and (c) one can clearly separate two shelves with the energies E = 1.514 eV (n = = 13) and 1.408 eV (n = 12). Thus, the considered TL peak is non-elementary, and a special feature of it is that the maximum with the higher energy glows at lower temperatures. The position of the TL peak n = 13 can be approximately estimated at 450 K from the beginning of the second shelf. The last fractional curve has a maximum at T = 476 K. The energy calculated from the 1/T-dependence of ln(I/n_t) for this curve is 1.41 eV, what corresponds to the second shelf energy. On the high-temperature tail of the 470 K peak, the low intensive one at 502 K is seen, for which the energy value E = 1.73 eV was received. It is in rather good accordance with E = 1.738 eV determined from (1) for n = 15.

Curve (a) in Fig. 5 shows the partially overlapped TL peaks received for the specimen, which was excited at room temperature. The calculated fractional energies are presented in Fig. 5 (b) as a dependence on the effective temperature T_{ef}. The energies of the shelves 1 and 3 corresponding to the first two clearly distinct peaks at 335 and 391 K are coincident: E_1 = 1.063 eV, E_3 = 1.066 eV; they correspond to the value n = 9. The energies of the shelves 2 and 4 are also coincident: E_2 = 1.118 eV, E_4 = = 1.119 eV. The shelf 4 places in the temperature region

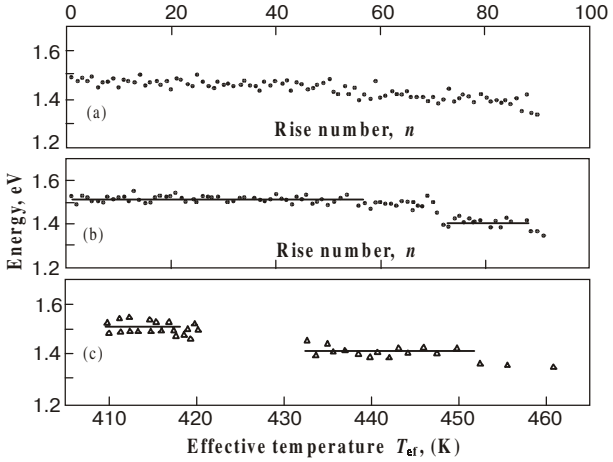

Fig. 4. Data on the fractional glowing of the nonelementary 474 K TL peak for the specimen No.2: (a) fractional energies versus the initial rise number (with the background); (b) the same dependence after excluding of the background; (c) the same versus the effective temperature.

of a 442 K peak glowing. The TL peak corresponding to the shelf 2 is not revealed in curve (a), but it can be observed at 367 K after subtraction of elementary peaks at 335 and 391 K from the total glow curve. It was noticed that the energies 1.118 and 1.119 eV do not correspond to any value determined by (1), but they are multiple to the integer number of $\hbar\omega_{TL}$ (n = 9, E = 1.121 eV). So, two energy values were found, namely 0.676 eV and 1.119 eV, which do not fit the regularity (1), but are multiple to the integer number of $\hbar\omega_{TL}$, that is they are described by the regularity corresponding to the two-dimensional oscillator.

We found one series starting with the 95 K peak and probably caused mostly by defects associated with oxygen complexes. Activation energies corresponding to the peaks at lower temperatures can form another series; this

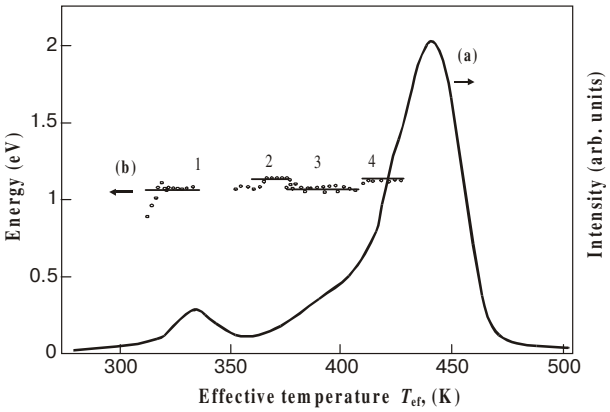

Fig. 5. (a) The TL peaks in the temperature range from 300 to 500 K; (b) data on the fractional glowing of these peaks.

series can be caused by other type of defects. The rough estimation of literary data revealed the possibility of the series with ~150 cm^{-1}, what corresponds to the only fundamental IR mode of NaCl. Now we have no opportunity to investigate the low-temperature region (< 80K).

