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Oscillator Rule of the Trap Activation Energies in NaCl Crystals

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Abstract: The energy spectra of traps in NaCl crystals have been 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, $E_n = \hbar\omega_{TL}(n+1/2)$, $\hbar\omega_{TL} = 903\,\mathrm{cm}^{-1}$. Contrary to other previously studied crystals with complex lattices, the corresponding line $\hbar\omega_{Ram} = \hbar\omega_{TL}$ was not found in Raman spectra of NaCl. It is assumed that the oscillator rule is governed by the polaron nature of traps. The trap activation energy is determined by the vibration level from which the transition of the charge carrier to the excited luminescence centre is made possible and depends on the distance between these centres.

Keywords: thermoluminescence, trap, initial rise method, activation energy, polaron, luminescence center
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1 Introduction

In recent investigations [1 to 7], we reported that as a result of careful investigation by the thermoluminescence (TL) method of the trap energy spectra in complex oxide and halide crystals the oscillator rule of the thermal activation trap energy has been found:

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

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

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In different crystals from one ($Ba_2NaNb_5O_{15}$, $YAlO_3$) to five ($Y_3Al_5O_{12}$) series have been 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 (excluding $YAlO_3$ crystal) $\hbar\omega_{TL}$ (see Table 1 and 2 for data on some of the crystals). 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 this model, a filled trap is a small polaron - either self-trapped or stabilized by the field of the intrinsic or impurity defects. The reason for that undoubtedly, is the existence of the oscillator rule (1), which points to the decisive role of the charge carrier interactions with lattice vibrations (fundamental or local) in the trap states formation. The crystals mentioned above have rather complex lattices where it is possible to separate out comparatively isolated ion groups (tetrahedra or octahedra) so that the interaction inside them is stronger than between the groups. These quasi-molecular complexes are of considerable importance in the proposed polaron model, especially because the phonons ($\hbar\omega_{TL} = \hbar\omega_{Ram}$) correspond, as a rule, to the high-frequency internal vibrations of the complexes. The crystal point defects as a whole are mostly determined by the defects of quasi-molecules too.

The recombination in a TL-process was described as due to 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 centre. The thermal activation energy is then determined by the vibrational level closest to the point of the geometrical intersection of the potential curves of the trap and luminescence centre.

This mechanism gives an opportunity to explain the existence of the series (1): since the luminescence centres and traps can be situated at different distances, different vibrational levels responsible for the transition of a charge correspond to them, and 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 thermoluminescence, *i.e.,* the absence of retrapping in all crystals under study, in as much as the occuring of retrapping signifies that the carriers are in delocalized states for a rather long time, which is absent for the given mechanism. Besides that, in the framework of the model great numbers of traps in investigated crystals are naturally explained: e.g., the series with $\hbar\omega_{TL} = 250\,\text{cm}^{-1}$ in $CsCdCl_3$ includes 27 different values of the activation energy (32 of them have been found all in all), 27 traps have been found in $Y_3Al_5O_{12}$. Such great quantities of the TL curves are 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 in detail TL-investigations of the trap energy spectra in NaCl crystals. In contrast to the above-mentioned crystals, NaCl has a simple lattice and therefore interesting in the context of the oscillator rules, specifically from the view-point of the generalization of the trap model. As it will be shown, the activation trap energies in NaCl also form the oscillator rule with $\hbar\omega_{TL}$ = 903 cm^{-1}. The results of investigation of the rule and the previous analysis of the possible mechanism of its origin are presented here. Much attention is given to the techniques of data handling.

2 Experimental details

The TL-experiments were carried out in the temperature range between 80 and 600 K. The linearity of a heating rate (0.15 K/sec) was regulated by the computer program. Because of the thermal sluggishness of a system the use of a feedback for stabilization of a heating rate was not effective, therefore the temperature dependence of heater current was approximated by a polynomial

$$I = I_0 + a_1 T + a_2(T - T_2)^2 + a_3(T - T_3)^2 \qquad (2)$$

where the parameters I_0, a_1, a_2, a_3, T_2, T_3 were matched in advance. This method was effective at heating from the lowest temperature of 80 K. Because of the small thermal capacity of a system at low temperatures, the transient process of heat transfer holds only 4-5 experimental points ($<$ 7 K), whereas at heating from room temperature (RT) a steady state value of the heating rate was possible during 15-20 experimental points ($<$ 20 K). Therefore heating always began from 80 K, even if the X–ray irradiation was performed at RT.

During the observation of the fractional curves the heater was driven by constant direct current, as heating rate variations have no influence on the form of fractional curves; where this influence is significant, the initial rise method is not correct.

Specimens of sizes around 0.5 × 10 × 10 mm placed in a vacuum cryostat were irradiated by X-rays (U = 50 kV, I = 20 mA) through a 0.25 mm thick beryllium window at 80 K over 10 min to obtain TL glow curves and over 20 min at the fractional glowing experiments. Samples were irradiated at room temperature to obtain the TL-peaks with $T >$ 300 K . Between the stages of the X-ray irradiation and the following TL measurements the samples were not removed from a cryostat. The registration of the TL was performed through a quartz window of a cryostat. At the appearance of the high-temperature TL peaks ($T >$ 400 K), the glass filter was set in front of the photomultiplier tube for stopping the thermal IR–radiation of the substrate. Both as grown and thermally treated (quenched and tempered in air or, in some cases, in vacuum at 610 K) specimens were used.

Our previous studies of many crystals indicate that single energy levels of traps occur in undoped or lightly doped specimens. The TL-peaks broaden and single levels smear into bands with increasing dopant concentrations. Accordingly, undoped crystals of NaCl were chosen for the investigation.

The crystals were grown by the Kyrhopulos method in air. The relative impurity content of specimens was obtained by the mass-spectrometer method. It turns out that the oxygen complexes are a dominant impurity in crystals being studied. We used specimens split off from undoped crystals (No.1 and No.2) which differ in uncontrolled impurities concentrations; in particular, the concentration of oxygen complexes is several times more in crystal No.1. More detailed analysis of impurity content was not performed. Only proper emission bands were observed in the spectra of X-ray-luminescence, which is indicative of the purity of crystals.

