

Thermal Activation Energies in NaCl and KCl Crystals

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Thermal activation energies were computed from various glow peaks of NaCl and KCl single crystals. The method developed in the preceding paper has been used successfully in these calculations. Good agreement was obtained with the results calculated from the initial rise of the glow peaks. Activation energies varied from 0.3 to 1.5 eV for various peaks in the glow curve of NaCl between 150 and 500°K. Similar results were obtained for KCl crystals. The kinetics of the processes was found to be nearly of first order.

INTRODUCTION

IN the preceding paper,¹ a method has been developed for the evaluation of thermal activation energies from glow peaks. In the present paper, use is being made of this method for computing the activation energies from the various glow peaks in the glow curves of NaCl and KCl. Activation energies were computed not only by the new method, but also by the method of initial rise.² Comparison of the results obtained by the two methods served as a check for the new method.

Much controversy exists as to the thermal activation energies in general, and those of NaCl in particular. Randall and Wilkins,³ and many other investigators,⁴ assumed the activation energies of the various peaks in a glow curve to be approximately proportional to the peak temperatures of the individual peaks. On the other hand, Hill and Schwed,⁵ and more recently also Bonfiglioli *et al.*,⁶ claimed that all the glow peaks in the glow curve of NaCl have the same activation energy. These authors have gone so far, as to build a model of the transitions involved in the emission of thermoluminescence, based on the assumption of equal activation energies for all the peaks in the glow curve.

It was, therefore, of special interest to concentrate in the present work on the evaluation of the activation energies of NaCl. KCl crystals were also examined, but in less detail. The results, described below, show that though peaks appearing at different temperatures may have the same activation energy this is not the case in general, and activation energies are by no means equal for *all* the glow peaks.

EXPERIMENTAL

The experimental procedure used to record the glow curves was essentially the same as described previously.⁷

¹ A. Halperin and A. A. Braner, preceding paper [Phys. Rev. **117**, 408 (1960)].

² See, for example, W. Hoogenstraaten, Philips Research Repts. **13**, 515 (1958).

³ J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 347 (1945).

⁴ See, for example, G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, Oxford, 1949); also reference 2.

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

⁶ Bonfiglioli, Brovetto, and Cortese, Phys. Rev. Letters **1**, 94 (1958); Phys. Rev. **114**, 951, 956 (1959).

⁷ Halperin, Braner, and Alexander, Phys. Rev. **108**, 928 (1957); A. A. Braner and A. Halperin, Phys. Rev. **108**, 932 (1957).

In brief, the crystal was mounted in a vacuum cryostat, which with the aid of a heating element could be heated up from liquid-air temperature to above 600°K. The light emitted by the crystal reached the detector (RCA IP28 photomultiplier) through a quartz window in the cryostat. The output from the amplifier⁸ was fed to a 50-mV Brown recorder, on which the glow curves were recorded. Temperatures were measured with a calibrated copper-constantan thermocouple with one junction fixed near the crystal, and the other in an ice bath. High speed of the recorder chart (about 2 inches per min) ensured high accuracy in the determination of temperatures at various points in the glow curve. Heating rates were kept within 10–20 deg/min, and with the mentioned speed of the recorder chart, temperature differences within a glow peak could be fixed with an accuracy of about 0.2 deg.

High sensitivity of the amplification system was used in the initial-rise measurements. This enabled high accuracy in the determination of relative intensities of the thermoluminescence at various points on the curves. In fact, for intense glow peaks, less than 1% of the total light sum of the peak was often enough to give an initial-rise curve with intensities from zero up to 100 scale divisions on the chart.

To examine the activation energies at different portions of the glow peaks, the crystal was allowed to cool back to some lower temperature, just when the first initial-rise curve reached the end of the chart (100 scale divisions). The crystal was then warmed up again till a second "initial-rise" curve was obtained from the next portion of the glow peak. Repetition of such cycles resulted in a whole series of initial-rise curves.

The glow peaks of NaCl and KCl have already been shown^{9,10} to appear as complex peaks with components differing from each other in spectral distribution. To reduce the disturbance due to this complexity, glow curves were recorded with optical filters, which separated the components. Perfect separation, however, could not be obtained because the spectral bands were

⁸ A. Halperin and A. A. Braner, Rev. Sci. Instr. **28**, 959 (1957).

