OPTICS. QUANTUM ELECTRONICS. HOLOGRAPHY

THERMOLUMINESCENCE STUDIES OF UNDOPED LiF CRYSTALS. 1. THE METHOD OF ANALYSIS OF COMPLICATED THERMOLUMINESCENCE PEAKS

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Undoped LiF crystals have been investigated by the methods of thermoluminescence (TL) in the temperature range of 80–200 K. A method of analysis of complicated TL peaks, which allows one to establish the cause of a peak broadening, i.e. to find whether the peak is an elementary one glowing in accordance with the second-order kinetics or a compound one formed by several closely situated elementary peaks, has been proposed. The method consists in studying the regularities of the peak maximum position and the peak half-width both considered as functions of the lightsum, which is modified in two manners, namely, by varying the excitation time and by heating the specimen excited at 80 K, to different intermediate temperatures, followed by its rapid cooling back to the initial excitation temperature and the registration of the residual TL peak. For a simple peak, both the ways must give identical results independently of the kinetics order. In the case of a compound peak, the corresponding dependences must be different. To illustrate the method, a broad TL peak at 141 K has been shown to be compound. Its low-temperature component is a superposition of two or more peaks, and the high-temperature one is an elementary peak that glows in accordance with a linear kinetics. The energies of thermal trap activation, which are responsible for the peak at 141 K, have been determined as well. The relevant traps can be characterized by three activation energy values: 0.48, 0.40 (the low-temperature components), and 0.32 eV (the high-temperature one).

1. Introduction

There are quite a few methods to determine the trap parameters from those of the TL curves [1–3], but all of them are applicable only to isolated or slightly overlapped TL peaks. In practice, we are often faced with substantially overlapped peaks merged into a single general maximum. A considerable width of such a peak sometimes provokes the researchers to deduce that it glows in accordance with the second-order kinetics, because a significant probability of retrapping induces the enhanced peak width, as compared with the case where the process runs in accordance with a linear kinetics. Here, we propose a simple test which allows the origin of TL-peak broadening to be established, i.e. to reveal whether it is really an elementary peak which glows in accordance with the second-order kinetics or is composed of several closely situated elementary peaks, which simulate a single general maximum.

LiF crystals, where an intensive TL peak with a maximum at 141 K (Fig. 1) is observed, were chosen

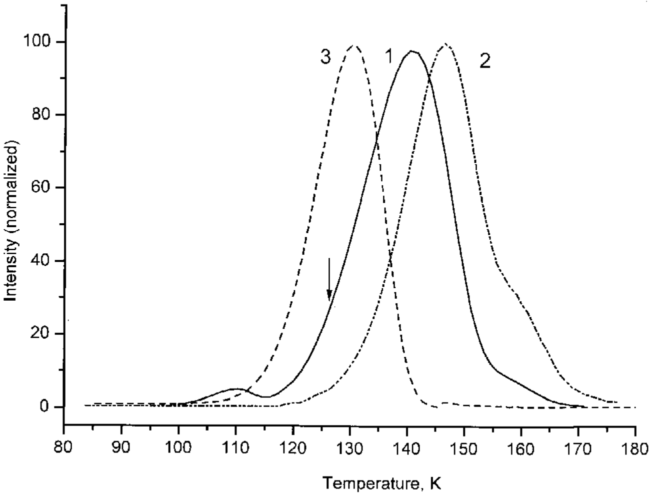

Fig. 1. Low-temperature thermoluminescence (TL) curves for LiF: initial specimen N 1 (*1*), the specimen preliminarily heated to 148 K (*2*), and specimen N 2 after γ-irradiation (*3*)

as objects of inquiry. This peak is characterized by a significant half-width $\delta = 16$ K and is assumed to be connected to the thermal release of self-trapped holes (V_k centers) [4]. LiF doped with Mg and Ti (TLD-100) is used in TL dosimetry, and a lot of works are devoted to the researches of its thermoluminescent properties. However, practically, all of them concern high-temperature TL($T > 300$ K), with low-temperature one ($T < 300$ K) being studied in few works [4–10]. Another problem that was resolved in the present work is the determination of the energies of thermal trap activation, which are responsible for the peak at 141 K, taking into account the structure of the latter.

