Photostimulated Thermoluminescence in Potassium Chloride Single Crystals*

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Thermoluminescence photostimulated over the spectral range 230–1000 mμ is investigated in KCl single crystals in the temperature range 90–270°K. The glow peaks are stimulated by rigorously monochromatic light of wavelength corresponding to the F, to the L, and to the tail of the K band. No V band stimulation is found; only electron traps are therefore involved in the process. Comparison of our stimulation spectra with the corresponding absorption and photoconductivity curves found by other authors shows that, besides the usual trapping through capture of photoelectrons from the conduction band, a second process takes place, namely tunneling from excited F centers; this happens for the glow band centered at ~215°K. The trap giving rise to the above band is assigned to F' centers, according to other works; further evidence is presented to support this identification.

INTRODUCTION

ONE of the purposes of thermoluminescence studies is to determine with certainty which type of carrier is responsible for a given glow peak. Most authors have tried to achieve this by seeking a correlation between emission and bleaching of color centers of known nature, such as V_1 or F' centers,[1,2] or by studying the emission spectra of the glow peaks and by assigning a given emission band to the recombination of one kind of carrier.[3]

A third very simple and direct way is to investigate the effect of filling traps with only one type of carrier, by means of experiments of photostimulated thermoluminescence. In such an experiment a crystal is x-rayed at a temperature T_A, then cooled in darkness to a temperature T_B, and subsequently illuminated with light of wavelength λ_s. If the temperature of the crystal is now increased, glow peaks appear at various characteristic temperatures in the range T_B–T_A, which would be absent had the crystal not been illuminated (Fig. 1). The general interpretation of the phenomenon, on the basis of common models, is rather simple: Empty traps, created by x rays at T_A, are filled at T_B with carriers excited by light of wavelength λ_s from color centers—either F- or V-type. When the sample is heated to T_A, these traps empty and the released carriers recombine with emitters and give glow peaks.[4] Previous results on the subject can be summarized as follows. Stoddard[5] experimented with NaCl; the crystal, x-rayed at dry-ice temperature, was illuminated at liquid-nitrogen temperature (LNT) with radiation of wavelength 400–1000 mμ; all the peaks of conventional thermoluminescence were re-excited with a maximum of efficiency using F light. Braner and Israeli[6] extended the research to various alkali halides; they found that only some of the glow peaks were re-excited by F light; those missing were obtained by illumination in the V bands. From these findings they concluded that it is possible to dis-

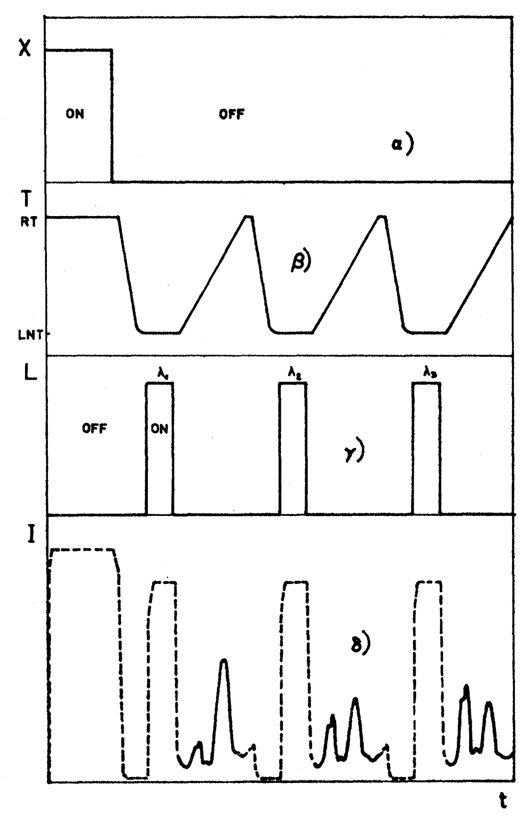

FIG. 1. Schematic diagram of the procedure for obtaining stimulation spectrum: (α) x rays; (β) temperature; (γ) light; (δ) emission.