⁹ A. Halperin and N. Kristianpoller, J. Opt. Soc. Am. **48**, 996 (1958).

¹⁰ Halperin, Kristianpoller, and A. Ben-Zvi, Phys. Rev. **116**, 1081 (1959).

partly overlapping. In addition, for some of the peaks, there are different components having the same spectral distribution.¹¹

To get a single peak, the lower temperature components had, therefore, to be cleaned away. This was effected by warming up the crystal to a temperature near the maximum of the peak to be measured, when only the higher temperature component remained on cooling back the crystal. The series of initial-rise curves mentioned above was usually obtained as a "by-product" of the cleaning procedure. Some of the crystals were treated thermally, by keeping them for a given period at 500–600°C before they were taken for the measurements. This treatment enhanced most of the peaks.^{10,12} without changing the activation energies. Only long heating periods caused minor changes in the activation energies, which resulted from changes in the relative intensities of the different components within one complex peak. The advantage in using the heat treated crystals was that a very large number of initial-rise curves could be obtained from one peak without using too high amplification.

The crystals used were synthetic KCl and NaCl crystals grown by the Harshaw Chemical Company. They were cleaved into small plates (about 6×7×1 mm). X-irradiation, etc., was as described previously.⁷

THEORETICAL

The theory outlined in the preceding paper¹ provided simple formulas for the evaluation of the activation energy E from the glow peaks. For submodel II treated in that paper, namely for the case of excitation from the trap into the conduction band, the general shape of the formula was

$$E = (q/\delta)kT_g^2(1-\Delta), \quad (1)$$

where k is Boltzmann's constant, T_g —the temperature of the maximum of the peak in °K, δ —the half-width towards the falloff of the peak (see Fig. 3, reference 1), $\Delta = 2kT_g/E$ is a correction factor ($\Delta \ll 1$), and q depends on the shape of the glow peak and on the kinetics of the process. This factor was calculated for a variety of specific cases. For a first-order process q is expressed by

$$q_1 = [1.72\mu_g/(1-\mu_g)](1-1.58\Delta), \quad (2)$$

and for most cases of second-order processes it is given with good approximation by

$$q_2 = [2\mu_g/(1-\mu_g)](1-2\Delta). \quad (3)$$

Here $\mu_g = \delta/w$, where w is the half-intensity width of the peak (Fig. 3, reference 1). The symmetry factor μ_g is characteristic of the type of the kinetics involved in the process. Values of μ_g equal to or smaller than $e^{-1}(1+\Delta)$ should be obtained for first-order processes, while values larger than $e^{-1}(1+\Delta)$ (and usually of

about 0.5) correspond to second-order processes. It should, however, be noted that weak shoulders at the high-temperature side of the peak will result in an apparent increase in the μ_g values, and care should be taken not to misinterpret such high μ_g values as indicating a second-order process. Nevertheless, the μ_g values give valuable information regarding the nature of the kinetics.

Formulas (2) and (3) can be further simplified by introducing the half-width at the low-temperature side of the peak: $\tau = w - \delta$. Substitution of τ and $\mu_g = \delta/w$ in the formulas will then result in the following working formulas:

$$E_1 = (1.72/\tau)kT_g^2(1-2.58\Delta), \quad (4)$$

for first-order processes, and

$$E_2 = (2/\tau)kT_g^2(1-3\Delta), \quad (5)$$

for second-order processes. Expressions containing higher powers of Δ have been neglected.

Only the values of τ and T_g are needed for the evaluation of the activation energies by Eqs. (4) and (5), and these are readily obtained from the recorded glow peaks. An advantage of this method is that the first half of the peak is sufficient for the evaluation of E , so that shoulders due to satellites towards higher temperatures do not influence the calculated E values, provided that the disturbing peaks are not as strong as to change the peak temperature.

The method of initial rise, which was used for comparison of the results, is based on the fact that for all types of kinetics, the intensity of thermoluminescence can be expressed in the form of

$$I = F \exp(-E/kT), \quad (6)$$

where F is a function of the number of full traps and that of empty centers, and contains also the probabilities of the transitions involved.¹³ F can be taken as constant for the initial part of the glow peak, when the change in the numbers of trapped carriers and empty centers may be neglected. We obtain then

$$\ln I = -E/kT + \text{constant}, \quad (7)$$

and plotting $\ln I$ versus $1/T$ should give a straight line, from the slope of which E is readily calculated.

