

Effects of Illumination on the Thermoluminescence of Alkali Halides

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Illumination with monochromatic light into the F - or V -absorption bands of KBr, KI, NaCl, and KCl single crystals at liquid nitrogen temperature (LNT), after x irradiation at room temperature (RT), "re-excites" different glow curves in the region between LNT and RT. F illumination produces a set of electron thermoluminescence peaks, and V light a set of hole peaks. Both sets of peaks add up to the regular glow curve obtained after x irradiation at LNT. The results are consistent with existing models of the thermoluminescence process.

INTRODUCTION

THE thermoluminescence of alkali halides has been the subject of investigations for a long time. Recently, a paper by Stoddard¹ reported some results, which apparently contradicted the existing models of the thermoluminescence process.

If a crystal at a temperature below 600°K is irradiated with x rays and then warmed, a number of luminescence glow peaks will be observed up to about 600°K. No thermoluminescence will be detected in the temperature region below the temperature of irradiation if the crystal is cooled down in darkness after x irradiation. It has been shown, however, by Stoddard that thermoluminescence can also be obtained at temperatures below the temperature of irradiation after the following treatment: A NaCl crystal at, say, room temperature (RT) is irradiated with x rays, then cooled down in darkness to liquid nitrogen temperature (LNT) and subsequently illuminated with light into the F -absorption band. When the temperature of the crystal is raised again, glow peaks will appear at various characteristic temperatures between LNT and RT. We have looked for this effect in the past but without success. After Stoddard's experiments we renewed our search and found the conditions for obtaining it.

The present paper describes how such a "re-excitation" of glow peaks is procured. It is shown that the glow curves obtained are different from those after x irradiation at LNT: Appropriate illumination of the cooled sample with F light was found to produce only part of the glow peaks. The "missing" glow peaks were obtained by illumination with light absorbed in the V_2 or V_3 bands. The results were verified for a number of alkali-halide crystals and made possible the distinction between luminescence glow peaks caused by thermal release of electrons and those caused by holes.

It is concluded that the observed effects are in agreement with current models of thermoluminescence.^{2,3}

¹ A. E. Stoddard, Phys. Rev. **120**, 114 (1960).

² A. Halperin and A. A. Braner, Phys. Rev. **117**, 408 (1960).

³ A. Halperin, A. A. Braner, and N. Kristianpoller, *Proceedings of the International Conference on Color Centers and Crystal Luminescence, Torino, Italy, 1960* (Litografia E. Gili, Torino, 1961) p. 35.

EXPERIMENTAL

The specimens used were single crystals of potassium bromide, potassium iodide, sodium chloride, and potassium chloride obtained from the Harshaw Chemical Company. Most of the crystals were used in the as-received or slightly aged condition and cleaved into small plates of approximately 8 mm×6 mm×1 mm.

The crystals were irradiated with x rays, in the absence of light, inside a vacuum cryostat as previously described.⁴ They were illuminated as necessary with monochromatic light from a Hilger 246D quartz monochromator and a Mazda MD/E 250W mercury lamp. Filters were selected which reduced the stray light.

The temperature of the specimen was raised uniformly at a constant rate of 10°K per min using an electronically controlled heating device.⁵ The constant and reproducible heating rate is of great importance in these experiments when glow curves taken in very diverse conditions are to be compared. The temperature of the glow peak maximum (T_g) is dependent on the heating rate,⁶ and the recordings of two different glow curves can be superposed only if the mode of heating has been identical. Temperature readings were made with a calibrated copper-constantan thermocouple with one junction fixed near the crystal and the other one in an ice bath.

An EMI 6256B photomultiplier which has a low dark current and high sensitivity in the uv and visible regions of the spectrum served as a detector. The photocurrent was measured with a Keithly model 410 microammeter and recorded with a Brown recorder. Glow intensities are hence given in arbitrary units.

The procedure for obtaining the glow curve was as follows. For "normal" glow curves: (1) sample cooled in vacuum to LNT (77°K); (2) irradiation with x rays at LNT; (3) heat at a linear rate (10°K per min) and record the glow curve. For glow curves with illumination effects: (a) irradiation with x rays at RT; (b) sample cooled in darkness to LNT; (c) illumination into the proper absorption band; (d) heat the crystal and record the glow curve.

