

A method for analysis of complex thermoluminescence peaks: 141 K peak in LiF as an example

A.F.Gumenjuk, S.Yu.Kutovyi

Physics Faculty, T.Shevchenko Kyiv National University,
2 Acad. Glushkov Ave., 03022 Kyiv, Ukraine

Undoped LiF crystals have been studied by thermoluminescence (TL) methods in the temperature range of 80 to 200 K. A method for analysis of complex thermoluminescence peaks has been proposed taking the broad 141 K TL peak as an example. The method enables to establish the cause of the peak broadening, that is, to establish if the peak is elementary one (emitted according to quadratic kinetics) or a complex peak formed by several closely positioned elementary peaks forming a common maximum. The 141 K TL peak has been shown to consist of several simple peaks. The low-temperature component results from superposition of two or more peaks while the high-temperature one is an elementary peak ($T_{max} = 145$ K) with linear decay kinetics. On the high temperature shoulder of this peak, a low intensity peak with a maximum at about 160 K is present. The trap activation energies are determined for the 141 K peak taking its structure into account.

Нелегированные кристаллы LiF исследованы методом термолюминесценции (ТЛ) в температурном интервале 80–200 К. На примере исследования широкого пика 141 К предложен метод анализа сложных пиков ТЛ, который позволяет установить причину уширения пика, т.е., определить, является ли он элементарным пиком, высвечивающимся по квадратичной кинетике, или же состоит из нескольких близко расположенных элементарных пиков, образующих один совместный максимум. Показано, что пик ТЛ 141 К образован совокупностью нескольких элементарных пиков. Низкотемпературная составляющая пика 141 К является суперпозицией двух или более пиков, а высокотемпературная составляющая представляет собой элементарный пик ($T_{max} = 145$ К), который высвечивается по линейной кинетике. На высокотемпературном крыле этого пика находится еще один пик низкой интенсивности ($T_{max} \sim 160$ К). Определены энергии активации ловушек, образующих пик ТЛ 141 К с учетом его структуры.

Numerous methods are used to determine trap parameters from thermoluminescence (TL) curves [1–3], but all of them are applicable only to isolated or slightly overlapped TL peaks. In practice, strongly overlapped peaks that form a single maximum are often observed. The large halfwidth of such a peak provokes sometimes the conclusion that the peak decay is characterized by second order kinetics, since the considerable retrapping probability increases the peak width as compared to the linear kinetics case. Here, we propose a simple test permitting to establish the cause of the peak broadening, that is, to establish if the peak

is an elementary one decaying by second order kinetics or the peak is complex one formed by several close elementary peaks forming a single common maximum.

As the study object, a LiF crystal was chosen, where an intense TL peak with a maximum at 141 K is observed (Fig. 1). The peak has a large halfwidth ($\delta = 16$ K) and is associated usually with the thermal release of self-trapped holes (V_k centers) [4]. LiF doped with Mg and Ti (TLD-100) is used in the thermoluminescence dosimetry, and there are many works aimed at the LiF thermoluminescence properties. But almost all of them deal with high-temperature TL

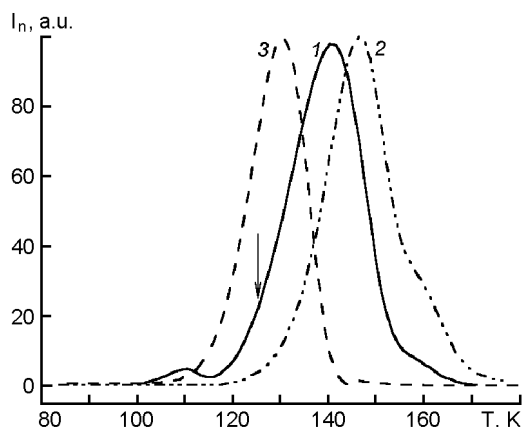


Fig. 1. Low-temperature TL curves of LiF. 1, initial sample No.1; 2, the sample preliminary heated to 148 K; 3, sample No.2 after γ -irradiation.