RESULTS

(i) NaCl

The glow curves of the NaCl crystals examined in the present work have already been described.¹⁰ The main peaks were found to appear at 170, 235, 335, and at about 500°K.

We start with the peak at about 170°K. The wavelength of the main spectral band emitted in this region is about 0.36 μ (see reference 10) in crystals not treated

¹¹ See in the results below; also in reference 10.

¹² A. Halperin and M. Schlesinger, Phys. Rev. **113**, 762 (1959).

¹³ For the form of F see, for example, Eqs. (1.4) and (5.2), reference 1.

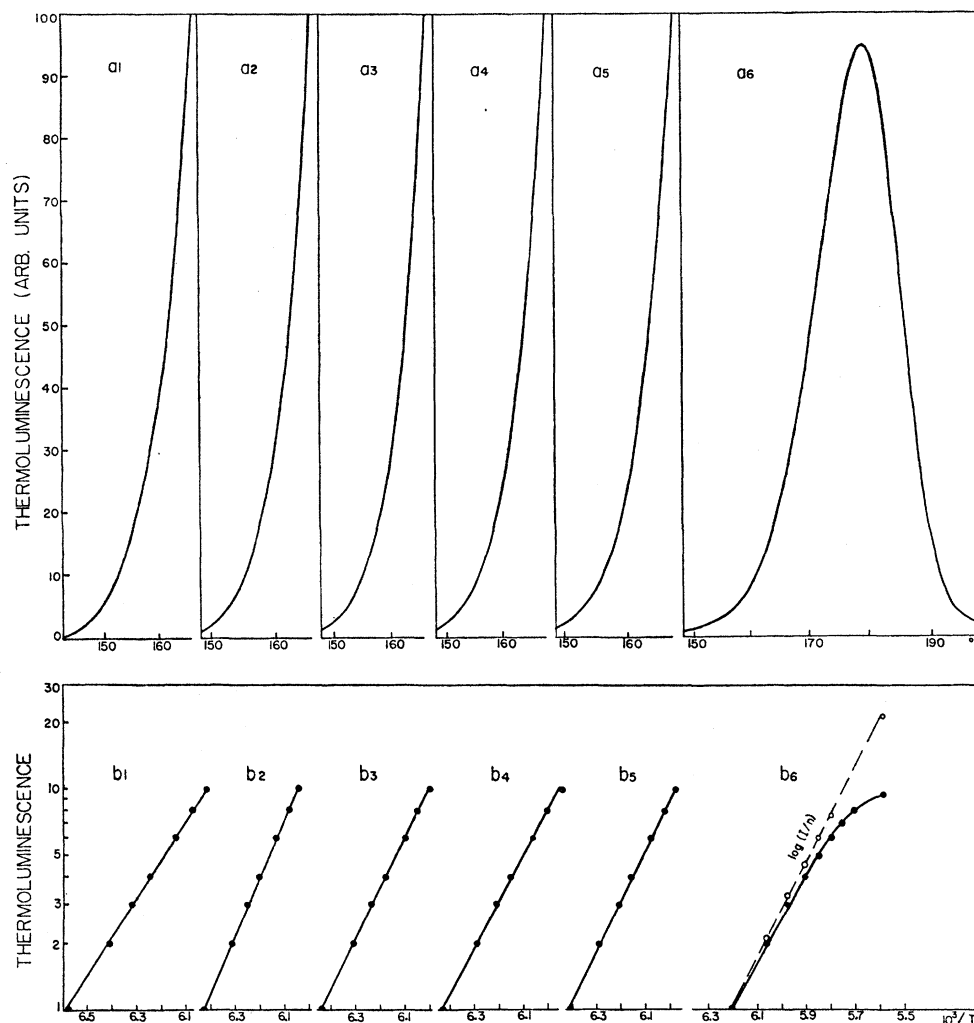


FIG. 1. (a) A series of initial rise curves and glow peak for NaCl at 170°K. (b) The corresponding $\ln I$ versus $1/T$ plots.

thermally. After long periods of heat treatment a band above 0.40μ with a glow maximum at about 155°K becomes the dominating one. An ultraviolet transmitting filter (Chance 0X1) was inserted in front of the photomultiplier in order to eliminate the visible components of the glow.

