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# Thermoluminescence in Lithium Fluoride*

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Thermoluminescence has been studied in LiF crystals which were produced by a variety of growth conditions. X-ray, $Co^{60}$ gamma-ray, and/or optical excitation have been used to both populate and/or produce defects. Collectively, as many as 28 different glow peaks are observed in the range 20–550°K. However, in any one sample only about 15 of these peaks occur. The glow curves cover a range in intensity, the ratio of the strongest to weakest peaks is about $10^4$, and the strongest thermoluminescence occurs near 140°K. No one glow peak is common to all samples. Some of the factors which determine the presence or absence of a glow peak are discussed. The activation energies of the major peaks have been determined by several methods. The four peaks at 115, 147, 154, and 255°K, and possibly others, follow first-order kinetics. Typical peak temperatures (°K), pre-exponential factors ($sec^{-1}$), and activation energies (eV) are 119, $2.7\times10^{10}$, 0.28; 133, $3.1\times10^{3}$, 0.14; 147, $8.3\times10^{3}$, 0.17; 158, $3.4\times10^{7}$, 0.29; 194, $1.8\times10^{6}$, 0.31; 255, $4.7\times10^{8}$, 0.53. The peaks at 115, 158, 194, and 255°K, and possibly others, result from electron untrapping, since they can be populated by both x irradiation and by electrons released upon irradiating a colored crystal with *F*-band light. The peak at 68°K has been observed only after optical re-excitation. Several of the glow peaks have been corelated with impurities, ESR data, etc. These corelations suggest specific models for the defects associated with particular glow peaks. The peak at 115°K appears to result from the *H* center. The peak at 133°K is impurity-sensitive and is probably caused by the untrapping of a hole from the $V_K$ center. A Mg impurity produces peaks between 430 and 490°K, whereas Mn, Ti, Zr, or Ce merely enhance the 133°K peak.

## I. INTRODUCTION

THERMOLUMINESCENCE and thermally stimulated currents in lithium fluoride have been observed by many authors.[1–12] The reported results differ greatly. Factors which might contribute to these differences are the effects of impurities, detector sensitivity, and differences in heating rates used during the observation of the glow peaks. In this work an attempt is made to clarify some of the ambiguities previously reported.

Comparisons of the work of different authors is confusing, most often because they have used different heating rates for glow-curve measurement. Typically, the temperature of a glow maximum may change as much as 25°K when the heating rate is changed from 0.5 to 20°/min. Consequently, to effect comparisons between this work and previously published results, the dependence of peak temperature on heating rate has been determined. Also, detailed measurements have been made on the shape, activation energy, and untrapping kinetics of the larger peaks.

An example of isothermal-decay analysis will be presented for one crystal, and the activation energies derived from this are compared with those found from different types of analyses[13] of glow curves. Comparison of glow curves and ESR data provides some specific models for the untrapping processes associated with some of the glow peaks. From these results and experiments using additively doped crystals, it is concluded that the major glow peaks arise from intrinsic shallow trapping levels. LiF thermoluminescence results were compared with those obtained using other alkali halides under the same conditions. Evidence was obtained indicating that in the various alkali halides a correlation exists between lattice parameter and the temperature at which each specific defect releases its charge.

## II. EXPERIMENTAL

Thermoluminescence measurements in the range 15 to 320°K were performed in the apparatus described by McSweeney, Levy, and Townsend.[14] Heating rates from 0.5 to 15°K/min were used. At rates of less than 12°K/min the slope of the heating curve was constant to better than 2%. The deviations in temperature from the desired temperature-versus-time curve were less

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TABLE I. A summary of glow peaks in LiF.[a]