($T > 300$ K) and only few works are devoted to study of the low-temperature TL of LiF ($T < 300$ K) [4–10]. Another problem being solved in this work was to determine the activation energies of the traps forming the 141 K peak, taking into account the peak structure.

The TL experiments were carried out in the temperature range between 80 and 200 K. The constant heating rate ($0.2 \text{ K/s} \pm 5\%$) was regulated by a computer program. The samples of about $0.5 \times 8 \times 8 \text{ mm}^3$ size placed in a vacuum cryostat were irradiated with X-rays ($U = 50 \text{ kV}$, $I = 12 \text{ mA}$) through a 0.5 mm thick beryllium window. Between the X-ray irradiation and the following TL measurements, the samples were not removed from the cryostat. The TL was recorded through a quartz window of the cryostat. The samples were split off from undoped LiF crystals grown for optical usage (optical windows) and for investigations. The samples differ in uncontrolled impurities concentrations; no detailed analysis of impurity content was performed. Sample No.2 was irradiated preliminary by γ - Co^{60} at room temperature, it has a dark cherry color. We did not use dosimetric material LiF:Mg:Ti (TLD-100), because we found on many examples that at considerable dopant concentrations (10^{17} – 10^{18} cm^{-3}) the trap activation energy spectrum is not discrete, that is with increasing of dopant concentrations the TL peaks broaden and single levels smear into bands.

The trap activation energies were determined using the fractional TL method. The essence of the method variation used here

consists in registration of initial TL curve section for a singly-excited sample under slow heating followed by rapid cooling back to the initial temperature. After recording of the data, the sample was heated again with the TL intensity registration and so forth. The cycles of heating and cooling were repeated up to the total decay of one or several closely located TL peaks. To attain about the same maximal intensities of initial slopes, the sample was heated up in each next cycle to a temperature something higher than in previous one. The advantage of this method is the opportunity to obtain for certain intense peaks more than a hundred of uniform data, that substantially improves the determination accuracy of the trap activation energies. Besides, dividing the energy determination into stages of fractional curve registration and the corresponding energy calculation therefrom provides a thorough mathematical processing of experimental data. All this makes it possible to determine the trap activation energy to within the root-mean-square (RMS) of 1 to 4 meV.

The computerized data processing program includes a sequence of procedures, some of those are briefly described in [11]. Here, we mention only the background subtraction. The procedure was developed specially for the analysis of the 176 K TL peak in NaCl [11], where the "intrinsic" TL curve is followed by a relatively intense emission of the tunnel origin, which decays slowly. In LiF, a background accompanies the 141 K TL peak emission. At recording of the overview TL curve (Fig. 1), the background is barely noticeable. Since the recording of fractional curves is carried out at the measuring apparatus sensibility increased by a factor of 10 to 100, the background increases respectively. Immediately ($\Delta t < 5 \text{ s}$) after the sample cooling to the initial temperature, the background intensity may attain 30 % of the fractional curve maximal intensity. The fast component of the background was eliminated by conditioning of samples at 80 K for $t \geq 2 \text{ min}$ before the next fractional heating. The slow background component was excluded by this procedure in assumption of its constancy for the whole initial rise. The data obtained from the initial rises were processed using another program which permitted to gain the fractional energy dependences vs. the serial number of the initial rise, n . The trap activation energy was determined if the above dependences exhibit a plateau. An op-

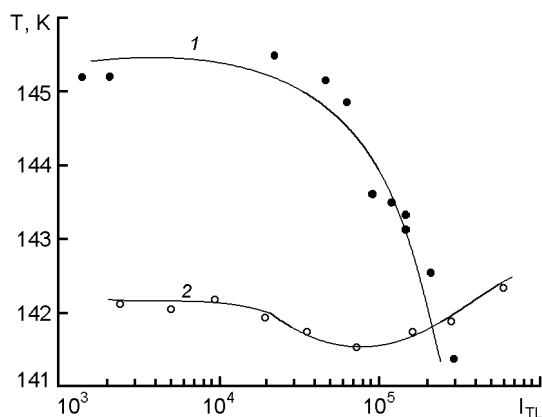


Fig. 2. Dependence of the main peak T_m on the light sum: 1 — variation of the excitation time; 2 — partial annealing.

portunity to obtain several tens of uniform values of fractional energies improves substantially the determination accuracy of the trap activation energy.

