

## Thermoluminescence of X-Ray-Colored KCl Single Crystals

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Thermoluminescence curves of KCl single crystals have been recorded. Twelve glow peaks were obtained in the temperature range of 90–600°K. The glow peaks seem to show regularity with regard to their peak temperatures, spectral emission and sensitivity to optical bleaching in the *F* band. Effects of aging of the crystals are reported. Activation energies for several peaks as calculated from the results are also given.

### INTRODUCTION

**T**HERMOLUMINESCENCE of colored alkali halides has been studied by many investigators.<sup>1–6</sup> Glow curves were obtained, which exhibited many peaks during the warming up of the crystal. The origin of most of these peaks seems, as yet, to be unknown.<sup>7</sup>

Some investigators have used powder samples for their luminescence glow experiments, which might have complicated the results. Others have restricted their measurements to temperatures above room temperature. In the present work, glow curves were recorded for single crystals of KCl and for a temperature range from liquid-air temperature up to above 600°K.

Well defined peaks were obtained in our experiments, and this enabled us to notice some regularities concerning the grouping of the peaks in the complexity of the glow curves.

Of interest is also the relation found between the process of thermal glow and that of thermal bleaching

of the colored crystals. The latter experiments are to be described in the following paper.<sup>8</sup>

### EXPERIMENTAL

The crystals under examination were placed in a vacuum Dewar system where they could be cooled to liquid-air temperature and warmed up to 700°K. The construction of this system was complicated more than was needed for the glow experiments in order to meet the special requirements of the thermal-bleaching experiments. Details, including also detection, amplification, and recording devices, are therefore given in Paper II.

The specimens used were synthetic single crystals of KCl grown by the Harshaw Chemical Company, from which plates 5×6 mm and about 1 mm thick were cleaved. Irradiation was performed in the dark with the crystal inside the evacuated cryostat. Crystals were put at nearest access (3–4 cm) to the window of a General Electric x-ray tube operated at 45 kvp, 14 ma with a copper target or at 45 kvp, 20 ma with a molybdenum target.

### RESULTS

#### (a) General Features of the Glow Curves

The recorder tracing of a glow curve of a KCl crystal as obtained after 8 minutes of x-irradiation at liquid-air temperature, is reproduced in Fig. 1. It seems advantageous to divide the peaks appearing in the glow curve into four groups: Group *A*—containing the peaks appearing in the temperature range 100–200°K; group *B*—from 200 to 350°K; group *C*—from 350 to 450°K and group *D*—from 450 to 575°K. Each of these groups will be shown to contain three glow peaks. Approximate peak temperatures ( $T_g$ ), as obtained from experiments described below, are given in Table I.

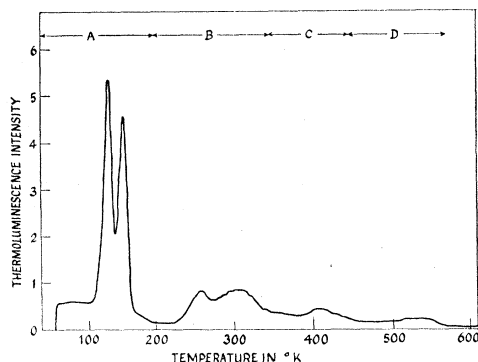


FIG. 1. Recorder tracing of a glow curve of a KCl crystal colored by 8 minutes of x-irradiation (Mo target, 45 kvp, 20 ma) at liquid-air temperature. The crystal had been subjected previously to only a few minutes of x-irradiation. (The heating rate was about 30°/min.)

<sup>1</sup> F. Urbach, Wien. Ber. (IIA) **139**, 353 (1930); F. Urbach and G. Schwartz, Wien. Ber. (IIA) **139**, 483 (1930).

<sup>2</sup> J. A. Ghormley and H. A. Levy, J. Phys. Chem. **56**, 548 (1952).

<sup>3</sup> H. N. Bose, Proc. Phys. Soc. (London) **B68**, 249 (1955).

<sup>4</sup> J. Sharma, Phys. Rev. **85**, 692 (1952); **87**, 535 (1952); **101**, 1295 (1956).