Typical TL-curves are plotted in Fig.1. The positions of the TL peaks are given in the next to last column of Table 3. 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 to 7]. It consists of observation at high sensitivity of the recording channel of initial TL-curve portions of the singly-excited specimen by slow heating, followed by rapid cooling back to the initial temperature. The cycles of heating and cooling were repeated up to the total glowing of one or several near TL peaks. For certain intense peaks one could obtain more than a hundred of the initial portions of the TL-peak. It provides the opportunity to determine the trap activation energy with an accuracy of 1{3 meV, and it is more accurate than by any other single stage methods.

3 Experimental data handling

Data handling was performed by a special computer program. Based on the temperature dependence of the intensity $I = I_0 \exp(-E/kT)$, the parameters of a straight line $\ln I = A - E/kT$ were found. The energy E was calculated by averaging over all pairs of adjacent points and the constant A over all m points: $A_i = (1/m)\sum(\ln I_i + E/kT_i)$. The criterion for the choice of E value was a minimum of a root-mean square (RMS) deviation of experimental and calculated (that is the straight line points) values of $\ln I$.

3.1 Subtraction of the background.

Among the procedures used for data handling, the procedure of the background subtraction was the most important for NaCl. It was found that in NaCl the \proper" TL curves are followed by glowing which varies slowly with the temperature.

The occurrence of the background has received much attention (see, e.g., [8]). The background was barely noticeable in the review TL curve. Since the recording of fractional curves is carried out at amplification by a factor of 10 to 100, the background increases correspondingly (relative to the TL intensity). The handling of the TL peaks without regard for the background underestimated (by $\approx 0.05 - 0.1$ eV) values of the energy. The fast component of the background was eliminated by conditioning the specimens for $1 - 2$ min before the next fractional heating. The slow background component was excluded by the program due to its assumed constancy across all of the initial rise. To do this the intensities of all points were decreased by a certain predetermined value and the energy and RMS were calculated. The process was repeated until the RMS passed through the minimum.

An example of the procedure for one of the initial rises of the 176 K TL peak is given in Fig.2. The curve (a) presents the dependence of $\ln I$ versus $1/T$ together with the background, while the straight line (b) presents the same dependence after the subtraction of the background value corresponding to the minimum RMS. The energy calculated for the three last points on the curve (a) is only 0.390 eV, while the value obtained from the straight line (b) is 0.494 eV. The curve with the minimum (d) in the inset shows the qualitative change of the RMS as the background is subtracted.

3.2 Exclusion of some experimental points.

The procedure for the exclusion of the low-temperature points should be mentioned. This is necessary due to a small value of the signal to noise ratio for these points. According to the procedure, experimental points were sequentially excluded (beginning from the first) and after each exclusion the energy and RMS were calculated. As a rule, the minimum of the RMS was achieved after exclusion of no more than five points out of the total number of about 30–50 experimental points.

At final stages of glowing the criteria of a constant illumination is not valid and the initial rise method is not correct. For such cases a similar procedure was used, but now some high-temperature points were excluded, beginning with the last one.

It should be noted that the exclusion of some experimental points was not arbitrary and that this exclusion has no significant effect on the results.

3.3 Determination of the trap energies from the fractional glowing data.

The data obtained from the initial rises was handled by another program which enabled us to take advantage of the behavior of the fractional energy versus the ordinal number of the initial rise n or versus the rise effective temperature T_{ef}. The latter was calculated for a maximum intensity of fractional curves (I = 2000.0). With this choice, the temperature value T_{ef} for the last rises were close to the temperature of the investigated TL peak maximum T_m.

The trap activation energy was determined if the above dependencies exhibited a plateau. The initial rise ordinal number dependence of the fractional energy for the TL peak at 176 K in an as-grown specimen from the crystal No. 2 is given in Fig. 3 (a). The energy determined from the plateau is E = 0.502 eV at the RMS value of $\pm$0.001 eV. The relative values of the subtracted background are marked by the triangles (b), the solid line (c) corresponds to the illumination which was left after each glowing cycle. Practically the same value was obtained for the quenched specimen : E = 0.505 eV (not shown in Figure).

From these data it follows that: 1) the fractional curve glowing method under close data handling enables us to determine the trap activation energies with high accuracy (e.g., RMS $\sim$ 0.001 eV for the discussed 176 K TL peak). The occurrence of a plateau can indicate in particular that possible thermally activated trap modification in the sample between each measured points is not very important for the method employed; otherwise $\sim 30 - 50$ points could not fit *one* plateau, *i.e.*, one activation energy E related to one trap. This modification probably changes the intensities of the TL-peaks but it does not lead to changes in the activation energies; 2) the procedure of the background subtraction is correct since as seen from Figure 3, the energies determined from initial rises fit well in the plateau even though the background considerably decreases (from an initial value $\sim$ 0.15 of a maximum initial rise intensity I_s to about zero ($\sim 0.01 I_s$) in final glow cycles). It should be noted that without the frequent background subtraction, we would not have been able to separate the plateau: since the occurrence of the plateau is indicative of *a specific* trap glowing, the importance of the background subtraction in the proper determination of the activation energy is clearly seen. 3) for the 176 K TL peak considered here, there exists the direct correlation between the background intensity and the rest of the illumination.

A dependence similar to that shown in Fig.3 (a) is presented on the inset (Fig.3), but as a function of T_{ef}. It consists of two plateaus which are nearly equal in energies: E_1 = 0.502 eV and E_2 = 0.503 eV, one of them ends at T_{ef} = 173 K, corresponding to the 176 K TL peak, while the second ends at 215 K. It is seen from Fig.1 that the latter value corresponds to the next low intensive peak at 210 K. The boundary between the two peaks can be detected also on the fracture in the illumination plot (see Fig.3 (c)). The nonuniformity of the points distributed in the former plateau (see inset) are caused by the amplification coefficient decreasing correspondingly by a factor of $\sqrt{10}$ and 10 for the purpose of obtaining a reasonable number of fractional curves.

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 equal activation energies. Another pair of such TL peaks is discussed below.

The trap activation energies determined by the fractional glowing method are given in the third column of Table 3.

3.4 The total curve fitting method.

The energies of certain intense and rather isolated TL peaks were also determined from slopes of a straight line (for the first order kinetics) $1/T$-dependence of $\ln(I/n_{\mathrm{t}})$, where n_{t} is the rest of the illumination.