⁴ A. A. Braner and A. Halperin, Phys. Rev. **108**, 932 (1957).

⁵ A. Halperin, M. Leibovitz, and M. Schlesinger, Rev. Sci. Instr. **33**, 1168 (1962).

⁶ A. Halperin and N. Kristianpoller, J. Opt. Soc. Am. **48**, 996 (1958).

TABLE I. Peak temperatures T_g (in °K) of glow peaks in KBr. X -regular X glow, F -re-excited F glow, V -re-excited V glow. Temperatures in parentheses are of peaks unresolved in the X glow. Heating rate: $dT/dt=10^\circ\text{K}/\text{min}$.

X	108	136	148	(161)	167	176	(189)	194	(210)	(215)	220	(226)	244
F			148	161		176		194	210		220		244
V	108	136			167		189			215		226	

RESULTS

One main difficulty in studying the effect of re-excitation of thermoluminescence is its extremely low intensity. Regular thermoluminescence is quite weak, and the re-excited glow is an effect of about two orders of magnitude smaller.

A series of experiments gave us the optimal conditions for re-excitation. Figure 1 illustrates the dependence of the effect on the energy of the x rays. These results are for a KBr crystal irradiated with x rays for 30 min (at RT) and bleached to obtain re-excitation with F light ($625\text{ m}\mu$) for 10 min (at LNT). The 148°K glow peak intensity is plotted as a function of peak voltage on the x-ray tube. This effect reaches a maximum at about 50 kvp and drops to zero at 200 kvp. By keeping the voltage constant and varying the irradiation dose, one obtains a dependence with a maximum at very short irradiation times which falls off at larger doses. In most of our experiments which will be described below the x-irradiation conditions were 35 kvp, 14 ma, Cu target with 10 to 30 min of irradiation.

The efficiency of the bleaching light dose goes also through a maximum and decreases with longer bleaching times. Generally, a time of 8–10 min proved satisfactory with our light source, but sometimes shorter or longer illuminations were also applied to enhance certain glow peaks.

1. KBr

Potassium bromide proved to be a specially good material for studying the effect. Figure 2, curve a,

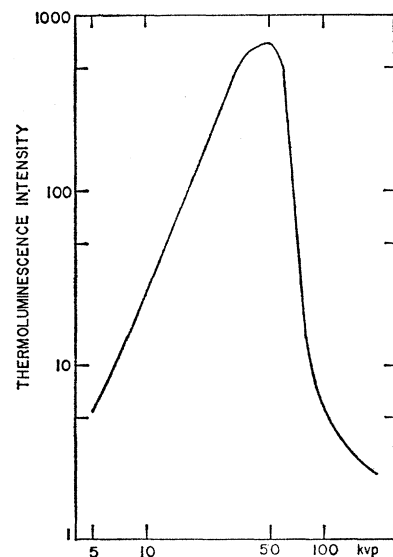


FIG. 1. The intensity of the 148°K re-excited glow peaks in KBr as a function of x-ray energy. x irradiation for 30 min at RT and subsequent bleaching with F light at LNT.

shows a regular glow curve (X glow) for KBr between LNT and RT. The effect of illumination with light in the F band (F glow) is illustrated in Fig. 2, curve b. Comparison of the F and X glows reveals the absence of a number of glow peaks. The missing peaks were obtained after illumination of the crystal with light in

TABLE II. The same as Table I but for KI. The 195°K peak was not detected in the re-excited glow.

X	97	114	122	136	(146)	158	180	195	(212)	216	(231)	237
F			122		146		180	?		216	231	
V	97	114		136		158		?	212			237

the V_2 band ($265\text{ m}\mu$).⁷ The resulting glow (V glow) is shown in Fig. 2 curve c. The peak temperatures T_g of the measured glow are listed in Table I. The temperatures in parentheses are those of peaks resolved in the re-excited glow but were barely visible as shoulders in the X glow.