2. Experimental Techniques and Data Handling

2.1. Equipment and specimens

The TL researches of LiF crystals were carried out in the temperature interval of 80—200 K. The rate of specimen heating was 0.2 K/s and was maintained by a computer program in the range of ±5%. Specimens $0.5 \times 8 \times 8$ mm^3 in size were placed into a vacuum cryostat and were excited by X-ray irradiation ($U = 50$ kV, $I = 12$ mA) through a small 0.5-mm-thick beryllium window. Specimens were cleaved off from the specially undoped LiF crystals grown for optical applications (optical windows) and scientific researches. Specimen No.2 was preliminarily irradiated with the help of a γ-Co^{60} source at room temperature. We did not use dosimetric-grade material Li:Mg:Ti (TLD-100), because we had been convinced by many examples that the trap energies cease to be discrete at a significant concentration of impurities ($10^{17} - 10^{18}$ cm^{-3}).

2.2. Calculation of energies from fractional-TL curves

The energies of trap activation were determined by the initial rise method. The essence of the variant of this method, which was applied by us, is that, after the registration of the initial section of the TL curve, the specimen was quickly cooled down to the initial temperature. After recording the obtained data into a file, the specimen was heated up again, the TL signal was registered once more, and the cycle was repeated iteratively. In order to provide approximately the identical maximal intensities of fractional curves, the specimen was heated up in each following cycle to a temperature that was somewhat higher than that in the previous cycle. The advantage of the initial rise method lies in the fact that it allows one to obtain dozens of uniform results, which essentially raises the ultimate accuracy of the trap energy values. Moreover, separating the registration stage from the mathematical handling of experimental data in time allows one to carry out the latter rather thoroughly. All this makes it possible to determine the trap energies with a standard deviation (SD) of 1—4 meV.

A specially developed computer program of data handling provides a number of procedures, which were described in our work [11]. Here, we mention only the background exclusion procedure initially created for the analysis of the TL peak at 176 K in NaCl [11]. This peak is accompanied by a rather intensive glowing of the tunnel origin which eventually slowly fades. In LiF, the tunnel background accompanies the glowing of the TL peak at 141 K. When the review TL curve is being recorded (Fig. 1), it is practically imperceptible. The registration of the fractional curves was carried out at a higher sensitivity of the recording equipment (by 1—2 orders of magnitude), which caused an increase of the background intensity with respect to the maximal intensity value of the fractional curve. Immediately after the cooling of the specimen ($\Delta t < 5$ s), the background intensity can reach the 30%-level of the fractional curve maximum. The fast component of the background was eliminated by holding the specimen at a temperature of 80 K for $t \geq 2$ min, and the slow one was excluded through the procedure described above. Then, using the results obtained from the analysis of the fractional curves and with the help of another computer program, the dependence of the fractional energy on the ordinal number of the curve was plotted. The trap activation energy was determined as the value of the plateau on the plot. An opportunity to obtain dozens of uniform values for the fractional energy allows it to be determined with rather a small SD (1—4 meV).

3. Results and Their Discussion

3.1. Research of the 141-K peak TL kinetics

In Fig. 1, the low-temperature parts of the LiF-TL curves are shown. Curve *1* with a maximum at $T_m = 141$ K corresponds to the initial specimen No. 1. Curve *2* with $T_m = 146$ K was obtained after a preliminary heating of the excited specimen up to 148 K, followed by a fast cooling down to 80 K. Curve *3* with $T_m = 130$ K corresponds to specimen No. 2 which was irradiated by γ-Co^{60} at room temperature before X-ray excitation.