The low-temperature part of the TL-curve LiF is plotted in Fig. 1. Curve 1 with a maximum at $T_m = 141$ K corresponds to the as-grown sample No.1, curve 2 ($T_m = 146$ K) is obtained after preliminary heating of the excited sample to 148 K, followed by rapid cooling back to 80 K. Curve 3 ($T_m = 130$ K) corresponds to the sample No.2 which was irradiated by γ -Co⁶⁰ at room temperature prior to X-ray excitation.

The dependence of the main TL peak maximum position on the sample preliminary treating method and its large halfwidth ($\delta = 16$ K) may be due to two different causes: (1) the TL peak is not elementary, that is, it consists of two or more simple peaks; 2) the appreciable retrapping probability of released carriers resulting in a delayed TL process. The asymmetry parameter $\mu = (T_2 - T_m)/(T_2 - T_1)$ (T_1, T_2 are the temperatures at the half-height of the peak at its low- and high-temperature sides, respectively) lies within limits of 0.42 to 0.43, depending on the sample and the excitation conditions, that is close to the value $\mu = 0.42$ characteristic for the first-order kinetics [1].

To elucidate the cause of the peak broadening, we applied a simple test which consists in study of dependences of the peak maximum location and its halfwidth as functions of the light sum which changed in two manners: (1) by varying of the excitation time; (2) by heating of the sample excited in standard conditions ($T_{exc} = 80$ K,

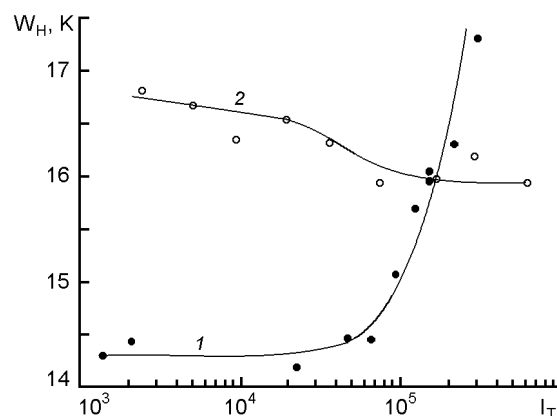


Fig. 3. Dependence of the 141 K TL peak halfwidth on the light sum: 1 — variation of the excitation time; 2 — partial cleaning.

$\tau_{exc} = 12$ min) up to different intermediate temperatures, followed by rapid cooling back to the initial excitation temperature and subsequent registration of the rest TL peak. If the peak is a simple one, then both manners of the light sum changing must give identical results independently of the kinetics order, but in the case of a complex peak, the corresponding dependences must be different. In fact, if the peak is complex and the concentration of the filled traps changes by the preliminary partial heating (annealing), then the traps related to the low-temperature peak are mostly emptied. Therefore, as the total peak intensity decreases, the peak maximum must shift itself towards higher temperatures, and its halfwidth must decrease. At variation of the excitation time, these parameters may change in both directions, depending on the relations between the filling rates of different types of traps during the excitation.

Results of this study for the sample No.1 are presented in Figs. 2 and 3. It follows from these data that the 141 K TL peak consists of several close elementary (simple) peaks. As the light sum decreases due to heating up to an intermediate temperature (Figs. 2, 3, curves 1), parameters T_m and δ change fast at first and after the light sum becomes decreased by a factor of about 10, are flattened out. Independence of the T_m position of the light sum points that the high-temperature component of the peak is an elementary one ($T_m = 145$ K and $\delta = 14$ K) which decays according to linear kinetics. This peak obtained by partial annealing (preliminary heating to 148 K) is presented in Fig. 1 (curve 2). On a high temperature

shoulder of the peak, there is a low-intensity peak with a maximum at about 160 K is; it always follows the main 141 K TL peak [4–10].