A low-temperature part of a chosen TL peak was cleared by heating of a specimen to a corresponding temperature followed by rapid cooling. From a high temperature part the TL peak chosen for calculation was bounded by a position of the intensity minimum. In Fig.4 the curve (a) shows this dependence for the TL peak at 332 K (quenched specimen No.2). The deviation of the high temperature points from a straight line can be caused both by the increasing contribution of the next TL peak and the understated value of the rest of the illumination, because of the cropping of the tail of the TL peak investigated. In the curve (a) the sharply increasing portion (1) is caused primarily by a contribution of the next TL peak intensity, whereas the part of a curve with a lesser slope (2) indicates that the illumination appeared too large at the cost of the next TL peak contribution. Then, in calculating the energy, the points which formed the sharply increasing portion were excluded by the procedure of the energy determination and for the purpose of straightening the line, the required correction of the illumination was performed. The procedure was repeated as necessary. In the final stages of the illumination-fitting, the procedure of high-temperature points exclusion was used, which gave the opportunity to reveal the tiny deviations from straight line. The final calculated result is shown in the curve (b), which is slightly displaced on the vertical axis for the sake of clarity. The energy E = 1.066 ± 0.020 eV determined from the rectilinear portion of the line (b) is in good agreement with a corresponding value obtained by the fractional glowing method (Table 3, n = 9, E = 1.064 eV).

The energy values calculated by this method for some TL peaks are given in the fourth column of Table 3. The values of the temperature maximums T_m and pre-exponential factors for corresponding TL peaks are given in the next columns. Reliable values of the energy for the high-temperature ($T >$ 330 K) TL peaks cannot be obtained by this method due to considerable overlapping of the peaks.

3.5 The oscillator series in NaCl.

It is seen from Table 3 that the trap activation energies fit the oscillator rule (1), as in the cases of all other crystals investigated earlier. One oscillator series had a rather large value of $\hbar\omega_{TL}$, namely 0.1121 eV (903 cm^{-1}). In the second column of Table 3 the energies calculated from (1) are given. The fractional glowing method data were used as the most accurate, in determining the vibration quantum number, with the exception of the TL peak 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 peaks are identified by the corresponding values of the vibration quantum number n.

n = 1. The TL peak at 96 K could not be investigated satisfactorily by the fractional glowing method because of its small intensity. The activation energy E = 0.167±0.005 eV calculated by the total curve fitting method coincides very closely with the value expected from (1) at n = 1.

The next TL peak at 121 K is also of low intensity and also considerably overlaps with the following TL peak at 163 K. The energy determined by the fractional glowing method is $\sim$ 0.19 eV, and that obtained from the total curve fitting method is 0.17–0.20 eV. These values are much closer to the energy value for the previous peak than to the energy calculated from (1) for the next quantum number value n = 2, namely, E = 0.28 eV.

n = 3. The TL peak at 176 K is non-elementary in our specimens. There is a peak additional to the primary peak in the low temperature tail, as is exemplified also by its considerable asymmetry: the ratio between the high-temperature and total half-widths of the TL peak is only μ = 0.37, compared to the “standard" value μ = 0.42 for the first-order kinetics. This additional 163 K peak was separated from a total TL peak and its energy determined from the $1/T$-dependence of $\ln(I/n_t)$ and averaged over five values obtained from variously treated specimens is 0.393 $\pm$ 0.005 eV. We can infer from Fig.3 the influence of the additional TL peak at 163 K on the results of the main 176 K peak fractional glowing. Therefore the energy determined from the first two points is 0.386 eV, the next values of the fractional energies are increasing monotonically and fall within the plateau beginning only from the eighth initial rise.

$n = 6, 7$. The TL peak at 260 K in as-grown specimens is comparable to the previous peak at 241 K in intensity and considerably overlaps with it (Fig.1). The data on the fractional glowing dependent on the effective temperature T_{ef} in the range of 200–270 K is given in Fig.5 . The fractional energy values obtained for the as-grown specimens from crystal No.1 are indicated by open circles, and those obtained from crystal No.2 by triangles. The first plateau energy E = 0.617 eV is caused by the previous peak (241 K) contribution. The next plateau (b) is available in both crystals (E = 0.679 and 0.673 eV for No.1 and No.2, respectively). These values do not fit the rule (1) but correspond rather exactly to the integer number of $\hbar\omega_{TL}$: n = 5, E = 0.672 eV. The energy values from the plateau (c), E = 0.736 eV, specimens from No.1, provide a satisfactory fit to the rule (1) for n = 6 (the calculated energy is E = 0.728 eV). For the thermally untreated specimen from crystal No.2 a set of monotonically increasing energy values was obtained; we can, with some uncertainty, separate out two plateaus with the energies E = 0.82 and 0.87 eV, which are close to the calculated value of 0.84 eV for n = 7. This result is not included in Table 3.

n = 11. In specimens from crystal No.1 a peak at 408 K with E = 1.292 eV is observed, while in specimens from crystal No.2 practically the same energy E = 1.300 eV was found for the TL peak at 442 K. The glowing of these peaks in both crystals is accompanied by the background, the relative value of which decreases from 0.02 to zero.

$n = 12, 13$. The data on the 474 K TL peak fractional glowing (as-grown specimens from crystal No.1) are given in Fig.6. The initial rise number dependence of the fractional energies without the subtraction of the background is presented in Fig.6 (a). In Fig.6 (b) and (c) the same dependencies after the background subtraction are shown (depending on the initial rise number and the effective temperature T_{ef}, respectively). The break on curve (a) is caused by an amplification decrease by a factor of $\sqrt{10}$. In Fig.6 (a) a monotonic decrease of the fractional energies values from 1.47 eV to 1.40 eV is observed, whereas in Fig.6 (b) and (c) two plateaus with the energies E = 1.514 eV (n = 13) and 1.408 eV (n = 12) clearly stand out. Thus, the TL peak under consideration is non-elementary, and has the special feature 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 plateau. 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, which corresponds to the second plateau energy. The one of low intensity at 502 K is seen on the high-temperature tail of the 470 K peak, for which the energy value E = 1.73 eV was obtained. It is in rather good agreement with E = 1.738 eV determined from (1) for n = 15.

n = (?). Curve (a) in Fig.7 shows partially overlapped TL peaks obtained on the as-grown specimen from the crystal No.2 which was excited at room temperature. The calculated fractional energies are presented in Fig.7 (b) as a function of the effective temperature T_{ef}. The energies of the plateaus *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 plateaus *2* and *4* are also coincident: E_2 = 1.118 eV, E_4 = 1.119 eV. The plateau *4* is placed in the temperature region of a 442 K peak glowing. The TL peak corresponding to the plateau *2* does not reveal itself in curve (a), but it can be observed at 367 K after the substraction of the elementary peaks at 335 and 391 K from the total glow curve.