4. Discussion

4.1. On the fractional curve glowing method. We consider it necessary to emphasize that the oscillator regularity (1) in NaCl and other crystals [1-6] was revealed owing to using the fractional curve method. The main advantage of it is an opportunity to obtain a considerable amount of uniform data on activation energies. Small values of the RMS are caused by just that circumstance, since the RMS decreases as the body of data increases. It is clear that errors connected with the thermocouple calibration, temperature gradients, *etc*, are not taken into account here. Other methods are, effectively, one-fold, therefore they can not compete with the fractional curve method in accuracy. For example, to attain such accuracy by the method of the heating rate variation, it is necessary to receive several tens of the TL curves at different fixed heating rates, what is rather complicated technical problem.

4.2. On the TL mechanism in NaCl. This mechanism involves both electronic and ionic rearrangement and usually it is difficult to separate clearly their contributions in the TL processes. There are several hypotheses concerning the trap nature in alkali halides, specifically in NaCl crystals. Neither of our experiments show exactly the nature of particles released from traps, but considering that all found activation energies fit the oscillator dependence (1) it may be deduced that in at least undoped NaCl crystals all traps providing glow in the temperature range from 80 to 500 K have a certain component in their composition which defines the local vibration 0.112 eV.

Contrary to the previously investigated crystals where for all series the correspondence between $\hbar\omega_{TL}$ and $\hbar\omega_{Ram}$ quanta was found, in NaCl corresponding $\hbar\omega_{Ram}$ was not detected. Since the highest Raman modes are no more than about 540 cm^{-1} (the second-order Raman lines [7]), the only fundamental mode 162 cm^{-1} is IR-active [7], thus the energy $\hbar\omega_{TL}$=0.112 eV must correspond to the local vibration caused by the defect. It is possible that in NaCl $\hbar\omega_{TL}$ corresponds to a local mode of one of the oxygen defects, which are the main uncontrolled impurity in NaCl and have vibration frequencies in the range between 800 and 1000 cm^{-1}. Estimations based on the literary data show that the best suitable frequencies may correspond to the complexes O_3^{2-}(about 910 cm^{-1}) or the bent O-Cl-O (about 915 cm^{-1}).

The results on NaCl confirmed the previously proposed model, which explains the TL process as a thermal charge release out of the parabolic potential well from a level which is governed by the distance between a trap and a luminescence center. We have not found the alternative mechanisms, which could explain the great number of traps in earlier investigated crystals. In NaCl the number of different activation energies is comparatively small – something more than 10. Taking into account a tendency of alkali halides to form proper defects and different aggregates of defects, the traditional band mechanism of the TL seems to be possible, too. Both mechanisms may act simultaneously, that is the activation energy is defined both the trap nature (the polaron potential well in the energy scale) and the trap position relative to the neighboring luminescence center (which determines the position of the vibration level for charge tunnelling).

4.3. On the oscillator dimensionality. Here the model of the one-dimensional harmonic oscillator was used for interpretation. The results for the three-dimensional oscillator can be presented by using the factor 3/2 instead of 1/2 in formula (1), and lowering by 1 the values of the quantum number n in the Table. But the occurrence of a trap with E = 0.167 eV argues for the one-dimensional model. Really, this activation energy corresponds to the emptying of a trap from the excited vibration level n = 1, whereas for the three-dimensional oscillator this activation energy must correspond to the ground (thermally unexcited) level n = 0.

The energy values 0.676 eV and 1.119 eV do not fit the regularity (1), but they are multiple to the integer number of $\hbar\omega_{TL}$. One can concede that in this case the two-dimensional oscillator $E = \hbar\omega_{TL}(n+1)$ is realized, where n = 5 and 9.

The availability of double energy values corresponding to the half-integer number of $\hbar\omega_{TL}$ (n = 4,11, Table) at first sight can be attributed to exhibition of the three-dimensional oscillator with n = 3,10. But the existing of two traps with equal activation energies E = 1.118 eV corresponding to the two-dimensional oscillator is in contradiction with above assumption. It is likely that existing of equal activation energies relating to different TL peaks may be caused by certain differences in structure of traps which lead to different probabilities of charge tunneling.

Conclusions

The performed experiments revealed that in undoped NaCl crystals the trap activation energies form a single oscillator series with a vibration quantum $\hbar\omega_{TL}$=0.112 eV (903 cm^{-1}). Considering our preceding results for several crystals and independent data of other workers it can be done the conclusion that the oscillator regularity results from the strong electron–lattice interaction in crystals with mainly ionic bonds. This regularity is not unique feature of certain crystals but reflects rather common property of them.

In NaCl we have obtain the direct (that is from the TL experiments but not the Raman lines symmetry analysis) evidence of the one-dimensionality of the oscillator. The exhibition of the two-dimensional oscillator we have also observed first just in NaCl.

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