| Crystal | Supplier and method of growth | Irradiation treatment | Range of measurement | Nominal-peak temperature measured at 6°K/min | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 26 | 29.5 | 35.5 | 46 | 54 | 68 | 115 | 122 | 133 | 147 | 158 | 175 | 194 | 202 | 225 | 255 | 275 | 294 | 315 | 338 | 370 | 400 | 417 | 440 | 453 | 483 | 500 | 550 |
| 2 | Harshaw | uv light at 80° following $\gamma$ irradiation at 300° | 80–300 | | | | | | | | | | (150) | | | X | ? | X | X | X | | | | | | | | | | | |
| 17 | Harshaw | x ray at 10° | 10–280 | X | X | X | X | X | | | | | X | | | | ? | X | X | X | | | | | | | | | | | |
| | | Re-excited with uv at 10° | 10–120 | | ? | | X | | X | X | | | | | | | | | | | | | | | | | | | | | |
| 21 | Semi-Elements Mg doped | $\gamma$ ray at 80° | 80–570 | | | | | | | X | | X | ? | | | X | | X | X | X | X | ? | (355) | | X | | X | X | X | X | X |
| | | x ray at 80° | 80–320 | | | | | | | X | | X | | | | X | | X | X | X | X | | | | | | | | | | |
| | | x ray at 185° | 185–320 | | | | | | | | | | | | | X | | X | X | X | X | | | | | | | | | | |
| | | x ray at 220° | 220–320 | | | | | | | | | | | | | | | | X | X | X | | | | | | | | | | |
| 26 | Semi-Elements Mn doped | x ray at 80° | 80–270 | | | | | | | X | | X | X | X | | X | | | X | | | | | | | | | | | | |
| | | Re-excited with uv 80° | 80–270 | | | | | | | X | | | | X | | X | | | | | | | | | | | | | | | |
| | | $\gamma$ ray at 80° | 80–570 | | | | | | | X | | | X | | | X | | | X | | X | X | X | X | X | X | ? | | | ? | |
| 26 A | Semi-Elements Mn doped | x ray at 80° | 80–320 | | | | | | | X | | X | X | | | X | | | X | | | | | | | | | | | | |
| 30 | Mervyn Instruments—under $N_2$ | x ray at 80° | 80–300 | | | | | | | X | X | X | X | X | X | X | | (236) | | X | | | | | | | | | | | |
| | | Re-excited with uv at 80° | 80–300 | | | | | | | X | | | | X | | X | | | | | | | | | | | | | | | |
| | | $\gamma$ irradiated $5\times10^6$ R at 300°K | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | x ray at 80° | 80–300 | | | | | | | X | | X | X | | X | X | | (242) | | (258) | (284) | | | | | | | | | | |
| | | Re-excited with uv at 80° | 80–300 | | | | | | | X | | | (150) | | | ? | | | | ? | | | | | | | | | | | |
| 32 | Harshaw —under A and zone refined | $\gamma$ ray at 80° | 80–570 | | | | | | | | | | X | | ? | | X | ? | X | | X | X | X | ? | ? | X | ? | ? | ? | | |

[a] The question mark (?) signifies a shoulder or weak signal.

than ±0.2°K. Slightly larger errors occur at higher heating rates. Measurements were also made between 77 and 500°K in a manually controlled furnace.

Crystals from the following sources were used: (1) Harshaw LiF cleaved from a single block; (2) crystals grown under different conditions by Mervyn Instruments Ltd.; (3) additively doped crystals prepared by Semi-Elements Inc.

Crystals which were reasonably free from steps on the surfaces were obtained by cleaving them at 100°C. Gamma irradiations were performed in a $Co^{60}$ source at $2.2\times10^5$ R/h. X irradiations were obtained from a 63-kV peak tungsten anode tube which produced a flux of 266 R/h at the specimen. Optical illuminations were made with a low-pressure mercury arc which was filtered for selected wavelength ranges.

## III. RESULTS

### A. Introduction

The thermoluminescence curves from various crystals show considerable differences and the results from two specimens are presented in Fig. 1. Number 32 is a zone refined crystal from Harshaw and No. 21 is a magnesium-doped crystal made by Semi-Elements. There are obviously a large number of unresolved glow peaks within each curve. Resolution of the curve into component peaks is possible because the heights of the glow peaks present differ relative to one another. The glow peaks are sensitive to the radiation dose, impurities, manufacturer, and even vary for crystals cut from a single block. As many as 28 different glow peaks occur in the range 20–550°K, and about 15 occur in a typical sample. Not even one of the peaks is common to all samples. The observed glow peaks and examples of their occurence in different samples are summarized in Table I.

### B. More Detailed Results

To specify a peak in the following the value given refers to the maximum temperature $T_m$ of a peak produced with a heating rate of 6°K/min. An example of the change of $T_m$ with heating rate is shown in Fig. 2.

Glow peaks were produced, upon heating, after either x or gamma irradiation. In some instances glow peaks could be reintroduced into the crystals by cooling the crystal (after the initial irradiation and heating) and illuminating with light. This has been termed re-excitation. Examples of both types of spectra are presented in Fig. 3 for crystal No. 26 after x irradiation and after re-excitation with light at 2537 Å.

The results in different temperature ranges are given below, in general without comment, and will be discussed in a later section.