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[1] D. Dutton and R. J. Maurer, Phys. Rev. **90**, 126 (1953).

[2] A. Halperin, A. A. Braner, M. Schlesinger, and N. Kristianpoller, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 724.

[3] A. Halperin, A. A. Braner, and N. Kristianpoller, Proceedings of the International Conference on Color Centers, Turin, 1960, p. 35 (unpublished).

[4] The phenomenon should not be confused with the thermoluminescence induced by uv excitation in the fundamental absorption of the crystal; in this last case both electrons and holes are excited by the ionizing radiation: The excitation mechanism is therefore analogous to the x-ray excitation.

[5] A. E. Stoddard, Phys. Rev. **120**, 114 (1960).

[6] A. A. Braner and M. Israeli, Phys. Rev. **132**, 2501 (1963).

tinguish between glow peaks caused by thermal release of electrons and glow peaks caused by thermal release of holes, consequently between electron traps and hole traps. More recently Tournon and Berge[7] studied the effect of irradiation with x ray and F light on the photostimulated thermoluminescence of LiF, and suggested that the electron traps are filled by tunneling of the electron from the $2p$ state of the F center.

A difficulty is associated with experiments of this kind: As is known, some of the color centers have an ionization quantum yield orders of magnitude lower than others, as pointed out by Braner and Israeli[6]; for instance, the V_3 with respect to the L bands in KCl. It may happen, therefore, that irradiation in the range of absorption bands which are nearly undetectable gives a large number of free carriers, while clearly defined absorption bands give a negligible contribution. Moreover, the interpretation of the results may be strongly affected by even weak stray light. The above considerations suggest that the phenomenon studied by the above quoted authors should be reconsidered before definite conclusions can be drawn.

In order to obtain reliable information on the kind of center which is stimulated by the exciting light, and hence unquestionable knowledge of the nature of traps (whether they are donors or acceptors), it is not sufficient to irradiate the crystal with light of a single wavelength. Rather it is necessary to carefully study the stimulation of thermoluminescence (TL) over the whole spectrum by repeating measurements at many stimulating wavelengths and employing a double monochromator with narrow bandwidth. The results should then be interpreted by comparing the intensity of the optically stimulated TL, as a function of exciting wavelength, with the corresponding photoconductivity curve and absorption spectrum.

In the present work we study the photostimulated thermoluminescence of KCl. The "stimulation spectrum" for the various glow peaks of the emission is considered for exciting radiation over the spectral range 230–1000 mμ.

The procedure for obtaining such a spectrum is as follows (Fig. 1): (a) irradiation of the sample at room temperature (RT); (b) cooling in darkness to LNT; (c) illumination with monochromatic λ_1 light at LNT; (d) warming up to RT, recording the glow curve; (e) recooling to LNT; (f) a second illumination with λ_2 light; (g) rewarming to RT; and so on, for various λ_s in the range to be explored.

The heights of the various peaks, normalized to equal values of the intensity incident on the sample, are then reported. By these means, we can say that a peak is excited by, say, F light only if its stimulation spectrum shows a band centered at the peak of the F-band absorption; more correctly, we shall say that its maximum stimulation efficiency is at F wavelength.

[7] J. Tournon and P. Berge, Phys. Stat. Solidi **5**, 117 (1964).