It turned out that the concentration of the filled traps corresponding to the total 141 K peak depends strictly linearly on the irradiation time (the straight line slope is $(\Delta \ln n)/(\Delta \ln t_{exp}) = 1.02$), within the range of used irradiation times ($t_{exp} = 16$ to 3600 s). The linearity of the dose dependence is indicative of the absence of saturation in the traps occupation. At the same time, the curve 2 in Fig. 3 indicates some decreasing of the total peak halfwidth with increasing irradiation time. Such behavior can be explained by decreasing of the traps filling rate for the 145 K peak with increasing of the irradiation dose. Considering also the linearity of the dose dependence for the total peak, it can be concluded that for the residual peak at 145 K, the saturation of the traps occupation occurs and, at the same time, the absence of saturation for the low-temperature component. The linear dose dependence evidences a high concentration of corresponding traps which are obviously caused by intrinsic defects created during the irradiation (in this case, the self-trapped holes [4]). The saturation for the high temperature component (145 K), on the contrary, indicates a limited concentration of corresponding traps, so those can be attributed to extrinsic defects.

Let us analyze the peculiarities of the 141 K peak halfwidth behavior at partial annealing assuming that the peak consists of two simple peaks only, these peaks decaying according to first order kinetics and being characterized by discrete trap energies. Without partial annealing, the TL peak halfwidth is defined by its intense low-temperature component. If the partial annealing is performed up to the temperature when the main contribution to the peak intensity is due to the high-temperature component, then it is just that component that defines the peak halfwidth. In the intermediate case, when about the same amounts of non-equilibrium charges remain in both types of traps, the both peak components contribute approximately equally to the total halfwidth, therefore, naturally, it must be the largest, if the components are slightly separated in temperature. In experiment (Fig. 3, curve 2), with increasing annealing temperature, a monotonous decrease followed by stabilization of the total peak halfwidth is observed only. Such be-

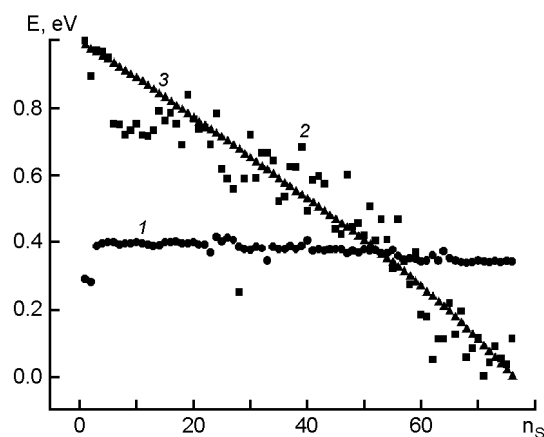


Fig. 4. The initial fractional curve dependences of the 141 K TL peak: 1 — initial fractional curve energy; 2 — background; 3 — light sum.

havior allows to admit that the low-temperature component is a superposition of two or more very close peaks. It is not impossible that a continuous distribution of the traps in energies and/or frequency factors is realized here.

In Fig. 4, the data on the preliminary fractional decay of the 141 K TL peak for the sample No.1 are presented. The plot 4(2) in Fig. 4 shows the energy dependence vs. the ordinal number of the initial fractional curve n ($n = 1$ to 76). This dependence is anomalous in the sense that as of the initial fractional curve number increases, the energy does not increase as it would be expected considering the complex peak structure but, on the contrary, decreases monotonously from 0.40 eV to 0.34 eV. As mentioned above, the 141 K peak is observed against a tunnel emission background; the slow component of this emission was excluded by the program procedure under assumption of its constancy for all the initial fractional curves, while its fast component was eliminated by conditioning the samples at 80 K for $t = 2$ min before the next fractional heating. At this conditioning time, the relative decrease of the background intensity during the registration of the initial fractional curve (~1 min) did not exceed 3 %. The background value normalized to unity is presented in Fig. 4, plot 2. Therein, the plot (line) 3 represents the light sum relative change after the registration of a next initial fractional curve. A good correlation between these two dependencies is worth to note.