A set of measurements with this arrangement is shown in Fig. 1(a), in which a series of initial-rise curves is given, including the final cleaned glow peak. The corresponding $\ln I$ versus $1/T$ plots are given, in the same order, in Fig. 1(b). All but the last curve form straight lines while the last one starts to curve on nearing the peak when the assumption $F = \text{constant}$ in Eq. (6) does not hold anymore.

Activation energies computed from the slopes of the curves were: 0.35, 0.51, 0.46, 0.41, 0.46, and 0.42 for curves 1 to 6 in Fig. 1(b), respectively. The value is considerably smaller on the beginning (0.35 ev), and fluctuates afterwards (probably due to experimental error) about the value 0.45 ev. The existence of a

component with a lower activation energy was indicated more clearly in some cases, when the $\ln I$ plots showed distinct deviations in slope on passing from the lower activation-energy components to the rest of the glow. An example is shown in Fig. 2. Here plots 1 to 4 belong to the first four initial rise curves out of a series of 13. In curve (1) there is a transition in slope from an activation energy of 0.30 ev to a higher one of 0.38 ev. The points on the next 3 curves of Fig. 2 fit well the straight lines with activation energies of 0.44, 0.42, and 0.42 ev. All the other members of this series (fifth to thirteenth) gave activation energies within the limits 0.42–0.48 ev.

Measurements were also taken with a combination of filters transmitting in the violet only (Wratten 34A+2B). Thermally untreated crystals gave practically the same results with the uv transmitting filter, and it seems that in these crystals only the tail of the 0.36μ band was measured. The results, however, differed for crystals submitted to prolonged heating

TABLE I. Results of initial-rise and glow-curve experiments for the 170°K peak in NaCl. Columns 2–5 give the experimental parameters obtained from the glow peaks. E_1 , E_2 , E , and E_0 stand for the thermal activation energies as obtained using formula (4), formula (5), the initial-rise method, and the Urbach-Lushchik formula, respectively.

	μ_g	$\tau^\circ\text{K}$	$T_g^\circ\text{K}$	Δ	E_1 ev	E_2 ev	E ev	E_0 ev
1	0.43	8.3	175	0.06	0.46	0.51	0.47	0.38
2	0.44	9.0	179	0.06	0.45	0.50	0.41	0.36
3	0.49	8.5	180	0.06	0.52	0.58	0.52	0.34
4	0.39	9.4	180	0.06	0.43	0.48	0.44	0.43
5	0.42	9.9	174	0.06	0.37	0.42	0.34	0.33
Average (20 measurements)	0.427	8.5	178	0.06	0.46 ± 0.02^a	0.52 ± 0.02^a	0.44 ± 0.02^a	0.40

^a Standard deviation based on 20 measurements.

periods. The first out of a series of initial-rise curves gave now a considerably higher activation energy, and the value dropped for the later curves in the series. This is shown in Fig. 3, in which activation energies are given as function of the fraction of the total light sum of the glow already emitted before the given measurement. Curve *a* (Fig. 3) was obtained with the uv transmitting filter, and curve *b* with the violet transmitting one. The crystal was in this case pretreated for 66 hours at 600°C. The two curves differ on the beginning but approach each other at the later part of the glow. It seems that the higher activation energy belongs to the violet peak at 155°K, which is exhausted first. The remaining part of the glow seems to belong to the 0.36 μ component, whose tail towards longer wavelengths is to some extent transmitted by the violet filter (W34A+2B).

We turn now to the activation energies computed from the formulas (4) and (5). The glow peaks obtained at the end of each series of initial-rise curves were usually used for these computations. Results for the peak at 170°K are summarized in Table I. Five typical examples are given in lines 1–5, after which the average obtained from 20 independent measurements is given. Activation energies obtained by the method of initial rise are given for comparison under E , and values obtained by the previously developed formula for first order kinetics⁷ ($E_0 = kT_g^2/\delta$) are given in the last column.