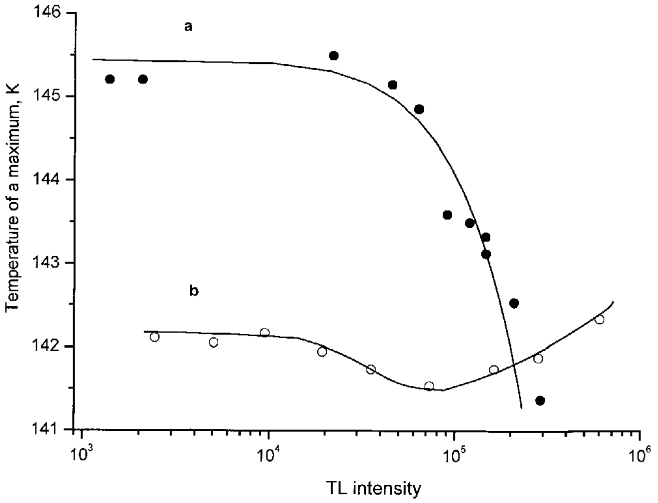

Fig. 2. Dependences of the temperature of the maximum of the main TL peak on the lightsum obtained by varying the excitation time (a) and by partial cleaning (b)

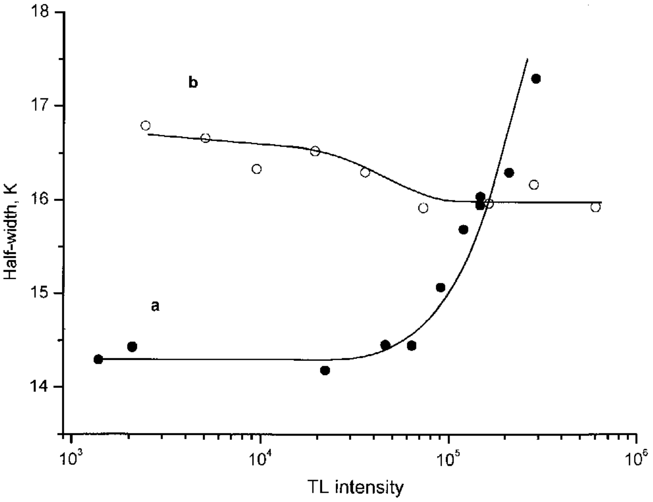

Fig. 3. The same as in Fig. 2, but for the width of the TL peak at 141 K

The dependence of the position of the main TL peak maximum on the manner of a preliminary treatment of the specimen and a significant half-width of the peak (δ = 16 K) can be caused by two different reasons: (i) the TL peak is nonelementary, i.e. it consists of two or more elementary peaks and (ii) there is a significant probability for the released carriers to be retrapped, which leads to a retardation of the TL process. The peak asymmetry parameter $\mu = (T_2 - T_m)/(T_2 - T_1)$, where T_1 and T_2 are the temperatures that correspond to the intensity equal to the half-maximum of the peak on its low- and high-temperature sides, respectively, varies in the range of 0.42–0.43, depending on the specimen and the excitation conditions, i.e. it is close to the value $\mu = 0.42$ which is characteristic of a linear kinetics of TL [1].

To elucidate the mechanism of broadening for this peak, we applied a simple test which consists in analyzing the peak maximum position and the peak width as functions of the lightsum which was varied in two ways: (i) by varying the excitation time and (ii) by heating the specimen excited at 80 K to different intermediate temperatures with the following fast cooling to the temperature of excitation and the further registration of the residual peak.

If the TL peak is elementary, both ways should yield identical results irrespective of the kinetics type. But, in the case of the compound peak, the corresponding dependences must differ. Really, if the peak is not elementary and the concentration of the trapped carriers is changed by a preliminary partial heating (annealing), then those traps are mainly emptied, which are connected to the low-temperature peak. Therefore, with a reduction of the general-peak intensity, its maximum position has to shift towards higher temperatures and its width has to decrease. If the excitation time is varied, these parameters can change in both directions, depending on a relation between the filling rates for the traps of different kinds during the excitation.