EXPERIMENTAL

The specimens used were single crystals of KCl, grown by the Kyropoulos method in dry nitrogen atmosphere and cleaved into platelets approximately $8\times6\times1$ mm. The sample was mounted on a metal vacuum cryostat and x-irradiated at room temperature in the dark with a W-target OEG 50 Macklett tube with beryllium window, operated at 50 kV, 40 mA; the x rays were filtered with an Al plate 1 mm thick, to eliminate the soft component and to obtain a more uniform absorption. The x-irradiation time at RT was generally 15 min. The concentration of F centers generated in the crystal was about 3×10^{16}/cm^3. A 1000-W Hanovia hydrogen discharge tube, model 471 A 0320, and a 1000-W Wolfram lamp were used for illumination in the ultraviolet and visible portions of the spectrum, respectively. The light from these sources was monochromatized with a Zeiss quartz double monochromator. Generally, very narrow slits (0.08 mm, with a bandwidth of $\sim$1 mμ for F light) and short illumination times were used. The light emitted by the crystal was detected with a 9558 QA trialkali EMI photomultiplier of wide spectral response (200–800 mμ) and low dark current; the current was measured with a Keithley model 414 micromicroammeter and recorded with a Speedomax recorder.

The same sample was used for several repeated runs; this is justified by the observation that, with our low illumination doses, many cycles could be carried out on the same crystal before saturation effects appeared. This was checked periodically during the course of the measurements by noting that the emission stimulated by a constant and very low intensity of F light either was constant or changed only slightly.

Since the intensity of the light incident on the crystal (keeping the slit width constant) depends on the wavelength, it was necessary to use correction plots (lamp +monochromator response versus λ_s) in constructing our stimulation spectra. The heights of the peaks were assumed to vary linearly with the stimulation intensity at a given wavelength. As reported later (point c, Fig. 3) this is justified at our low illumination doses. With the reported slit widths, the illumination time was generally 1 min.

RESULTS

(a) The main features of the shape of the glow curves are the same in x-ray and in photostimulated thermoluminescence, at least for low x-ray doses (Fig. 2); the peaks appearing in one of the curves also appear in the other one, although the intensity ratios differ. The temperature maxima, reported in Table I with their approximate relative intensities, agree reasonably well with the results obtained by other authors.[1,6,8]

In spite of the general agreement between the x- and the light-excited glow curves, we cannot state with

[8] F. Fischer, Z. Physik **163**, 401 (1961).

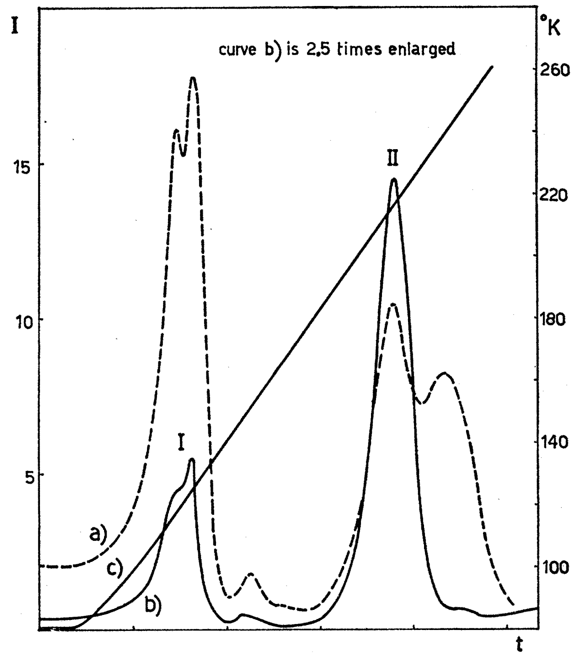

FIG. 2. Glow curves of a KCl crystal: (a) after 10 min of x irradiation at LNT; (b) after 15 min of x irradiation at RT and 1 min of 410 mμ light at LNT (slit width 1 mm); (c) temperature versus time; (I in arbitrary units).

certainty that all the peaks of the conventional TL are actually re-excited by light; a careful analysis of the activation energy would be necessary to identify the corresponding peaks in both cases. We did not find, however, the difference observed by Braner and Israeli[6] between *F* and x-ray stimulation. Moreover, we performed very intense stimulation at $\lambda_s = 215$ mμ, but we found no evidence of new glow peaks. Our results can better be compared with those obtained by Stoddard on NaCl[5]; see however point (b).