The E_0 values are the lowest and give the largest

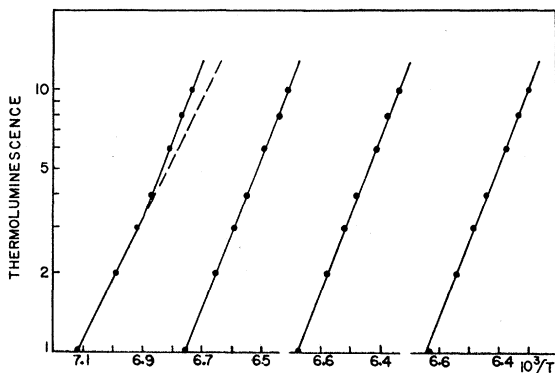


FIG. 2. The first 4 initial rise curves out of a series of 13 for NaCl at 170°K. Curve (1) exhibits a transition in slope.

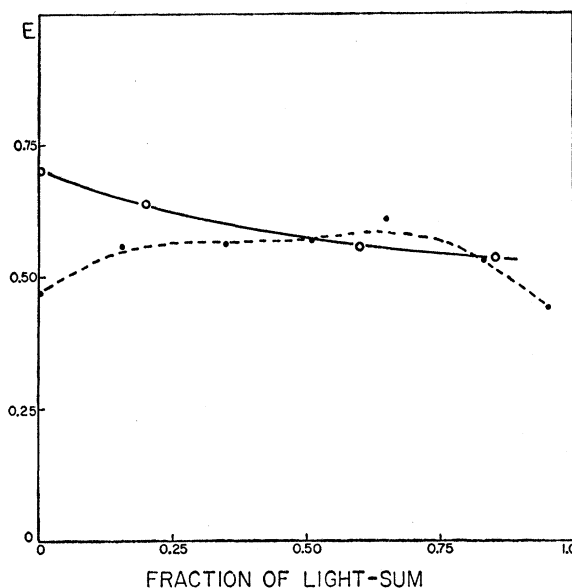


FIG. 3. The activation energy of a NaCl glow peak at 170°K as a function of the light sum emitted prior to each measurement in a series of initial rise curves. (a) dashed curve with an uv transmitting filter, (b) full curve with a violet transmitting filter.

scattering (see also Table III). The average values for the activation energy were found to be: 0.44 eV by the method of initial rise, 0.46 eV assuming first-order kinetics, and 0.52 eV on assuming second-order kinetics, each with a standard deviation of ± 0.02 eV. This indicates that the process is of first order, an assumption which is further supported by the comparatively low μ_g values.

The average value was found to be below 0.43. Assuming $\rho=1$ (see preceding paper), a μ_g value of about 0.40 corresponds to first-order kinetics, and $\mu_g=0.53$ to second-order kinetics. Taking in account that the measured μ_g values are affected by shoulders towards higher temperatures (e.g., example 3, Table I), so that the true μ_g values are still lower, we conclude that the kinetics is nearly of first order.

More evidence for this view is obtained from the initial-rise curves. As stated above, the $\ln I$ versus $1/T$ curves should deviate from the straight line on nearing the peak, when F can no more be considered as constant. For first order kinetics, however, $F_1 = F/n$ should then

TABLE II. The variation of activation energy in a series of initial-rise experiments in NaCl. Column I the activation energy of the first member, II and III—middle members IV—last members of the series.

I	II	III	IV
0.61	0.65	0.67	0.72
0.49	0.52	0.70	0.67
0.51	0.65	0.81	0.71
0.56	0.67	0.74	0.69
0.57	0.67	0.67	0.77
0.54	0.64	0.71	0.65

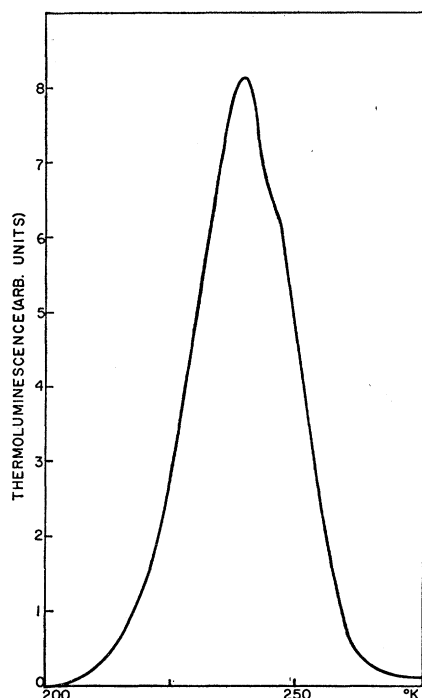


FIG. 4. A glow peak of NaCl at 235°K exhibiting a shoulder to the high-temperature side, which resulted in an apparent μ_g value of 0.49.

be constant. This was indeed found to be the case as shown in Fig. 1(b) curve 6. Here the dashed line describes $\ln(I/n)$ as function of $1/T$, and the resulting straight line is characteristic of first-order kinetics.