Note that the energies 1.118 and 1.119 eV do not correspond to any value determined by (1), but they are related to the integer multiple of $\hbar\omega_{TL}$: $\hbar\omega_{TL}(9 + 1)$ = 1.121 eV. Two energy values were thus found, 0.676 eV and 1.119 eV, which do not fit the rule (1), but are related to the integer multiple of $\hbar\omega_{TL}$, that is they are described by the rule $E = \hbar\omega_{TL}(n + 1)$ 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 series can be caused by other type of defects. The rough estimation of literary data revealed the possibility of a series with $\sim$ 150 cm^{-1}, which corresponds to the only fundamental (IR) mode of NaCl. Now we have no opportunity to investigate the low-temperature region ($<$ 80 K).

4 Discussion

4.1 On the fractional curve glowing method.

We must emphasize that the oscillator rule (1) in NaCl and other crystals [1 to 7] was revealed by using the fractional curve method. The main advantage of it is the opportunity to obtain a considerable amount of uniform data on activation energies. Small values of the RMS (0.001–0.005 eV) result from both the reproducibility of the results and the proper mathematical handling of the experimental data. The criteria for all methods of the data handling except the procedure of the high-temperature points exclusion was a minimum of a RMS. Of special importance was the procedure of the background subtraction. The background follows all TL-peaks exept the peaks corresponding to n = 9, 10 (E = 1.064, 1.178 eV). It is believed that failure to take the background into account had led to very understated energy values and, correspondingly, frequency factors obtained by the isothermal light–decay curves method [20,21]. It is clear that errors connected with the thermocouple calibration, temperature gradients etc. are not taken into account here, but the rather exact correspondence of the energy values to the oscillator rule (1) indicates that these errors have no significance.

Other methods of the energy determination are, in essence, one-fold, hence they cannot 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 obtain several tens of the TL curves at different fixed heating rates, which is a rather complicated technical problem.

The initial rise method was repeatedly proposed for investigations of the trap energy spectra in different crystals (see, for example, [9 to 11]). The slow linear heating of a specimen was followed by the low temperature oscillations with the determination of the fractional energy during the experiment just after the appearance of each oscillation. By dividing the energy determination in stages of the fractional curve appearance and by proper energy calculation from it, we were able to perform a thorough mathematical analysis of experimental data and thus obtain more reliable values. Of special concern is the procedure of background subtraction in the case of low-temperature ($T <$ 300 K) TL peaks: the proper performance of this procedure by the traditional initial rise method is not possible.

A variant of the total glow peak method (with light intensity fitting) used by us in the energy determination from the $1/T$-dependence of ln(I/n_{t}) also gives good but less accurate results in comparison with the fractional glow method. For the total glow peak method to be successful, it is sufficient for only a part of the TL peak (as a rule, it is a region near its maximum) to be free of the near TL peak's influence. This method can be applied successfully in the case of partially overlapped TL peaks with the properly corrected remaining illumination instead of the more cumbersome initial rise method.

4.2 On the TL mechanism in NaCl.

This mechanism involves both electronic and ionic rearrangement and is usually difficult to separate their contributions clearly in the TL processes. There are several hypotheses concerning the trap nature in alkali halides, specifically in NaCl crystals.

According to the most advanced of them, the mechanism of the TL is governed by: 1) the recombination of electrons (released from F centers and other defects) with holes at luminescence centers [11 to 13] or with double holes centers [14]; 2) F centers are the recombination centers for holes which are thermally released from traps [15,16]; 3) the release of holes (V_k centers) and interstitials (H centers) trapped together in the form of Cl_3^- ion followed by recombination [17 to 19]; 4) the recombination with F centers of halogen interstitial atoms (stabilized by different defects) which are thermally released from traps (the ion model [20,21]). This model seems to be more convincing for the case of NaCl.

Although our experiments do not show the exact nature of the particles released from traps, considering that all observed activation energies fit the oscillator dependence, rule (1), it may be inferred that in at least pure NaCl crystals all traps glowing in the temperature range from 80 to 500 K have a certain component in their composition which defines the local vibration 0.112 eV.

The results of earlier work [21] confirmed implicitly the local nature of the TL mechanism, *i.e.,* the occurrence of different emission spectra for different TL peaks. In fact, with the band mechanism of the TL, the thermally released carriers are distributed more or less evenly among all available channels of recombination, therefore the spectra having the identical nature (electronic or hole or ionic ones) must be coincident. With the local mechanism, the radiation must reflect the definite nature of the defect.

Contrary to the previously investigated crystals [1 to 7] where for all series the correspondence between $\hbar\omega_{TL}$ and $\hbar\omega_{Ram}$ quanta (the first or sometimes second-order Raman lines or local Raman modes) was found, the corresponding $\hbar\omega_{Ram}$ was not detected in NaCl. Since the highest observed Raman modes are no more than about 540 cm^{-1} (the second-order Raman lines [22]), the only fundamental mode 162 cm^{-1} is IR-active [23], and in a simple lattice of NaCl it is impossible to separate out the quasimolecular complexes as in the other investigated crystals, thus the energy $\hbar\omega_{TL}$ = 0.112 eV must correspond to the local vibration caused by the certain defect.