(b) According to other authors, the photostimulated TL depends on the stimulating wavelength λ_s; although the maximum stimulation wavelength is not the same for all the peaks, we found that every glow peak is re-excited simultaneously by any given λ_s; we did not find therefore any peak re-excited exclusively by a given wavelength.

(c) Let us consider only the two main peaks of the re-excitation emission that are present also in the conventional experiment: peak I, at about 120 °K, and peak II, at about 215 °K [peak I is a composite one, but its components (at 115 and 125 °K) are nearly equal and vary in the same way; therefore it can be taken here as a single peak]. Figure 3 shows a plot of the maximum intensities of peaks I and II versus the length of illumination at two different stimulation wavelengths [*F* light (543 mμ) and 420 mμ]; *F* light is much more effective than 420-mμ light in re-exciting peak II, and 420-mμ light is more effective than *F* light in re-exciting peak I.

(d) Stimulation spectra of both peaks in the region 230–1000 mμ are plotted in Fig. 4; the peak I spectrum follows quite well the absorption spectrum[9] for an additively colored crystal (Fig. 5, curve a) in the uv region, and shows a stimulation maximum also at about 410 mμ; the peak II spectrum, which in the uv has a similar plot, shows a strong enhancement of stimulation efficiency in the *F* region.

(e) Stimulation spectra are obtained on the same sample by successive cycles of illumination and heating because, as often noticed, different samples endanger reproducibility. It is necessary, therefore, to ensure that the results are not affected by saturation effects. We checked at various wavelengths, and found that with

TABLE I. Temperature maxima and intensities of thermoluminescence glow peaks in KCl single crystals, x-rayed at LNT or photostimulated at $\lambda_s = 420$ mμ at LNT. (Slit width, 1 mm.)

T_{max}	115°K	125°K	148°K	215°K	238°K
X-rayed for 10 sec at LNT.	72	80	9	50	40
Photostimulated at $\lambda_s = 420$ mμ for 1 min at LNT.	8	10	1	28	1

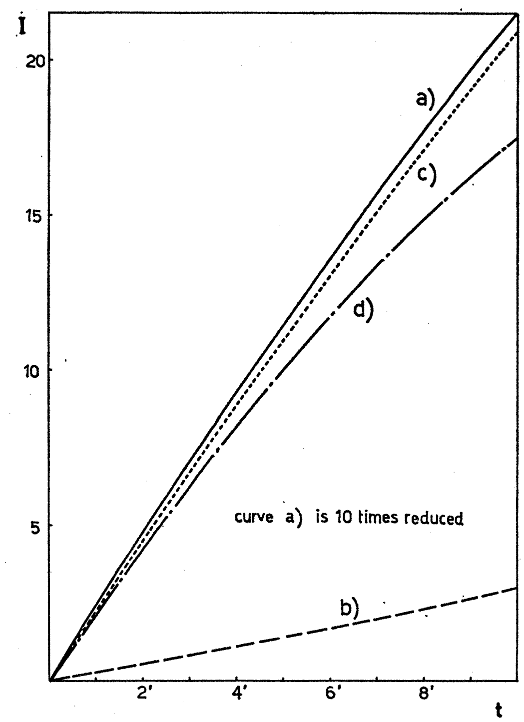

FIG. 3. Maximum intensities of peaks I and II as a function of illumination dose, for two different stimulations: (a) peak II, $\lambda_s = 543$ mμ, slit width=0.1 mm; (b) peak I, *idem*; (c) peak II, $\lambda_s = 420$ mμ, slit width=0.15 mm; (d) peak I, *idem* (I in arbitrary units).

[9] F. Lüty, Z. Physik **160**, 1 (1960).