The results of these researches for sample No. 1 are depicted in Figs. 2 and 3, from which it follows that the TL peak at 141 K is composed by several neighbor overlapped elementary peaks. At the lightsum reduction due to the heating of the specimen to the intermediate temperature (Figs. 2 and 3, curves a), the parameters T_m and δ quickly change firstly and then, after the almost 10-fold reduction of the lightsum, reach their saturation levels. The lightsum-independent temperature position of the maximum means that the high-temperature component consists of an elementary peak (T_m = 145 K, δ = 14 K) which glows according to a linear kinetics. This peak obtained by the previous heating of the specimen up to 148 K is presented in Fig. 1 by curve *2*. On its high-temperature side, there is a TL peak of low-intensity with a maximum at about 160 K which permanently accompanies the dominant peak at 141 K [4–10].

The concentration of the filled traps, which are responsible for the resulting TL peak at 141 K, turned out to depend strictly linearly on the exposure time within the limits of the applied exposure intervals t_{ex} = 16 − 3600 s (the slope of the straight line

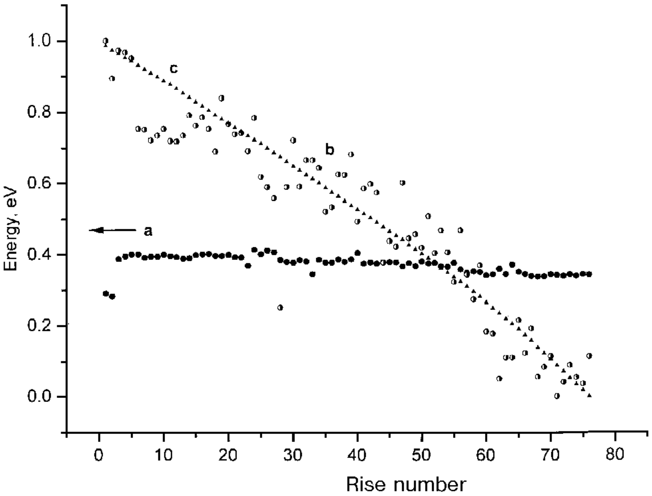

Fig. 4. Dependences of the fractional energy (a), the background (b), and the lightsum (c) on the ordinal number of the fractional curve of the TL peak at 141 K

$(\Delta \ln n)/(\Delta \ln t_{\mathrm{ex}}) = 1.02$). The linearity of the dose-dependences testifies for the absence of a saturation in the population of traps. At the same time, curve b in Fig. 3 denotes some reduction of the width of the general peak with increase in the exposure time. Such a behavior can be explained by diminishing the trap filling rate for the peak at 145 K with increase in the exposure dose. Taking also into account the linear character of the dose-dependence of the general peak, one may draw a conclusion that, for the residual peak at 145 K, the saturation of the population of relevant traps and the absence of a saturation for the low-temperature component are observed simultaneously. The linear dose-dependence indicates a significant concentration of corresponding traps, which are probably induced by own defects that are created during irradiation; in the present case, these are self-trapped holes [4]. The saturation of the high-temperature component (145 K), on the contrary, testifies for the limited concentration of corresponding traps. Therefore, we may attribute the impurity nature to them.

Let us analyze the features in the behavior of the 141-K peak width at its partial cleaning, in an assumption that the peak is made up by the superposition of only two elementary peaks which are characterized by discrete energies of traps and glow in accordance with a linear kinetics. In the absence of partial cleaning, the width of the thermal peak is defined by its intensive low-temperature component. If a partial cleaning is carried out up to the temperature, at which the high-temperature component makes a dominant contribution into the intensity, it is this component that is responsible for the peak width. In the intermediate case where the approximately identical quantities of nonequilibrium charges remain in the traps of both kinds, both the peaks will make comparable contributions into the general width. Therefore, the last must be maximal if, of course, those peaks are somewhat diverse in temperature. The experiment evidences for only a monotonous reduction of the peak width and its further stabilization with increase in the cleaning temperature (Fig. 3, curve b). Such a behavior allows us to assume that the low-temperature component is a result of the superposition of two or more peaks. Here, a permanent redistribution of traps in energy and/or frequency might take place.