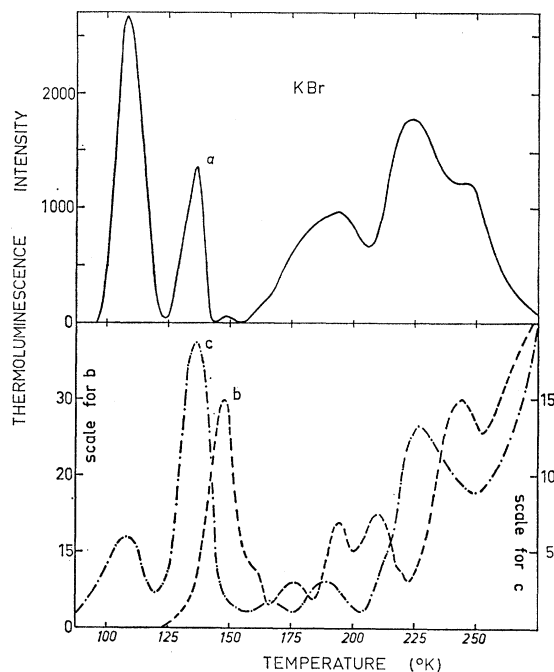


FIG. 2. Glow curves of a KBr crystal. Curve a represents regular glow curves after x irradiation at LNT (X glow). Curve b—re-excited glow with F light (F glow). Curve c—re-excited glow with V light (V glow).

⁷ H. Dorendorf, Z. Physik 126, 317 (1951).

TABLE III. The same as Table I but for NaCl.

<i>X</i>	101	104	110	129	(160)	(177)	182	(206)	213	(216)	237	(243)
<i>F</i>	101	104	110	129	160		182			216		243
<i>V</i>						177		206	213		237	

2. KI

In potassium iodide the *F* band is centered at 660 mμ and two of the *V* bands present after x irradiation at RT are *V*₂ (355 mμ) and *V*₃ (290 mμ).⁸ The results for KI are summed up in Fig. 3 and Table II. Large variations in glow intensity caused the introduction of different scales in Fig. 3. Figure 3 curves a₁ to a₃ apply to an *X* glow obtained from a virgin crystal. Figure 3 curve a₂' is from a slightly aged crystal. The effects of *F* illumination are shown in curve b and those of *V*₃ light in curve c. *V*₂ illumination had an effect similar to that of *V*₃ light. The arrow in curve b indicates the position of the 180°K peak with an intensity of 133 arbitrary units.

3. NaCl

A normal glow curve for NaCl is given in Fig. 4. The re-excited glow after *F* illumination (458 mμ) and after *V*₂ illumination (223 mμ) are given in Fig. 5, curves b and c, respectively. The peak temperatures are listed

in Table III. Illumination with *V*₃ light (210 mμ) gave results similar to those obtained with *V*₂ light. The *V*-glow peaks are few and positioned near the *F*-glow peaks.

4. KCl

The results for potassium chloride were similar to those for the other alkali halides investigated, but they are not as complete. Table IV gives a list of glow peaks for KCl. *F* light (546 mμ) resulted in a broad peak at

TABLE IV. The same as Table I but for KCl.