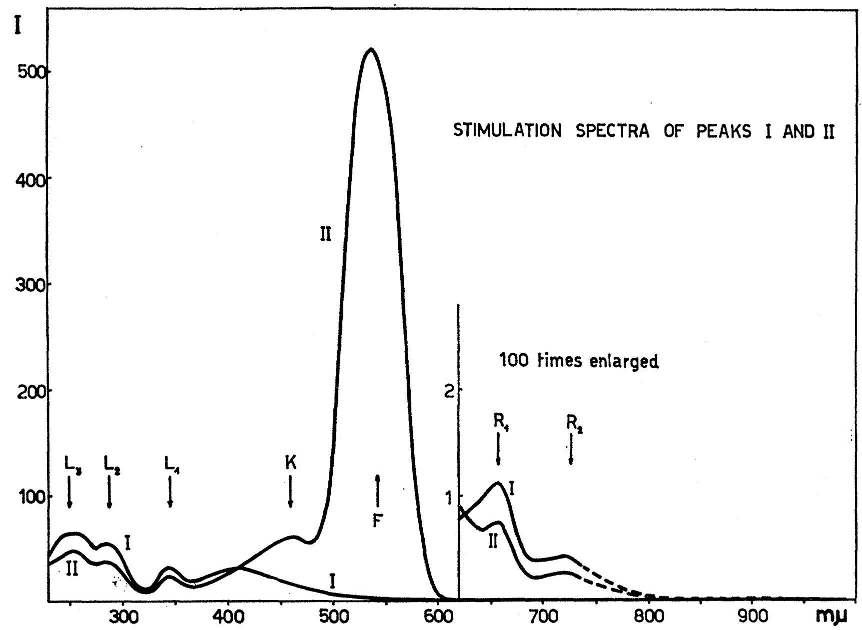

FIG. 4. Stimulation spectra of peaks I and II (the dashed region shows only the rough behavior of the spectrum). The position of the electronic absorption bands is also shown (I in arbitrary units).

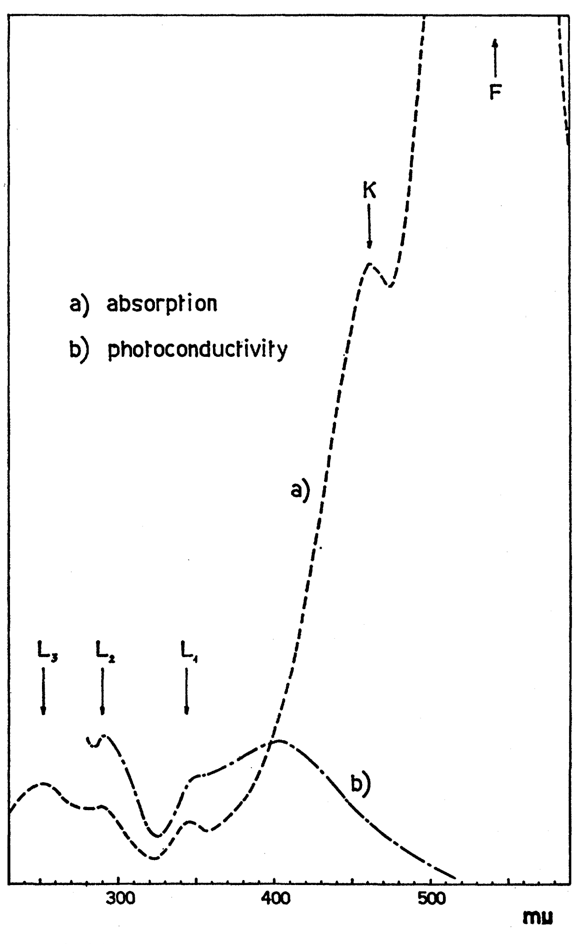

FIG. 5. (a) Absorption spectrum, as reported by Lüty Ref. 9; (b) photoconductivity (stimulation spectrum) as reported by Wild and Brown Ref. 11.

our intensities the heights of the peaks vary linearly with the dose. This is shown in Fig. 3 for $\lambda_s = 543$ mμ and $\lambda_s = 420$ mμ. Saturation effects appear at greater doses. Figure 6 shows a plot of the height of peak II in repeated runs with increasing time of F illumination. We also report a check curve (dashed) obtained by stimulating with a constant low dose.