<sup>5</sup> J. J. Hill and P. Schwed, J. Chem. Phys. **23**, 652 (1955).

<sup>6</sup> M. L. Katz, J. Exptl. Theoret. Phys. (U.S.S.R.) **18**, 501 (1948).

<sup>7</sup> See pp. 46, 73 of the review by F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

TABLE I. Temperatures in °K for the different glow peaks of the thermoluminescence curve.

Group	A			B			C			D		
Peak	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>
$T_g$ °K	125	145	170	250	280	315	360	390	415	480	520	560

<sup>8</sup> A. A. Braner and A. Halperin [Phys. Rev. **108**, 932 (1957)], following paper. This paper will be further referred to as Paper II.

In Fig. 1 the first two peaks of group *A* ( $A_1, A_2$ ), are well resolved.  $A_3$  is very weak and appears in this case only as an extended tail of  $A_2$  towards higher temperatures. In group *B* the three peaks can still be noticed. Almost no sign of the individual peaks of groups *C*, *D* can, however, be noticed in Fig. 1.

There are several methods which help to get individual peaks better resolved. One method, frequently used by many investigators<sup>2,5,9,10</sup> is to keep the crystal for some time at a temperature somewhat below the peak to be resolved. Lower peaks are then absent in the glow curve obtained on subsequent cooling and reheating the crystal. This method is particularly successful for the highest peak in each group (e.g.,  $A_3$ ,  $B_3$ ). Other methods will follow from the results to be given.

Remarkable is the regularity in the distribution of the peaks.  $B_1$  peaks at twice,  $C_1$  at three times, and  $D_1$

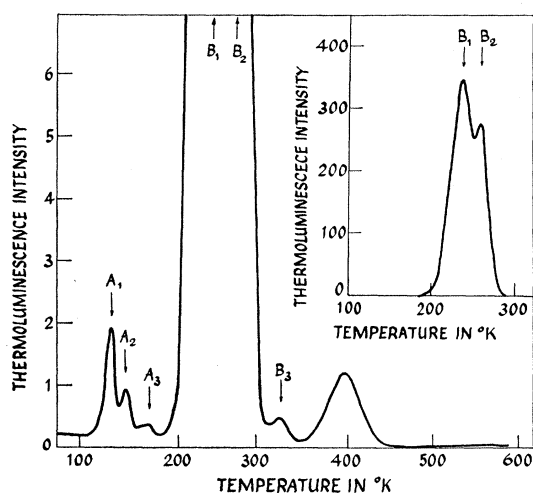


FIG. 2. A glow curve of an aged KCl crystal, having in its history some 50 hours of x-irradiation in about 40 cycles of cooling, x-irradiation, and warming up to 600°K. The enormous increase in the peaks  $B_1, B_2$  is shown by a curve given on reduced ordinates in the upper right corner of the figure. (The heating rate was about 30°/min.)

at four times the peak temperature of  $A_1$  (within experimental error). There is also regularity in the temperature intervals within each group. These are about 25° for group *A*, about 30° for groups *B* and *C*, and about 40° for group *D*.

### (b) Effects of Thermal and Irradiation History of the Crystal

The glow curve shown in Fig. 1 is of the type exhibited by virgin crystals, not subjected to subsequent cycles of irradiation, heating, and cooling. Subjection to many such cycles results in changes in the intensity distribution of the peaks in the glow curve.

<sup>9</sup> C. B. Lushchik, J. Exptl. Theoret. Phys. (U.S.S.R.) **30**, 488 (1956) [translation: Soviet Phys. JETP **3**, 390 (1956)].

<sup>10</sup> J. S. Johnson, Jr., and F. E. Williams, J. Opt. Soc. Am. **39**, 709 (1949).

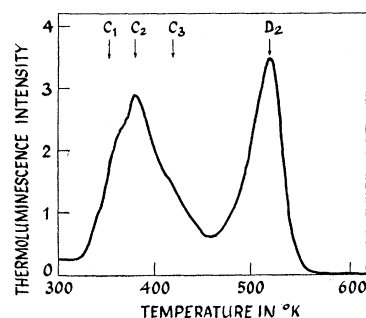


FIG. 3. A glow curve obtained after 3 hours of x-irradiation (Cu target, 45 kvp, 14 ma) at room temperature. (The heating rate was about 30°/min.)