The experiment described above has occurred too continuous and so it was not

performed to the complete glowing of the 141 K peak. The maximum temperature attained at the last initial rise registration ($n = 76$) was 126 K only (an arrow in Fig. 1). The purpose of a next experiment was to determine the boundary activation energies for this complicated peak. The excitation time was increased three times and the device sensitivity ten times. The calculation results are presented in Fig. 5, plot 1. The energies determined from 50 initial rises fit the plateau with value $E = 0.404 \pm 0.001$ eV. Then the sample was heated to 145 K without registration of the glowing intensity and cooled rapidly. The rest of light sum was glowed in 5 cycles, the energy of the high temperature component (145 K) of the complicated peak determined from these initial rises was $E = 0.323 \pm 0.004$ eV, Fig. 5, plot 1. Besides the program manner the background can be excluded by conditioning of the sample at 80 K for a long time after next initial rise recording. After conditioning over one hour the background value did not exceed 0.2 % of the maximum intensity of an initial rise. The energies calculated considering the rest background has occurred considerably large: $E = 0.48$ eV, Fig. 5, plot 2.

The low intensity 113 K peak is situated at the low-temperature shoulder of the main 141 K peak, therefore, the trap activation energy determined by the initial rise method must be overvalued. In Fig. 5, plot 1, the emission of the 113 K peak is indicated by two first points with the energy ~ 0.29 eV. At especially selected experiment conditions (a short experiment duration and a high device sensitivity), the obtained trap energy values increased monotonously within the range of 0.25 to 0.4 eV. So the energy of the 133 K peak can be estimated as $E < 0.25$ eV. The intensity of the 160 K TL peak occurred too small so we could not determine the corresponding trap energy.

The existence of background accompanying the low-temperature TL in LiF is obviously caused by a low mobility of holes released from the V_k centers and simultaneously by the possibility of the V_k centers to do thermoactivated jumps at low (~ 80 K) temperatures through the rotation of the F_2^- molecule. At registration of the next initial fractional curve, only a fraction of holes released from V_k centers attains the recombination centers due to the insignificant mobility thereof. Another fraction of holes after moving from their antecedent positions does not recombine and is frozen

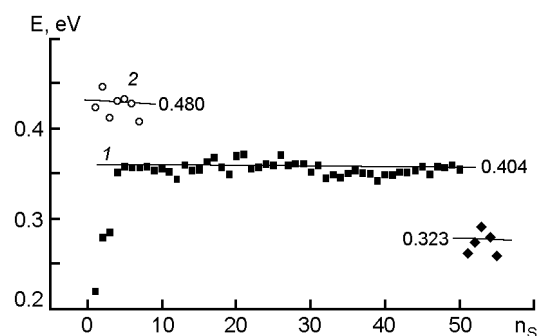


Fig. 5. Determination of energies of the 141 K TL peak. Conditioning before registration: 1 — 2 min; 2 — 60 min.

after the sample cooling. A fraction of these displaced holes is caught up near to the recombination centers and has opportunity to recombine with those after one or a few thermoactivated rotation jumps or by tunneling immediately into an excited state of the luminescence center. The number of holes released in a fractional cycle is proportional to the number of filled traps what provides the correlation between the subtracted background intensity and the rest of light sum.