(f) Figure 7 shows a comparison of three glow curves, the first one obtained with F illumination, the second and third ones with different doses of $F+F'$ illumination (F' stimulation alone has a negligible effect because the sample does not contain F' centers). It appears from

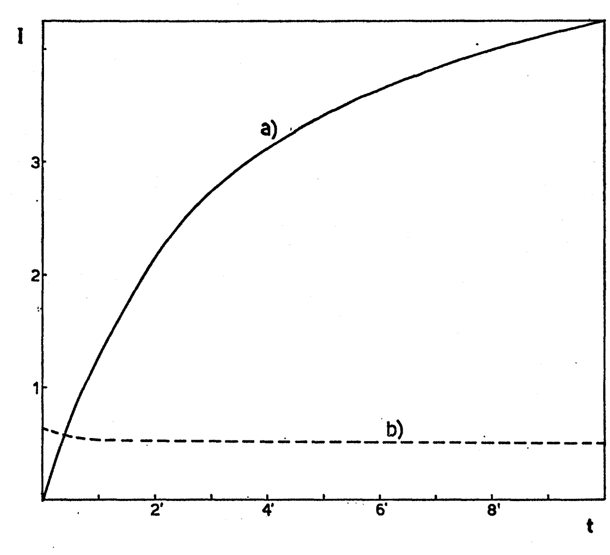

FIG. 6. (a) Intensity of peak II as a function of F-light dose (slit width 0.2 mm); (b) check curve, 10 times enlarged (slit width 0.1 mm F-light dose 1_min); (I in arbitrary units).

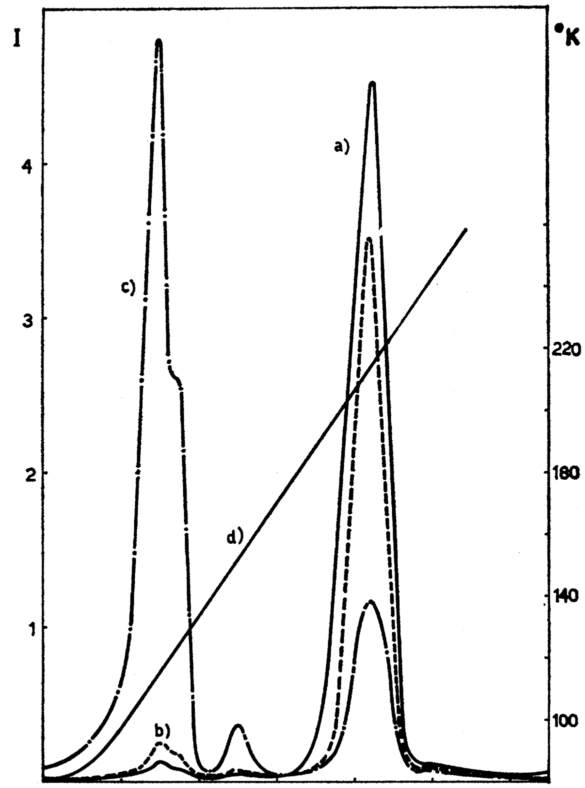

FIG. 7. Re-excited glow curves: (a) after 5 min of F light (slit width 0.1 mm) at LNT; (b) after 5 min of F light (slit width 0.1 mm) followed by 5 min F' light (slit width 0.1 mm) at LNT; (c) after 5 min of F light (slit width 0.1 mm) followed by 5 min F' light (slit width 1 mm) at LNT; (d) temperature-time curve (I in arbitrary units).