3.2. Determination of trap parameters

The results of the preliminary fractional glowing of the TL peak at 141 K obtained for specimen N 1 are displayed in Fig. 4. Curve a illustrates the dependence of the energy on the ordinal number of the fractional curve ($n = 1 \div 76$). This dependence is abnormal in the sense that the energy does not grow with increase in the fractional curve number, as was expected taking into account the complex nature of the peak, but, on the contrary, monotonously falls down from 0.40 to 0.34 eV. As was mentioned above, the peak at 141 K is observed against the luminescent background of the tunnel nature which was subtracted by a specially developed program in the calculation of the energy. The fast component of the background was excluded by holding the specimen at 80 K for 2 min before the registration of each fractional curve. At the indicated holding time, the relative reduction of the background intensity during the registration of the fractional curve (about 1 min) did not exceed 3%. The background intensity normalized to 1 is shown by curve b. Curve c displays the relative variation of the lightsum after the registration of the next fractional curve. A good correlation between those dependences should be emphasized.

The described experiment turned out too long and has not been carried out till the complete fading of the peak at 141 K. The maximal temperature achieved upon the recording of the last curve ($n = 76$), is 126 K only (denoted by an arrow in Fig. 1). The following experiment was aimed at finding the threshold activation energies of this compound peak. The time of specimen excitation was increased three times, and the sensitivity of recording systems was enhanced 10 times. The results of calculations of the fractional energies are shown in Fig. 5,a. The energy values determined from 50 fractional curves fell onto the plateau $E = (0.404 \pm 0.001)$ eV. Then the specimen was heated up to a temperature of 145 K without the registration of glowing and quickly cooled down. The rest of the lightsum was exhausted during 5 cycles which were used to find the energy of the high-temperature (at 145 K) peak component $E = (0.323 \pm 0.004)$ eV (Fig. 5,*a*).

In addition to the computer-aided way, the background can be diminished by holding the specimen at 80 K for a long time after the registration of the next fraction. After conditioning the specimen for 1 h., the background intensity did not exceed 0.2% of the fractional curve maximum. The energies, calculated with the compensation of the residual background, turned out essentially larger: $E = 0.48$ eV (Fig. 5,*b*).

The low-intensity TL peak at 113 K is situated on the low-temperature side of the main peak at 141 K. Therefore, the activation energies of the corresponding traps, which were determined by the initial rise method, must have the overestimated values. Two first points in Fig. 4,*a* with energies of about 0.29 eV correspond to the glowing of this peak. Special conditions of the experiment, namely the small excitation time and high sensitivity of the registration system, ensured the monotonous increase of the energy in the range 0.25–0.40 eV for initial fractional curves. The energy of this peak can be therefore estimated as $E < 0.25$ eV. The intensity of the TL peak at 160 K turned out too small in our specimens, so that we failed to determine the energies of corresponding traps.

The presence of the background, which accompanies the low-temperature TL in LiF, may be caused by a low mobility of holes released from V_k centers and, at the same time, by the opportunity for V_k centers to execute thermally induced jumps at low (about 80 K) temperatures through the rotation of the F_2^--molecule axis. Upon recording the next fractional curve, due to the insignificant mobility of holes released from V_k centers, only some of them reach the centers of recombination. Other part of holes, having shifted from their previous locations and having no time to recombine, become frozen after the specimen being cooled. Some of those displaced holes appear closely to recombination centers and have an opportunity to recombine with them after one or more thermally induced rotation jumps or to tunnel directly into the excited state of the luminescence center. The number of holes released in a fractional cycle is proportional to the number of filled traps, which defines the correlation between the intensity of the background to be excluded and the residue of the lightsum.