Figure 2 illustrates this effect. It shows the glow curve of an aged crystal which had in its history some 40 cycles and about 50 hours of x-irradiation. The intensity scale in Fig. 2 is about half that in Fig. 1 and the time of irradiation was only 2 minutes compared to 8 minutes for the curve in Fig. 1. The peaks  $B_1, B_2$  (250, 280°K) increased enormously in intensity and are shown on a reduced scale in the upper right corner of the figure. Peaks  $A_3$  and  $B_3$  have also increased and are now clearly seen. Other peaks do not seem to have changed appreciably. These changes depend also on the type of irradiation. More cycles of irradiation and bleaching with a copper target (45 kvp, 14 ma) did not result in such drastic changes in intensity. The effects tend to saturation. Measurements were, therefore, carried out mostly for aged crystals for which results of successive experiments could be compared.

Peaks at higher temperatures appear very weak on short x-irradiation at low temperatures. They can be obtained at higher intensity either by irradiation at higher temperatures, or by prolonged irradiation at lower temperatures.<sup>1,5,11,12</sup>

Figure 3 was obtained after 3 hours of x-irradiation at room temperature. The peaks at 360 and 415°K appear now as shoulders on both sides of the peak at 390° and that at 520° is now the strongest. After 10 minutes of irradiation at above 400°K<sup>13</sup> (Fig. 4) the glow peak at 560°K appears in addition to that at 520°K.

Upon increasing the amount of irradiation in one experiment, the intensity of the peak at the highest temperature is known<sup>1,5</sup> to increase faster than that of

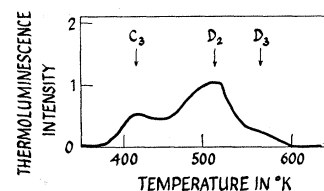


FIG. 4. A glow curve obtained after 10 minutes of x-irradiation at above 400°K (see reference 13). (The heating rate was about 30°/min.)

<sup>11</sup> J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 366 (1945).

<sup>12</sup> E. I. Adirivitsch, *Einige Fragen Zur Theorie der Lumineszenz der Kristalle* (Akademic-Verlag, Berlin, 1953), Chap. VI.

<sup>13</sup> Irradiation was started with the crystal at 500°K, but the temperature decreased to 400°K during irradiation.

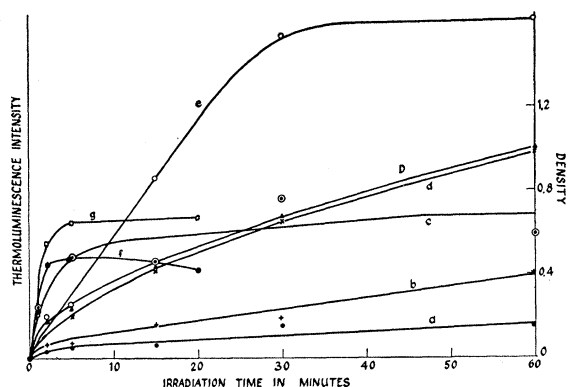


FIG. 5. Dependence of intensities of the different glow peaks on time of x-irradiation, *a*—for the peak at 170°K, *b*—325°K, *c*—125°K, *d*—145°K, *e*—390°K, *f*—280°K, and *g*—250°K. Ordinates for *f* and *g* were reduced by a factor of hundred. Optical densities at the peak of the *F* band are given for comparison (curve *D*).

lower peaks. This was confirmed in our experiments. On irradiation at room temperature the intensity of the peak at 390°K nearly reached saturation after 2 minutes, while that of the peak at 520°K remained very small for the first few minutes of irradiation and then started to rise linearly and showed only a slight deviation from linearity after 14 hours of irradiation.

Dependence of the intensities on irradiation time for crystals irradiated at liquid-air temperature is shown in Fig. 5. Optical densities at the peak of the *F* band are also plotted (curve *D*). The intensity of some of the peaks (145, 170, 315) rises in parallel with the increase in density, some reach saturation after only a few minutes, and others become saturated after longer irradiations. Peaks at higher temperatures (group *D*) were too weak to be measured. The peaks at 250, 280°K, on the other hand, were so intense that attenuation by a factor of hundred was necessary. Their intensities are therefore, given on a reduced scale.