The regularities in the energy spectra of traps forming the 141 K TL peak correlate, as a whole, with the above conclusions. The activation energy of the 141 K peak was determined in [10]. The energy determined by the total curve fitting method is $E_1 = 0.234$ eV, what is considerable less of the value obtained by us. This is caused obviously by taking no account for the complex structure (shape) of the peak and the intense background. The energy determined by the initial fractional curve method has occurred, to the contrary, too large: $E_2 = 0.428$ eV. A value similar to that can be obtained if the sample is conditioned for a long time ($t > 0.5$ h) before the next fractional heating and the background is not compensated. The cause of the energy value increasing for the 141 K peak from 0.404 eV to 0.480 eV after durable isothermal decay remains unknown. In the subsequent special studies, we shall try to elucidate the mechanism of the energy increasing.

So, when studying the broad 141 K TL peak, it has been found that the peak consists of several close simple peaks. The low-temperature component is a superposition of two or more very close peaks. The high-temperature component of the peak is elementary one ($T_m = 145$ K) which decays according to linear kinetics. At the high-tem-

perature shoulder of this peak, a low intensity peak with a maximum at ~160 K is disposed; it always follows the main 141 K TL peak. The trap activation energies were also determined for the 141 K peak taking into consideration its structure. The corresponding traps can be characterized by activation energies 0.48, 0.40 eV (the low-temperature components) and 0.32 eV (the high-temperature component). As a whole, a method has been proposed to analyze complex thermoluminescence peaks taking the 141 K TL peak as an example. The method makes it possible to establish the cause of the peak broadening, that is, to establish if the peak is elementary one decaying according to the second order kinetics or it is a complex one formed by several close elementary peaks forming a single common maximum.

References

1. G.F.J.Garlick, A.F.Gibson, *Proc. Phys. Soc.*, **60**, 574 (1948).
2. R.Chen, *Thermolum. Dosim.*, **1**, 49 (1984).
3. R.Chen, Y.Kirsh, *Analysis of Thermally Stimulated Process*, Pergamon Press, Oxford (1981).
4. E.B.Podgorsak, P.R.Moran, J.R.Cameron, *J. Appl. Phys.*, **42**, 2761 (1971).
5. P.D.Townsend, C.D.Clark, P.W.Levy, *Phys. Rev.*, **155**, 909 (1966).
6. J.L.Merz, P.S.Pershan, *Phys. Rev.*, **162**, 217 (1967).
7. D.W.Cooke, *J. Appl. Phys.*, **49**, 4206 (1978).
8. D.W.Cooke, J.F.Rhodes, *J. Appl. Phys.*, **52**, 4244 (1981).
9. V.K.Jain, *J. Phys. D:Appl. Phys.*, **19**, 1791 (1986).
10. V.K.Jain, M.S.Jahan, *Phys. Stat. Sol. (a)*, **102**, 725 (1987).
11. A.F.Gumenjuk, S.Yu.Kutovyi, *Centr. Europ. J. Phys.*, **1**, 307 (2003).

Метод аналізу складних піків термолюмінесценції на прикладі піка 141 К в LiF

А.Ф.Гуменюк, С.Ю.Кутовий

Нелеговані кристали LiF досліджено методами термолюмінесценції (ТЛ) в інтервалі температур 80–200 К. На прикладі дослідження широкого піка 141 К запропоновано метод аналізу складних піків ТЛ, який дозволяє встановити причину уширення піка, тобто встановити, чи це є елементарний пік, який висвічується за квадратичною кінетикою, чи він складається із декількох близько розміщених елементарних піків, які утворюють один спільний максимум. Показано, що пік ТЛ 141 К утворено накладанням декількох близьких елементарних піків. Низькотемпературна компонента піка 141 К є суперпозицією двох чи більше піків, а високотемпературна компонента являє собою елементарний пік ($T_{max} = 145$ К), який висвічується за лінійною кінетикою, на високотемпературному крилі якого знаходиться ще один малоінтенсивний пік ТЛ ($T_{max} \sim 160$ К). Визначено енергії термічної активації пасток, які створюють пік ТЛ 141 К з урахуванням його структури.