<i>X</i>	109	129	160	175	200	236
<i>F</i>	109		150		200	
<i>V</i>		118		175		236

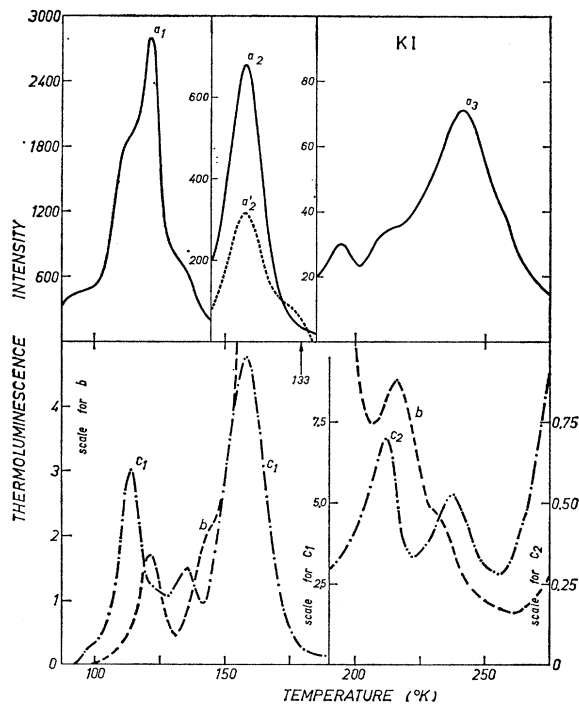


FIG. 3. The same as Fig. 2 but for KI. Curve a₂' represents the middle portion of the *X* glow of a slightly aged specimen. The other curves are for virgin crystals: b—*F* glow; c—*V*₃ glow. The glow at 180°K in curve b peaks with 133 intensity units.

⁸ H. N. Hersh, Phys. Rev. **105**, 1158, 1410 (1957).

109°K, and the strongest peak is located at 200°K. Certain experimental difficulties were encountered in obtaining *V*-glow curves. The *V*₃ absorption (212 mμ) is comparatively high,⁷ but the intensity of our light source is so low in this region of the spectrum that more than one hour of bleaching was necessary to produce the effect. During this one-hour stray light was sufficient to produce the strongest of the *F*-glow peaks. This was verified by introducing a thick plate of glass

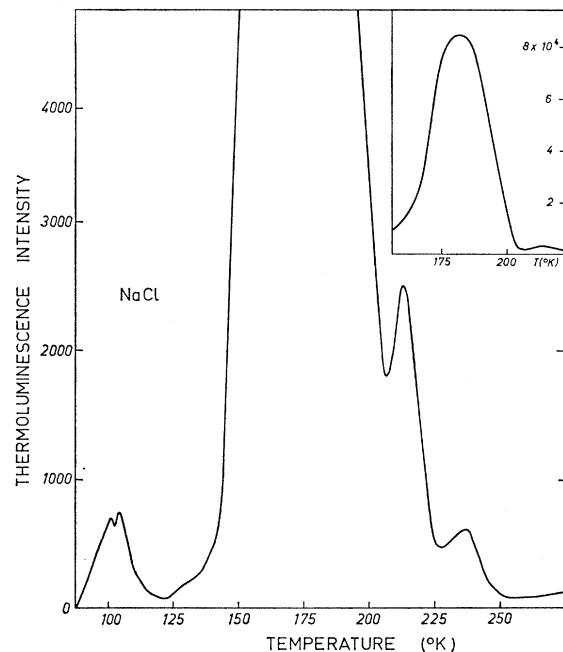


FIG. 4. The *X*-glow curve for NaCl.

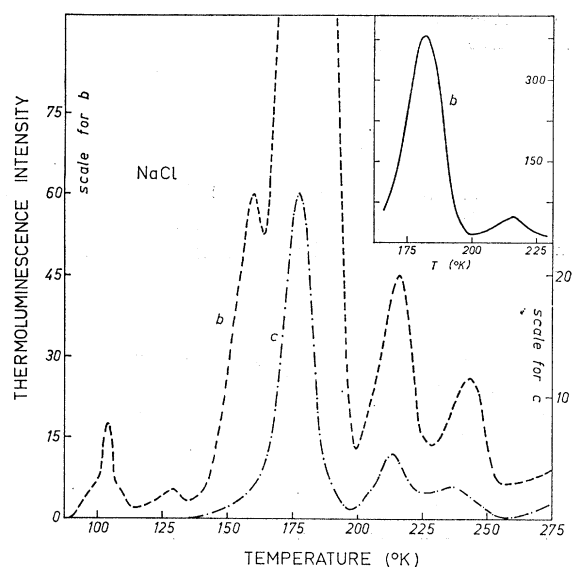


FIG. 5. The re-excited glow for NaCl. b— F glow
c— V_2 glow.

between the light source and the monochromator. Repeating the "V-light" bleaching experiment resulted in the disappearance of all true V -glow peaks and only F glow produced by stray light remained. The data presented in Table IV were obtained in this way. No curves for KCl were drawn.