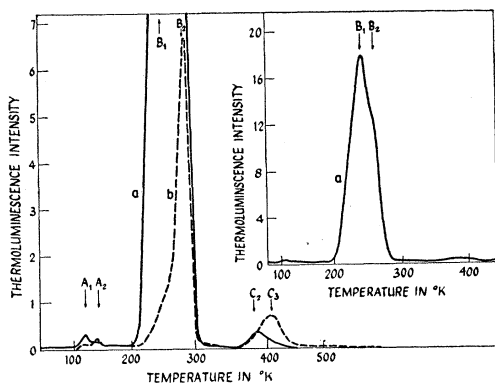


FIG. 6. Glow curves obtained by optical filtering, *a*—transmitted by a Chance OX7 filter (transmitting in the uv, 2500–4000 Å); *b*—transmitted by a Corning 3389 filter (absorbing the uv). (The heating rate was about 40°/min.) Curve *a* is given to the right with reduced coordinates.

### (c) Spectral Classification of the Glow Peaks

The small intensities of light emitted at a given luminescence peak, did not allow measurement of the exact spectral distribution of the light emitted at each peak. Optical filters were, therefore, used for color classification of the different peaks. The results show that the peaks may be classified according to their spectral emission into three groups: ultraviolet, blue, and green, as listed in Table II. The peaks at 170, 360, and 560°K were too weak and were not included in the color classification.

An example of glow curves obtained through filters is given in Fig. 6. Curve *a* was obtained with an ultraviolet transmitting filter (Chance OX7) while for curve *b* an ultraviolet absorbing filter (Corning 3389) was used. The differences in transmission are evident.

The results suggest another method for resolving peaks. Curve *b* in Fig. 6 is a good example.

### (d) Selective Optical Bleaching of Glow Peaks

The effect of irradiation in the *F* band on the glow curves was also studied. Green light (5460 Å) obtained by widely opening the slits of the Beckman DU monochromator, was allowed to fall on the x-irradiated crystal.

Figure 7 shows this effect for irradiation at liquid-air temperature, and Fig. 8 for irradiation at room temperature. It can be seen that the bleaching affects selectively some of the peaks while others (e.g., *A*<sub>2</sub>, *B*<sub>2</sub> and *C*<sub>3</sub>) show stronger resistance to bleaching in the *F* band. The selective bleaching suggests an additional method for resolving peaks.

## CONCLUSIONS

The glow curves obtained in the present work show some complexity, but they are in no way incidental. The regularity shown by the different peaks with regard to color, optical bleaching, and distribution through the temperature range may help in establishing a model to account for the behavior of the different peaks in the glow curves.

Classification of the peaks into groups seems to have deeper meaning for the groups *A* and *B* than just their appearance as separate groups on the glow curves. Both the groups have two intense peaks and a weak third one. The first peak in each group (*A*<sub>1</sub>, *B*<sub>1</sub>), emits in the ultraviolet, while the next emits mainly blue light. This suggests that common transitions are involved in the respective peaks of both the groups. On the other hand, the enormous rise in intensity of the peaks *B*<sub>1</sub>, *B*<sub>2</sub> on

TABLE II. Spectral distribution of the glow peaks for KCl.

<i>T</i> <sub>0</sub> °K	125	145	250	280	315	390	415	480	520
Color	uv	blue	uv	blue	blue	uv	blue	blue	green

aging the crystal was common for both these peaks. These should be attributed rather to an increase in the luminescence efficiency, and not to an increase in the number of electrons or holes involved. That this is so is shown in paper II, where in thermal bleaching experiments it was found that the decrease in density of the  $F$  band which accompanies the glow bursts at 250 and 280°K (the peaks  $B_1$  and  $B_2$ , respectively), was about the same for the aged crystal as for the virgin one.

It will also be shown in paper II that practically all the peaks in the glow curve are accompanied by a decrease in the  $F$  absorption. This gives a strong argument for our assumption that the peaks in the glow curve are not incidental, and they should be attributed to optical transitions between energy levels characteristic to the crystal lattice and to its defects.