It is possible that $\hbar\omega_{TL}$ in the case of NaCl corresponds to the local mode of one of the oxygen defects which are the main uncontrolled impurity in NaCl and have vibrational frequencies between 800 and 1000 cm^{-1}. The estimates based on existing data indicate that the most suitable frequencies may correspond to the complexes O_3^{2-} (about 910 cm^{-1}) or the bent O – Cl – O (about 915 cm^{-1}). Unfortunately, we have not found current investigations devoted to the study of the role of oxygen in the TL of NaCl crystals, but a recent study [24] dealt with the influence of oxygen centers on the TL of NaF crystals, where it was reported that oxygen centers (mostly $O^{2-}v_a^+$ complexes) can stabilize interstitial halogen atoms (H centres). This is important, in particular, for the ion model of Alvarez Rivaz *et al* [20,21].

While analyzing results on NaCl, we did not find any reason to reject 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 crystals (e.g., 32 in $CsCdCl_3$ or 27 in $Y_3Al_5O_{12}$) investigated earlier. Indeed it follows from the band model that between the stages of thermal release and recombination, the charge is in a free state for some time (here an electron in a polaron band) moving at considerable distances from the trap. In this case the influence of the recombination center on the energy trap parameters can be neglected, *i.e.,* each trap should be attributed to its "own" defect. It is therefore difficult to explain the availability of about 30 kinds of traps of considerable concentrations in undoped crystals, even considering primary defects and their aggregates.

The number of different activation energies in the case of NaCl is comparatively small — something exceeding 10. Taking into account a tendency of alkali halides to form primary defects and different aggregates of defects, the traditional band mechanism of the TL does not seem to be impossible. Both mechanisms may act together, *i.e.,* the activation energy is defined both by 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).

According to the accepted model the intensity of TL at tunneling of a charge carrier from the m^{th} vibration level is proportional to its population $n_m = n\,\exp\{-\hbar\omega(m + 1/2)/kT\}$, where n is the total concentration of full traps of a certain kind. Furthermore, the intensity is proportional to the probability of tunneling from this level and is determined by the penetrability of a potential barrier of a width l between the two potential pits, $D \sim \exp\{\alpha(l)\}$.

Compared to the m^{th} level, the $m - 1^{\text{th}}$ level has a larger barrier width but a higher population too. Therefore it is possible that the exponential decrease of the tunneling probability for the lower vibration levels is compensated by the exponential increase of their population. As a result, a thermal depopulation of a given center will be determined by more than one value of the activation energy. If this is the case then the TL curve is not described by a simple superposition of kinetically independent (with no re-trapping) mono-energetic TL peaks, because the depopulation channels have a common source which is a trap of a certain kind. This mechanism must be most characteristic of high-temperature TL peaks because more steep portions of parabolic curves correspond to a larger value of m and, consequently, to smaller values of the barrier width for the levels below. This may be the reason why we failed to expand the 470 K TL peak.

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 Table 1. But the occurrence of a trap with $E = 0.167$ eV argues for the one-dimensional model. Indeed, this activation energy corresponds to the emptying of a trap from the excited vibrational 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 rule (1), but are related to a multiple 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 occurrence of double energy values corresponding to the half-integer number of $\hbar\omega_{TL}$ ($n = 4, 11$, Table 3) at first sight, can be attributed to the exhibition of the three-dimensional oscillator with $n = 3, 10$. But the existence of two traps with equal activation energies $E = 1.118$ eV corresponding to the two-dimensional oscillator is in contradiction with the above assumption. It is likely that the existence of equal activation energies relating to different TL peaks may be caused by certain differences in the structure of traps which lead to different probabilities of charge tunneling.

4.4 Analyzing data of other published investigations.

Analyzing data of other published investigations, we have found many examples of the occurrence of the oscillator rule at the activation energy spectra. Thus in [25] the existence of four equidistant traps in AlN:O was pointed out. These values together with the author's two other values, and values estimated by us from the temperature positions of the peaks which were not investigated in [25] fit well into the oscillator rule with $\hbar\omega_{TL}$ = 0.057 eV and n = 1 − 12. To our knowledge, it is the only report about equidistant trap activation energies. Similar estimates of the data on activation energies in microcline [26] give the rule with $\hbar\omega_{TL}$ = 0.068 eV and n = 10, 14, 17, 19, 21, 22; in ZnS:Cu $\hbar\omega_{TL}$ = 0.076 eV, n = 3, 5 − 10; in CaS [27] $\hbar\omega_{TL}$ = 0.06 eV, n = 3, 5, 7, 12, 21. In LiF [28] the trap activation energies determined by the method of the heating rate variation can be described by the two-dimensional oscillator regularity with $\hbar\omega_{TL}$ = 0.159 eV and n = 6, 7, 9, 12. Other examples can be given.

4.5 On the nature of background.

The data concerning the background have appeared as a side effect of the energy trap calculations by the fractional glowing method. Despite the unregularity of these data, we can arrive at some conclusions about the background.

It appears that in the case of the background glowing, release occurs from all vibration levels of a trap, since the background intensity is proportional to the rest of the illumination; the carriers released in this way have to be of low mobility. As a working hypothesis, one can suggest that the contribution to the TL peak results from the recombination of thermally released electrons and holes, whereas the background is caused by the parallel tunneling process of the trap dissociation which produces interstitial (halide or oxygen) atoms; these atoms, as a consequence of their low mobility, cause slowly decaying glowing, hence the background is caused by the ionic component of recombination.

5 Conclusions

The experiments conducted have 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}). Taking into consideration our preceding results for several crystals, and independent data of other workers, we can conclude that the oscillator rule results from the strong electron-lattice interaction in crystals with mainly ionic bonds. This rule is not a unique feature of certain crystals but reflects a rather common property of them.

In NaCl we have obtained direct evidence (that is from the TL experiments but not the Raman lines symmetry analysis) of the one-dimensionality of the oscillator. It was also in the case of NaCl that we first observed the manifestation of the two-dimensional oscillator.

The mechanism of recombination that we have offered here, in our opinion, makes it possible to develop a new way of looking at the problem of the trap nature identification. It is well-known that doping often does not lead to the appearance of new TL-peaks but only changes the intensity of one or other existing peaks. According to our model, impurity can form several traps with activation energies fitted into the oscillator series. Moreover, if the impurities of substitution are of a different nature but occupy the equivalent sites without producing local vibrational modes, they can form series with either partially or totally coincident trap activation energies, although the temperature positions of corresponding TL peaks can differ considerably.