DISCUSSION

The reported results agree with the model of thermoluminescence previously proposed by Katz^{9,10} and discussed in earlier papers.²⁻⁴

The model involves a number of localized energy levels in the forbidden gap between the valence and conduction bands. Those near the conduction band serve as electron traps and are, if occupied, detected optically as F -type color centers. Other energy levels above the valence band may trap positive holes and become V -type centers.

Thermoluminescence arises in irradiated crystals from transitions involved in the process of recombination of electrons and holes after their thermal release from their corresponding trapping levels which are characterized by certain activation energies. An increase in temperature releases first electrons or holes from those filled centers which have the lowest activation energy. If the next higher activation energy is sufficiently far away, this will result in an isolated glow peak (T_g), otherwise overlap will occur. At any given temperature, T , shallow traps with $T_g < T$ will be empty, and deep traps with $T_g > T$ may be filled.

Up to this time, it was unknown which type of carrier is released at any characteristic temperature T_g . The basic idea of our experiments was to fill shallow traps with only one type of carrier. This was achieved through the experiments of re-excitation of glow peaks. In a crystal irradiated with x rays at RT, all the shallow traps with $T_g < RT$ will remain empty. Optical bleaching of only F centers with monochromatic light will result in a release of trapped electrons. If the crystal is cooled to LNT, a temperature below that at time of irradiation (RT) and then bleached some of those optically released electrons may become retrapped in shallow electron traps. The shallow hole traps remain empty. Now, on warming the crystal up to RT, only electrons will be released from trapping states and will recombine with sessile holes. The resulting glow curve (the F glow) will then show, up to RT, only those peaks caused by electrons.

Similarly when bleaching the colored crystal with V light, holes will be released and, if this is done at a temperature lower than that of irradiation, these holes may become retrapped in shallow hole traps. The resulting glow curve (the V glow) exhibits only peaks caused by holes.

Additional arguments for the above model were obtained by simultaneous thermoluminescence and thermostimulated conductivity measurements.¹¹ The re-excited electrical glow curves show large pronounced F peaks and very low, hardly measurable V peaks. As expected, the hole conductivity is about two orders of magnitude lower than that of electrons.

The particular experimental conditions required for the re-excitation of thermoluminescence and its very low intensity account for our past failure in obtaining the effect. Contrary to what one would expect the effect is obtained in only very slightly colored crystals and decreases with stronger coloration. Because of a fortunate combination of irradiation and illumination conditions, Stoddard¹ was able to observe the effect. He overcame the difficulty of low intensity by using a high heating rate of 120°C per min, compared to 10°C per min in our experiments. Such a high rate of heating, however, reduces the resolution of glow peaks and makes the comparison of peak temperatures in different curves even more difficult. By choosing sodium chloride as a sample for his experiments Stoddard came to the erroneous conclusion that *all* the low-temperature peaks were "excited" as a result of illumination in the F band at LNT. It is evident from Table III and Figs. 4 and 5, that in sodium chloride most of the low-temperature peaks are electron peaks. The hole peaks in turn are located at temperatures very close to those of electron peaks, hindering the resolution of peaks into two distinct groups.

This proximity of different peaks grouped around 175°K seems to be the reason for the scattering of

⁹ M. L. Katz, Dokl. Akad. Nauk SSSR 58, 1935 (1947).

¹⁰ M. L. Katz, *Luminescence and Electron-Hole Processes in Photochemically Colored Alkali-Halides* (Saratov University Publishing House, 1960), p. 139.

¹¹ A. A. Braner and T. Schlesinger (to be published).

thermal activation energies as calculated from the initial rise method in an earlier paper.¹² Stoddard¹ mentions the difficulty in F excitation of the -20°C peak. This peak corresponds to the group of peaks at $213\text{--}237^{\circ}\text{K}$ in our experiments.¹³ His difficulty is understandable because these peaks as shown are caused by holes and not electrons.