The glow burst at 235°K emits an almost pure uv band ($\sim 0.36 \mu$). No filters other than the uv transmitting one (OX1) were therefore used for this glow peak.

Using the initial-rise method as before revealed again a spread in activation energies within the glow peak. The E value obtained from the first initial-rise curve in a series was usually smaller compared to those obtained in the middle of the series. In most cases there was a decrease towards the end of the series. Examples are shown in Table II. Only four typical values of each series are given in the table. These include the first (under I), two values picked out from the middle of the series (under II and III), and the value obtained from the last curve in the series (under IV). The E values were above 0.5 ev for the first curve in a series, about 0.70 ev in the middle (the value 0.81 ev in example 3, Table II was a rare extreme case), and somewhat lower towards the end of the series.

The completed glow peaks at the end of each series were used, in addition, for evaluation of the activation energies from formulas (4) and (5). A few examples are given in Table III, and average values obtained from 24 measurements are given in the bottom of the table. Arguments similar to those given above on discussing the peak at 170°K, lead again to the conclusion that the process is nearly of first order. The average of the μ_g values was now nearly 0.45 compared to about 0.43 for the peak at 170°K. This, however, seems to have been caused by a more pronounced shoulder on the high-temperature side of the peak, and so does not indicate that the process is nearer to a second-order one. Figure 4 shows an example of the peak with a shoulder which caused a measured value of $\mu_g = 0.49$ (see example 5, Table III).

The peaks at and above room temperature were mostly too weak to be separated into components by using filters. The number of initial-rise curves in a series was therefore small, and a few hours of x-raying (at 45 kvp, 14 ma, Cu target) were needed to get more than two or three initial-rise curves in a series.

Results are summarized in Table IV. Average values are given for the peaks at 300, 335, and 490°K, and values for the peaks at lower temperatures are also repeated for convenience. In addition, extreme experimental values for the activation energies are given in brackets to give an idea of the spread. For the E values obtained from initial-rise curves, the spread includes all the members of the series. Only the last one, however, was taken in calculating the average E

TABLE III. Results of initial-rise and glow-curve experiments for the 235°K glow in NaCl.

	μ_g	$\tau^\circ\text{K}$	$T_g^\circ\text{K}$	Δ	E_1 ev	E_2 ev	E ev	E_0 ev
1	0.43	10.2	242	0.06	0.71	0.81	0.72	0.61
2	0.425	9.8	243	0.06	0.76	0.86	0.67	0.66
3	0.47	10.6	245	0.06	0.71	0.80	0.71	0.51
4	0.46	11.7	235	0.06	0.59	0.67	0.49	0.45
5	0.49	12.4	240	0.07	0.61	0.66	0.63	0.40
6	0.44	10.3	237	0.06	0.68	0.76	0.63	0.55
Average (24 measurements)	0.447	10.8	241	~ 0.065	0.67 ± 0.02^a	0.75 ± 0.02^a	0.67 ± 0.02^a	0.53

^a Standard deviation based on 24 measurements.

TABLE IV. Summary of the results for the various glow peaks obtained with NaCl. The figures in brackets are the extreme values obtained in the different measurements.