We would like to point out that the reported oscillator rule is a reliable experimental fact which we obtained for many crystals. However, we have no rigorous theory to support the findings presented here which are mainly experimental.

The oscillator rule at the trap energy spectra have been observed only in our investigations, if we do not take into consideration the report made in [25] where equidistance rule for some traps was observed in AlN:O but no proper conclusions were made. Since experimental data are not sufficient, we take a critical view of our conclusions. The only thing beyond question is that the rule (1) holds with high accuracy and is based on the polaron effect. The other conclusions are preliminary. We are interested in wide cooperation from other investigators to solve the problem and are ready to offer our software for data handling.

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Crystal	$\hbar\omega_{TL}, cm^{-1}$	$\hbar\omega_{Raman}, cm^{-1}$	n
$Ba_3NaNb_5O_{15}$	249	252	5–16, 20–23
$YAlO_3$	1048	—	1–16
	113	115	10–14
$CsCdCl_3$	250	248	12–20, 22–29, 31–33, 35–37, 39–42
	494	495	6–13
$CdWO_4$	516	521	6–11
	554	554	3,4,7–10
	550	545	3–12
$ZnWO_4$	581	578	5,6,10
	628	631	5–7,9
	782	786	1–3,6,8,11
	901	912	3–5,8
$Y_3Al_5O_{12}$	968	982	1–7
	1274	1309	6–10
	1347	1382	5–9

Table 1 Data on some crystals which were investigated. $\hbar\omega_{Raman}$ indicated by $^{II)}$ are the second-order Raman lines, those indicated by $^{L)}$ are additional, n are the vibrational numbers for investigated traps.

	$ZnWO_4$							$CdWO_4$					
	series 1		series 2		series 3			series 1		series 2		series 3	
n	E_a^{clc}	E_a^{exp}	E_a^{clc}	E_a^{exp}	E_a^{clc}	E_a^{exp}	n	E_a^{clc}	E_a^{exp}	E_a^{clc}	E_a^{exp}	E_a^{clc}	E_a^{exp}
3	0.239	—	0.252	—	0.272	0.270	3	0.215	—	0.224	—	0.241	0.242
4	0.307	0.305	0.324	—	0.350	0.355	4	0.276	—	0.288	—	0.309	0.308
5	0.375	0.377	0.396	0.394	0.428	0.428	5	0.337	—	0.352	—	0.378	—
6	0.443	0.441	0.467	0.469	0.506	0.507	6	0.399	0.398	0.416	0.415	0.447	—
7	0.512	0.507	0.539	—	0.584	0.583	7	0.460	0.459	0.480	0.481	0.515	0.517
8	0.580	0.583	0.611	—	0.661	—	8	0.521	0.521	0.544	0.542	0.584	0.582
9	0.648	0.646	0.683	—	0.739	0.738	9	0.583	0.584	0.607	0.609	0.653	0.652
10	0.716	0.713	0.755	0.752	0.817	0.810	10	0.644	0.643	0.671	0.671	0.722	0.721
11	0.784	0.791	0.827	—	0.894	—	11	0.705	0.707	0.735	0.735	0.790	—
12	0.853	0.860	0.899	—	0.972	—	12	0.762	0.767	0.799	—	0.859	—
13	0.921	—	0.971	—	1.050	—	13	0.834	0.828	0.863	—	0.928	—
$\hbar\omega$	0.0682		0.0720		0.0778		$\hbar\omega$	0.0613		0.0639		0.0687	

Table 2 Activation energies (E_a, eV) determined for $ZnWO_4$ and $CdWO_4$: E_a^{clc} from equation $E_a = \hbar\omega(n + 1/2)$; E_a^{exp} by fractional glowing method or by total glow peak method.

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

Table 3 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.

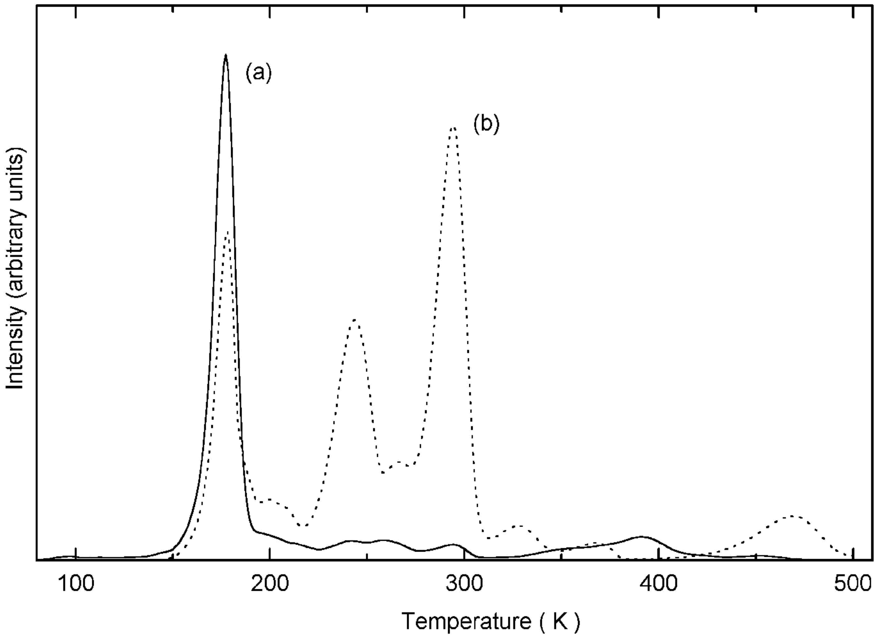

Fig. 1 Review thermoluminescence spectra of NaCl: (a) specimen No.2 (as-grown); (b) specimen No.1 (quenched).