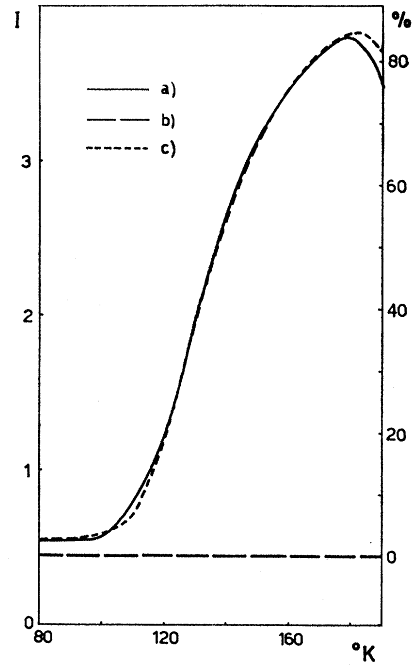

FIG. 8. (a) Intensity of peak II as a function of F illumination temperature; (b) intensity of the plateau due to tunneling effect; (c) Lüty's curve for the percent rate of F centers destroyed by F light with temperature.

the figure that in the second and third cases, peak II is decreased and peak I enhanced.

(g) Figure 8, curve a, shows a plot of the height of the peak II versus the temperature of F illumination: The F-stimulated glow peak is weak and constant at $T<95$ °K, while its intensity rises nearly exponentially at higher temperatures.

(h) The peaks that are not considered in this report because of their poor resolvability seem to follow the behavior of peak I; at any rate none of them shows a stimulation attributable to V centers.

(i) The study of the spectral composition of peaks I and II in the uv and visible region with the experimental apparatus already described[10] is rather difficult owing to the low emission intensity. By means of filters we observed that the intensities of the two peaks remain in a constant ratio: This suggests that the spectral composition and hence the recombination centers are the same.

DISCUSSION

In view of results (h) we limit the discussion to peaks I and II without loss of generality. The behavior of stimulation spectra, with maxima corresponding to electron bands, shows clearly that both traps I and II are electron traps. Nevertheless, these spectra show an interesting difference: Trap II captures F-stimulated electrons much more readily than trap I, whereas trap I is more effective in capturing L-stimulated electrons. Thus the electrons or the traps are somehow "differentiated" by the different stimulations, for otherwise the heights of the two peaks would always vary in the same ratio.

The band at about 410 mμ in the peak I spectrum, which has no corresponding absorption band, is rather puzzling; nevertheless the same band appears in the stimulation of the photoconductivity of KCl at low temperatures.[11] A comparison of our results with those of Wild and Brown (see Fig. 5, curve b of Ref. 11) is extremely meaningful. The stimulation spectrum of photoconductivity coincides with that of peak I and, far from the F region, also with that of peak II. This suggests that traps I and II capture electrons from the conduction band; the product $n\sigma$ (n = density of traps, σ = cross section) for trap I seems to be larger than for trap II.

Although trap I is filled only by this mechanism, trap II can capture electrons which tunnel from the first excited state of the F center. This is in agreement with the extremely low ionization quantum efficiency of the F center with F light at LNT and with the very high efficiency of stimulation of F light for the peak II.

[10] R. Fieschi, E. Panizza, and P. Scaramelli, Acta Phys. Polon., **26**, 645 (1964).

[11] R. L. Wild and F. C. Brown, Phys. Rev. **121**, 1296 (1961).

The temperature at which peak II appears corresponds to that of bleaching of F' centers. This suggests, in agreement with Dutton and Maurer,[12,1] that trap II can be identified with an F center. Electrons would tunnel between nearby F centers,[7,13,14] following a reaction of the following type:

$$(F)_{\text{ground state}}+\text{light} \rightarrow (F)_{\text{excited state}}$$
$$(F)_{\text{excited state}}+F \rightarrow \text{vacancy}+F'.$$

Electron tunneling like that assumed above for the $F \rightarrow F'$ conversion has been suggested by Markham, Platt, and Mador[13] to explain optical bleaching properties at low temperatures. The measurements were performed on KBr crystals x-irradiated at RT or additively colored: While bleaching effects are present in the former case, they are absent in the latter one. According to Markham, tunneling from F centers takes place only in x-rayed crystals owing to a nonuniform distribution of F centers.