T_g °K	μ_g	τ °K	Δ	E_1 ev	E_2 ev	E ev	Number of measurements
178	0.427	8.5	0.06	0.46 ± 0.02 (0.32–0.54)	0.52 ± 0.02 (0.36–0.61)	0.44 ± 0.02 (0.29–0.57)	20
241	0.447	10.8	0.06	0.67 ± 0.02 (0.53–0.76)	0.75 ± 0.02 (0.60–0.86)	0.67 ± 0.02 (0.43–0.86)	24
298	0.43	12.8	0.06	0.89 ± 0.02 (0.84–0.95)	1.00 ± 0.03 (0.94–1.07)	0.93 ± 0.05 (0.80–1.23)	6
339	0.43	13.3	0.05	1.12 ± 0.03 (0.86–1.28)	1.26 ± 0.04 (0.96–1.46)	1.12 ± 0.05 (0.78–1.47)	20
491	0.47	23.4	0.06	1.33 ± 0.03 (1.18–1.49)	1.51 ± 0.04 (1.33–1.68)	1.45 ± 0.06 (1.21–1.72)	10

value and the standard deviation, to enable comparison to the values obtained from formulas (4) and (5), which of course were obtained from the completed glow peak at the end of each series. Standard deviations are not given for T_g and τ , for both depend to some extent on the rate of heating and on the dose of x-rays to which the crystal has been subjected.

The behavior of the peaks above room temperature is generally the same as for the low-temperature ones, except for the peak at 490°K which exhibits a higher μ_g value. This is again partly due to high-temperature shoulders, but seems to indicate also a partly second-order process. This is shown also in Fig. 5, in which $\ln I$, $\ln(I/n)$, and $\ln(I/n^2)$ are plotted *versus* $1/T$. Deviations from the straight line indicate a process of an order higher than one though still lower than two. Some mixture of a second-order process could be noticed also for the peaks at lower temperature (e.g., at 350°K) but it was less pronounced.

(ii) KCl

KCl crystals were investigated in less detail than NaCl. The glow curves of the KCl crystals examined in the present work are described elsewhere.⁷ Their behavior, as far as it concerns the activation energies, is similar to that of NaCl as described in section (i) of the present work. In some cases, the spread in activation energies at a given temperature region was still larger than with NaCl. For the glow burst at about 250°K (which is in fact composed of at least three peaks emitting different wavelengths, see reference 9), activation energies in one series of 5 initial-rise curves were: 0.38, 0.52, 0.59, 0.63, and 0.80 ev. In general, however, the spread was considerably smaller than in this extreme example.

A summary of the results on KCl is presented in Table V. Data are given for the peaks at about 125, 140, 260, 360, and 390°K. The number of measurements was for some of the peaks too small to give standard deviations. The figures in the table give therefore in these cases only a rough indication of the error. As with NaCl, the μ_g values were slightly affected by shoulders at the high-temperature side of the peak. All the arguments mentioned in the case of NaCl lead

again to the conclusion that the process is nearly a first-order one.

DISCUSSION

The experimental results described in the present paper show good agreement between the activation energies determined by the method developed in the preceding paper and between those obtained by the method of initial rise. The new method gives no information about the spread of energies within a given glow burst as the method of initial rise does. Activation energies are, however, more readily obtained by the new method, and with better accuracy (see Tables IV and V). In addition, the type of the kinetics of the process is indicated by the symmetry of the

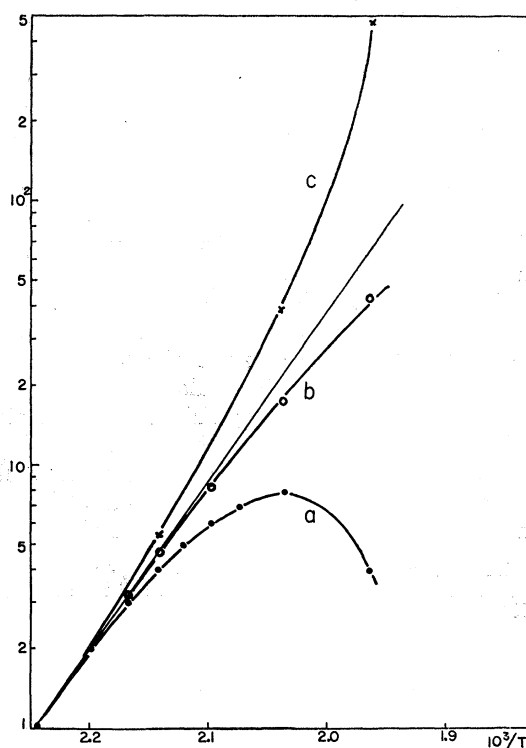


FIG. 5. A glow peak of NaCl at 490°K plotted *versus* $1/T$ with: (a) $\log I$, (b) $\log(I/n)$, and (c) $\log(I/n^2)$ in the ordinate.