The re-excitation of electron peaks will be achieved most efficiently with F light since there exists a much larger concentration of F centers compared to the concentration of other electron-excess centers. On the other hand, when bleaching the F centers, only a small number of optically released electrons will finally get retrapped in shallow traps. Most of these released electrons will recombine with holes in radiative and nonradiative transitions. This will reduce the total number of carriers available for thermoluminescence. If we also take into account the longevity of F centers,⁴ both the bleaching and excitation effects by Stoddard¹ will be explained.

Katz¹⁰ did not obtain any changes in glow curves of KCl after x-irradiating crystals at RT and following illumination with F light at liquid oxygen temperature. At RT F light produced relative intensity changes in glow peaks. This was correctly explained as a redistribution of electrons in traps.¹⁰

The results reported in this paper are additional proof against the single electron-excess center model proposed by Hill and Schwed,¹⁴ and Bonfiglioli *et al.*^{15,16}

The fact that the effect of re-excitation does not change in parallel with x-ray dose and energy, but reaches a maximum and then declines rapidly, is not unique to this effect and was also reported for F -light luminescence of alkali halides.¹⁷ This dependence is not well understood and no explanation will be offered. The relative intensities of the re-excited glow peaks change with varying excitation. In order to obtain more infor-

mation different irradiation and bleaching conditions were utilized throughout the work.

It is well known that the thermoluminescence of a crystal is dependent on its thermal history. The relative intensities of various glow peaks undergo considerable changes with heat treatment.¹⁸⁻²⁰ A similarity between aging and re-excitation effects is observed. In potassium bromide (Table I) the peaks at 148 and 136°K become measurable in the X glow of heat treated crystals only. In F and V glow, respectively, these peaks appear in virgin crystals and with a relatively high intensity. The same is true for the 180°K peak in potassium iodide (Fig. 3). This peak is the strongest one in the F glow, even of higher intensity than in the X glow of an aged crystal (Fig. 3, curve a_2'). On the other hand, the peak at 195°K in KI disappears in the X glow after short aging and is also not detectable in the re-excited glow. In sodium chloride (Table III) the peak at 206°K , hardly detectable in the V glow, appears in the X glow of virgin crystals only. All this indicates that x-ray coloration of the crystal influences it temporarily in a manner similar to the way in which aging influences an uncolored crystal.

CONCLUDING REMARKS

The method developed in this study has also been useful in distinguishing between hole and electron processes at temperatures higher than RT and after annealing. It may also prove applicable to other crystals.

It would be very interesting to measure the spectrum of the F and V glows, but their low intensity made it impossible up to this time. Knowledge of the spectrum and the sign of the carrier involved may supplement the information obtained by other methods in solving the problems of the mechanism of phosphors.

ACKNOWLEDGMENTS

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¹² A. Halperin, A. A. Braner, A. Ben-Zvi, and N. Kristianpoller, *Phys. Rev.* **117**, 416 (1960).

¹³ The change in heating rate causes a shift in glow-peak temperatures of about 10% (Ref. 6).

¹⁴ T. J. Hill and P. Schwed, *J. Chem. Phys.* **23**, 652 (1955).

¹⁵ G. Bonfiglioli, P. Brovetto, and C. Cortese, *Phys. Rev.* **114**, 951 (1959).

¹⁶ G. Bonfiglioli, P. Brovetto, and C. Cortese, *Proceedings of the International Conference on Color Centers and Crystal Luminescence, Torino, Italy, 1960* (Litografia E. Gili, Torino, 1961), p. 55.

¹⁷ A. Halperin and A. A. Braner, *International Symposium on Color Centers in Alkali-Halides, Stuttgart, Germany, 1962* (unpublished).

¹⁸ A. Halperin, A. A. Braner, and E. Alexander, *Phys. Rev.* **108**, 928 (1957).

¹⁹ A. Halperin and M. Schlesinger, *Phys. Rev.* **113**, 762 (1959).

²⁰ M. Schlesinger, Ph.D. thesis, The Hebrew University of Jerusalem, 1963 (unpublished).