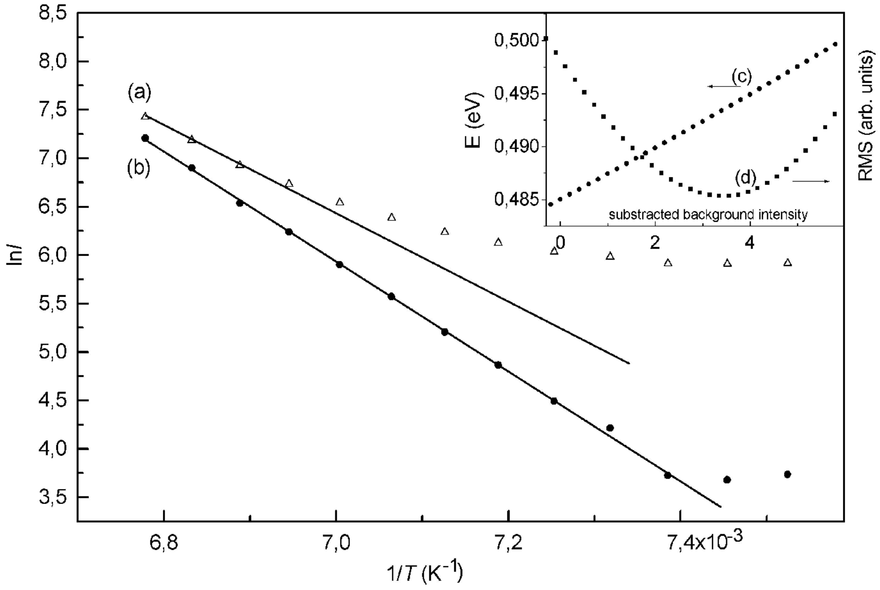

Fig. 2 An example of the background subtraction for the 176 K TL peak): (a) △ the initial $1/T$-dependence of $\ln I$ (with the background); (b) the same dependence after subtraction the background value which corresponds to the RMS minimum. On the insert: plots of the energy determined from the above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

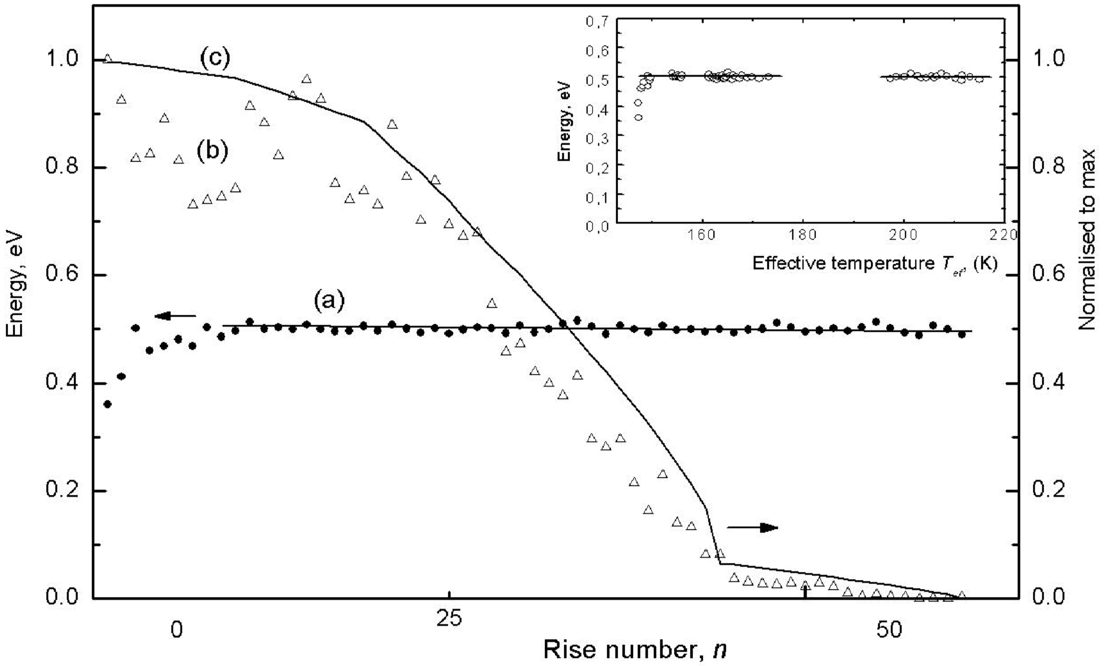

Fig. 3 Data on the fractional glowing of the 176 and 210 K TL peaks (as-grown specimen No.2). n is an ordinal number of the initial rise. The trap activation energy is determined from the shelf (line (a)) on the presented dependence; (b) △ the relative value of the subtracted background; (c) the rest of lightsum after each glowing cycle. On the insert: the dependence similat to (a) as a funcion of T_{ef}.

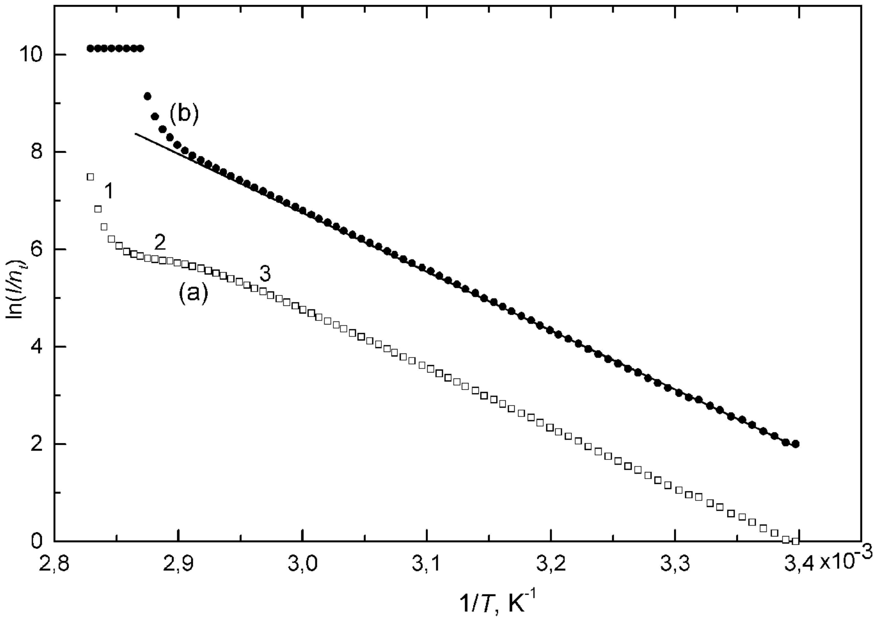

Fig. 4 The $1/T$-dependence of $\ln(I/n_\mathrm{t})$ for the 332 K TL peak: (a) an initial curve without exclusion of a next TL peak influence; (b) the above dependence after exclusion of a some high-temperature points and correction of a lightsum (●) and corrected straight line (—) from which the activation energy was determined. Specimen No.2, quenched.