TABLE V. Summary of the results for the various glow peaks obtained with KCl. The figures in brackets are the extreme values obtained in the different measurements.

$T_g^\circ\text{K}$	μ_g	$\tau^\circ\text{K}$	Δ	E_1 ev	E_2 ev	E ev	Number of measurements
126	0.425	6.9	0.09	0.26 ± 0.01 (0.22–0.27)	0.28 ± 0.01 (0.25–0.30)	0.24 ± 0.01 (0.20–0.26)	6
142	0.44	6.2	0.07	0.40 ± 0.01 (0.38–0.42)	0.44 ± 0.01 (0.42–0.46)	0.38 ± 0.03 (0.33–0.42)	3
262	0.47	11.2	0.06	0.77 ± 0.05 (0.68–0.85)	0.87 ± 0.05 (0.76–0.94)	0.72 ± 0.03 (0.38–0.80)	4
362	...	15.1	0.05	1.18 ± 0.06 (1.02–1.38)	1.32 ± 0.07 (1.06–1.57)	1.20 ± 0.07 (0.98–1.56)	7
392	0.42	19.2	0.06	1.0 ± 0.1 (0.85–1.17)	1.15 ± 0.1 (0.95–1.32)	0.9 ± 0.1 (0.81–1.03)	3

peaks as given by the μ_g value. However, effects of shoulders on the falloff of the glow peak should be eliminated when measuring the μ_g value. The method has already been applied¹⁴ successfully for the glow curves of ZnS crystals, in which case a typical second-order process was indicated. For NaCl and KCl, on the other hand, from the results of the present work, it appears that the process is nearly a first-order one, apparently with some tendency towards a second-order process for the peaks at higher temperatures. These results seem to be in agreement with Lushchik's¹⁵ who concluded that for all the alkali halides examined by him the probability for recombination was found to be large compared to that of retrapping, which is equivalent to a first-order process. It is, however, in contradiction to Bonfiglioli *et al.*⁶ who assumed a second-order process for the thermoluminescence of NaCl.

Other implications of the model given by Bonfiglioli *et al.* seem also not to be in agreement with our results. It has already been shown¹⁰ that different peaks in the glow curve often emit the same wavelength, while according to Bonfiglioli each peak must have its own wavelength. Our results in the present work do not verify another implication of that theory, namely that of a unique E value for all the peaks. It is difficult to explain why our *experimental* results differ from those obtained *experimentally* by Bonfiglioli as well as by Hill and Schwed,⁵ who obtained the same activation energy for all the peaks. It should first be noted that the value 1.28 eV obtained by Hill and Schwed differs considerably from the 0.72 eV obtained by Bonfiglioli. Both the mentioned investigators restricted their measurements to above room temperature. The range of activation energies, from about 0.3 to about 1.5 eV

in our measurements, was therefore reduced to 1.25–1.5 eV, which in light of the large spread of energies within each peak might explain the results obtained by Hill and Schwed. In fact, it happened often in our measurements that the activation energy on the beginning of a peak at some higher temperature was within the range of values obtained at some lower temperature (see Tables). The discrepancy between the value obtained by Hill and Schwed and that obtained by Bonfiglioli might, therefore, be explained on assuming that the latter measured the very initial rise of the glow peaks only, while the former did take points nearer to the maximum of the peak for the initial-rise curves.

It is an advantage of our method that the peaks should not necessarily be well isolated. An example was shown in Fig. 4, where good results were obtained in spite of the satellite towards higher temperatures. Also weak satellites to the lower temperature side do not interfere as long as they do not affect the half intensity point on this side of the peak. This is not the case with the initial-rise method, where such interference may lead to erroneous results.

Grossweiner¹⁶ has given a formula for the calculation of trap depths in first-order glow curves, which is similar to our formula (4). Our formulas are, however, more general as they cover various types of kinetics, and they seem to be more accurate as they include also the correction factor Δ . In addition, it should be borne in mind that the formulas used in the present work are only specific cases [and in case of formula (5) only an approximation] of the more general equations developed in the preceding paper.

ACKNOWLEDGMENT

We acknowledge with thanks the help of Mr. J. Ogdan in taking some of the glow curves.

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