More recently Costikas and Grossweiner[15] observed bleaching effects also on additively colored crystals. By assuming that the F centers in additively colored samples are uniformly distributed, the average distance between F centers for a concentration of 10^{17} cm^{-3} is found to be about 200 Å; this should make a tunneling mechanism very improbable. Further evidence of tunneling between near F centers is provided by Lüty's data (see Fig. 28 of Ref. 16) which shows that the low-temperature plateau rises with increasing F concentration. Our results (Fig. 4) seem to us to be conclusive evidence for such a process.

If the above identification is correct, F' stimulation immediately after F stimulation will ionize F' centers and will cause a filling of traps I at the expense of traps II. This is confirmed by measurements shown in f (Fig. 7).

Figure 8 supplies further evidence for the proposed model: Indeed the curve a is similar to those obtained for the $F \rightarrow F'$ transformations by Pohl's school[17] and more recently by Fedders, Hunger, and Lüty,[18] Lüty,[16] and Swank and Brown[19] in different experiments. This curve can be separated in two parts: the plateau (curve b), attributable to the F' formation with the tunnel mechanism, and the nearly exponential rise, attributable to the F' formation by the thermal ionization of the excited F center. This exponential rise, referred to the plateau as zero can be compared with the data of Lüty (see Fig. 13, Ref. 16) for the percentage rate of F centers destroyed by F light at different temperatures.

The saturation effect of the intensity of glow peak II (Fig. 6) when the stimulating doses of radiation increases, may be due to two phenomena:

(1) The number of available traps is limited and hence the maximum intensity is also limited.

(2) The stimulating radiation has the two competing effects of filling of traps through $F \rightarrow F'$ conversion and bleaching of F' centers (since the two absorption bands overlap), because the ionization quantum efficiency of F' centers is 1 at all temperatures.[17] We cannot distinguish, at the moment, between these mechanisms. A third phenomenon, the exhaustion of recombination centers, can be excluded as the main mechanism because of the fact that subsequent stimulation at low doses yields intensities comparable with the initial one (see the dashed curve of Fig. 6).

CONCLUSIONS

Through careful measurements of photostimulated TL in KCl in the range 90–270 °K we have obtained the following results:

(1) The glow peaks are stimulated only by light absorbed by electron centers.

(2) Filling of traps occurs either through capture of photoelectrons from the conduction band, or by tunneling of electrons from excited F centers to form F' centers.

(3) The glow peak at $T=215$ °K is due to the release of F' electrons.

The following conclusions can be drawn: Photostimulated glow peaks arise from the thermal release of trapped electrons distributed in distinct electron excess centers; the emission of light comes from the capture of these electrons from the conduction band by the same recombination centers.

We hope that a thorough study of this phenomenon, besides clarifying some aspects of thermoluminescence, may permit the development of a method that, on account of its sensitivity, could in some cases advantageously replace photoconductivity and absorption measurements in the study of electron processes in crystals.

ACKNOWLEDGMENTS

The authors are very grateful to Dr. R. Oggioni and Dr. G. Spinolo for useful discussions.

[12] The shift of peak maximum towards higher temperatures in our measurements is attributable to our higher warming rate of about 35°/min.

[13] J. J. Markham, H. T. Platt, and I. L. Mador, Phys. Rev. **93**, 597 (1953).

[14] J. J. Markham, *Report of Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955), p. 304.

[15] A. Costikas and L. I. Grossweiner, Phys. Rev. **126**, 1410 (1962).

[16] F. Lüty, *Elektrönenübergange in Farbzentren, Halbleiterprobleme VI* (Frederick Vieweg und Sohn, Braunschweig, Germany, 1961).

[17] See, for instance, H. Pick, Ann. Physik **31**, 365 (1938).

[18] H. Fedders, M. Hunger, and F. Lüty, J. Phys. Chem. Solids **22**, 299 (1961).

[19] R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).