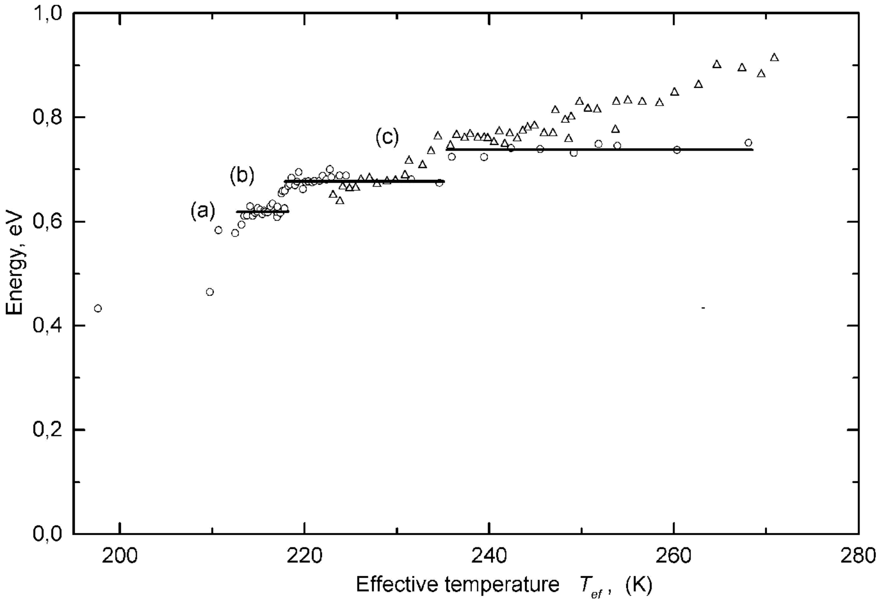

Fig. 5 Data on the fractional glowing in the range of 200–270 K: (○) – fractional energies versus the effective temperature T_{ef} for as-grown specimens from the crystal No.1; (△) – the same for No.2.

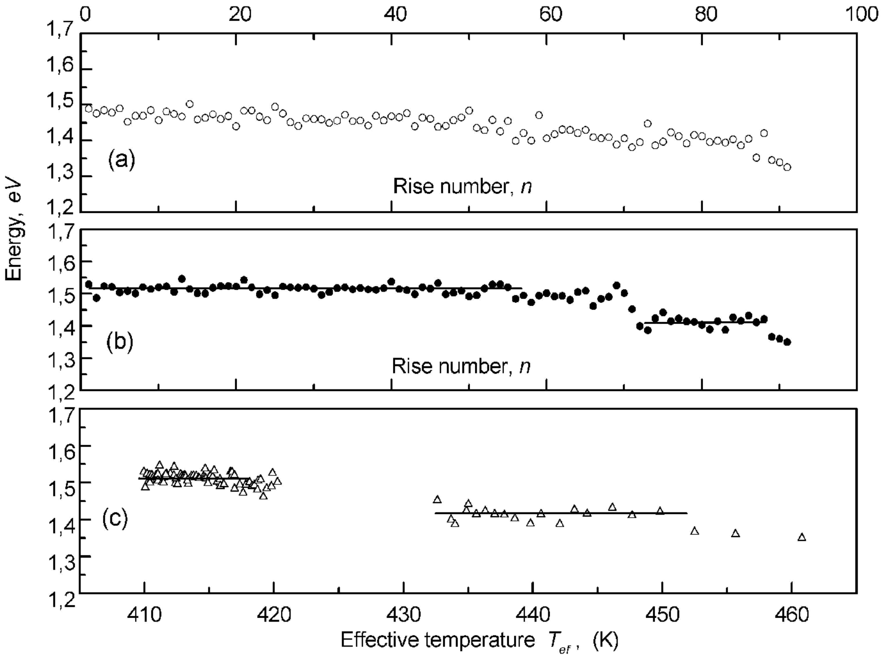

Fig. 6 Data on the fractional glowing of the nonelementary 474 K TL peak for as-grown specimen No.2: (a) fractional energies versus the initial rise number (with the background); (b) the same dependence after the background subtraction; (c) the same versus the effective temperature.

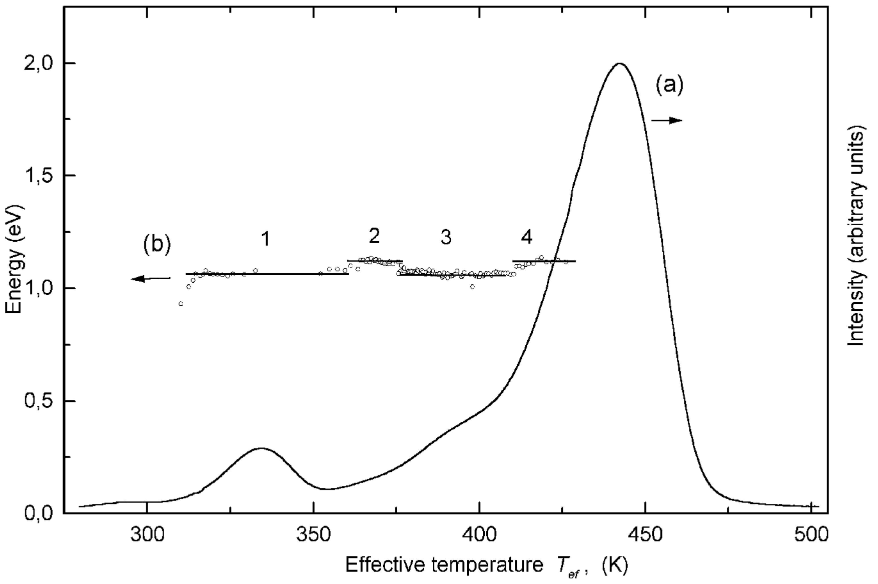

Fig. 7 (a) The TL peaks in the temperature range from 300 to 500 K; (b) data on the fractional glowing of these peaks. Specimen No.2, as-grown.