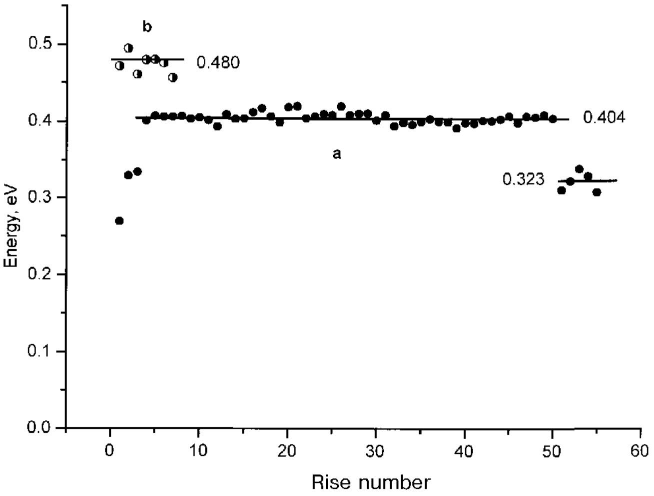

Fig. 5. Determination of the activation energies of the TL peak at 141 K making use of the specimen holding before the registration for 2 (*a*) and 60 min (*b*)

The regularities in the energy spectrum of traps, which are responsible for the peak at 141 K, correlate in general with the conclusions made in Section 3.. The activation energy of this peak was determined in work [10]. Analyzing the peak shape, we get $E_1 = 0.234$ eV which is considerably smaller than the value obtained by us. This may be a result of both neglecting the complicated nature of the peak and the presence of an intense background. The energy determined by the initial rise method, on the contrary, turned out too large: $E_2 = 0.428$ eV. The close value can be obtained for a specimen, if it was held for a long time ($t > 0.5$ h) before the registration and the background was not compensated. The reason for the energy growth from 0.404 to 0.480 eV for the peak at 141 K after its long isothermal fading is unknown. To elucidate the energy growth mechanism, special researches are needed.

4. Conclusions

Thus, upon the study of the broad TL peak at 141 K, it was established that this peak has a compound structure and is made up by the superposition of several close elementary peaks. The low-temperature component of the peak at 141 K is a superposition of two or more peaks. The high-temperature component is composed of an elementary peak ($T_m = 145$ K), which glows according to a linear kinetics, and another low-intensity TL peak ($T_m = 160$ K) situated on the high-temperature side of the first one. The energies of thermal activation of the traps which govern the TL peak at 141 K are determined taking into account its structure. Those traps can be characterized by three values of the activation energy, namely 0.48, 0.40 (the low-temperature components of the peak), and 0.32 eV (the high-temperature one).

We have proposed a method of analysis of complex TL peaks, which allows one to establish the cause of the peak broadening, i.e. to find whether the peak is an elementary one glowing in accordance with the second-order kinetics or a compound peak formed by several closely situated elementary peaks.

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ДОСЛІДЖЕННЯ ТЕРМОЛЮМІНЕСЦЕНЦІЇ НЕЛЕГОВАНИХ КРИСТАЛІВ LiF. 1. МЕТОД АНАЛІЗУ СКЛАДНИХ ПІКІВ ТЕРМОЛЮМІНЕСЦЕНЦІЇ

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Резюме

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 розширення піка, тобто встановити, чи це елементарний пік, який висвічується за квадратичною кінетикою, чи він складається із декількох близько розміщених елементарних піків, які утворюють один спільний максимум. Метод полягає у дослідженні закономірностей положення максимуму піка та його ширини як функцій світлосуми, яка змінювалась двома способами — варіацією часу збудження або ж прогріванням зразка, збудженого при 80 К, до різних проміжних температур із наступним швидким охолодженням до температури збудження та подальшою реєстрацією залишкового піка. Якщо пік елементарний, обидва способи повинні давати ідентичні результати незалежно від типу кінетики, якщо ж пік складний, то відповідні залежності повинні відрізнятися. Показано, що пік ТЛ 141 К складний, його низькотемпературна компонента є суперпозицією двох чи й більше піків, а високотемпературна являє собою елементарний пік, який висвічується за лінійною кінетикою. Також визначено енергії термічної активації пасток, які зумовлюють пік ТЛ 141 К. Відповідні пастки можна характеризувати трьома значеннями енергії активації — 0,48; 0,40 еВ (низькотемпературні компоненти піка) та 0,32 еВ (високотемпературна).