Additional work is needed before one tries to give a model for those transitions. It is intended now to measure the spectral distribution of the light bursts emitted for each of the peaks in the glow curve, and a liquid-air-cooled photomultiplier to be attached to the Beckman DU spectrophotometer is designed for this purpose.

It is also of importance to calculate the thermal activation energies for the different peaks. For this purpose each of the glow peaks should be isolated from neighboring peaks. This is being done now by using combinations of the methods indicated in the present paper.

Some of the activation energies were already calculated in preliminary work in this direction. Our calcula-

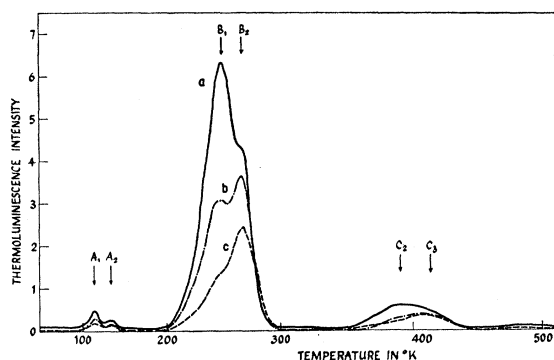


FIG. 7. Selective bleaching of the glow peaks by irradiation in the  $F$  band ( $\lambda 5460$ ),  $a$ —no light,  $b$ —obtained after 10 minutes of  $F$  irradiation,  $c$ —after 30 minutes of  $F$  irradiation. All the curves were obtained with an x-irradiation of 2 minutes, at liquid-air temperature. (The heating rate was about 20°/min.)

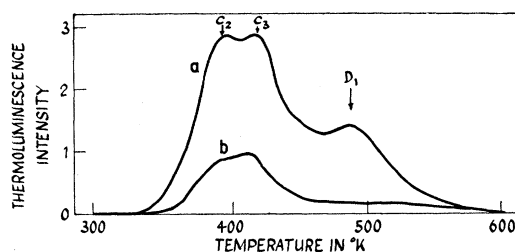


FIG. 8. The same as Fig. 7, but after 5 minutes of x-irradiation at room temperature.  $a$ —no  $F$  light,  $b$ —after 30 minutes of irradiation by  $F$  light. (The heating rate was about 20°/min.)

tions were carried out by a method suggested by Urbach<sup>14</sup> and with some modification due to Lushchik.<sup>9</sup> By this method the activation energy  $E_T$  of a glow burst at the temperature  $T_g$  is given with good approximation by

$$E_T = kT_g^2 / \delta_g,$$

where  $k$  is the Boltzmann constant and  $\delta_g = T_2 - T_g$ ,  $T_2$  being the temperature at half the intensity on the falloff of the peak.

Activation energies calculated by us hitherto were: 0.29 eV for  $T_g = 125^\circ\text{K}$ , 0.33 eV for  $145^\circ\text{K}$ , about 1 eV for  $420^\circ\text{K}$ , and not far from 1.5 eV for  $520^\circ\text{K}$ . These activation energies give for the frequency factor a value of the order of  $10^{10}$ – $10^{11}$   $\text{sec}^{-1}$ , which seems not to differ appreciably for the different peaks.

Our results seem to be in contradiction to those obtained for NaCl crystals by Hill and Schwed,<sup>5</sup> who came to the conclusion that the activation energies were constant for all the peaks in the glow curve (from room-temperature up to  $560^\circ\text{K}$ ). Although our work was on KCl crystals, it is believed that all the alkali halides behave similarly with respect to their glow curves. This was already confirmed in preliminary work on KBr crystals whose glow curves show striking similarity to glow curves obtained for KCl.

Extension of the work on the effect of optical bleaching on the glow curve to bleaching in other  $F$ -type as well as  $V$ -type and  $\alpha$ - and  $\beta$ -type bands is also planned; it is hoped that this will add to our knowledge concerning the processes involved in the thermoluminescence of the alkali halides.

<sup>14</sup> F. Urbach, *Preparation and Characteristics of Solid Luminescent Materials*, Cornell Symposium, New York, 1948 (John Wiley and Sons, Inc., New York, 1948).