#### *1. The Range 15 to 100°K*

In this temperature range the resolution of peaks is very sensitive to the heating rate. In order to resolve

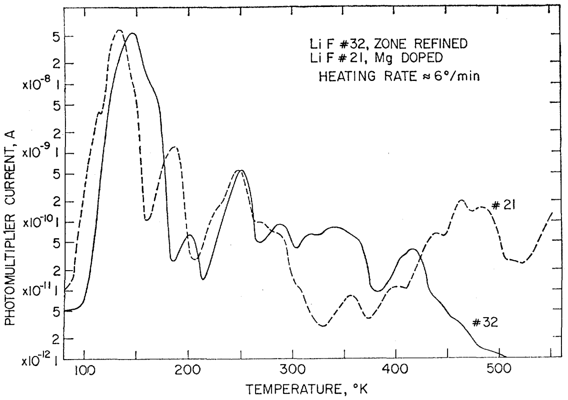

FIG. 1. Typical glow curves obtained from LiF crystals irradiated at 80°K with $10^4$ R of $Co^{60}$ gamma rays. The warm up rate was 6°K/min.

them it is essential to use very low warm up rates. For example, following x irradiation at 10°K, the spectrum can be resolved into six peaks at 20.8, 22.2, 24.0, 26.6, 31.2, and 34.0°K using a heating rate of 0.86°K/min, whereas at the higher rate of 6°K/min only 4 maxima are observed. The 2 peaks at 46 and 68°K are particularly interesting. In crystal No. 17 (see Table I) re-excitation of the glow peaks by irradiation with light in the F absorption band produces strong maxima near 46 and 68°K. Note that the 68°K peak was not observed in the x-ray-induced luminescence.

### *2. The Range 100 to 120°K*

In this range the peak near 115°K varies from 111 to 119°K in different samples, it is produced both by x and gamma irradiation, and is reintroduced by *F*-band light.

### *3. The Range 120 to 160°K*

The most intense observed thermoluminescence signal occurs near 147°K and results from the superposition of several strong glow peaks at 133, 147, and 158°K (see Fig. 1) which vary in relative intensity. In some of the spectra obtained it is possible to find cases where each of these three peaks is completely resolved. In more complicated spectra, selective annealing has been used to confirm which of the peaks are present. The 133°K peak appears to be influenced by impurities. It is the most intense peak observed in crystals 21, 26, and 26A which are additively doped with divalent cations, and in No. 35, a Ti-doped sample, it is the only glow peak in this temperature range.

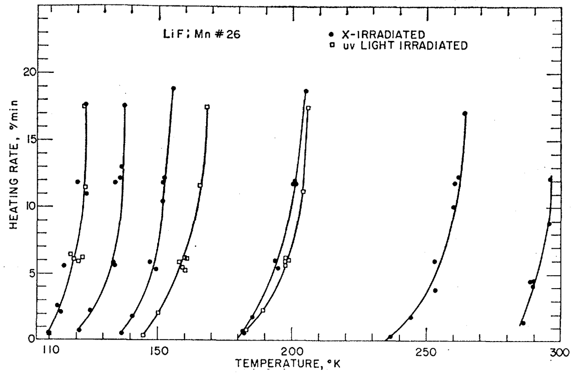

FIG. 2. The position of the glow-peak maxima, $T_m$, obtained as a function of heating rate. X-ray or uv-light irradiations were made at 80°K.

### *4. The Range 160 to 230°K*

The small peak at 202°K occurs in all the Harshaw crystals except the one grown in vacuum and is absent in crystals from all other sources. (This observation will be discussed later.) There appears to be a close connection between some of the peaks. Inspection of Table I reveals that following x or gamma irradiation the 194°K peak occurs only when a peak occurs at 133°K. The intensity of the 133°K peak is usually 30 times stronger than the 194°K peak. Re-excitation with *F*-band light introduced the 194°K but not the 133°K peak.

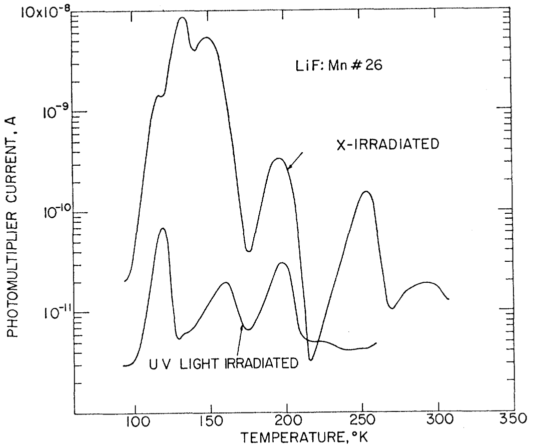

FIG. 3. A glow curve produced in LiF:Mn by x irradiation at 80°K and warming to 300°K and the glow curve produced by recooling the crystal to 80°K and irradiating it with light in the *F* absorption band. Both measurements were made at 6°K/min.

### *5. The Range 230 to 320°K*

The peak at 255°K is the largest in this region after x irradiation or by re-excitation with *F*-band light.

### *6. The Range 320 to 550°K*

All peaks in this range are weak. Magnesium-doped crystals show a set of peaks near 482°K (Fig. 1). The correlation of these peaks with magnesium has previously been discussed by Schulman[11] and by Pilcher, Schinke, and Friauf.[15]

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[15] F. Pilcher, D. Schinke, and R. J. Friauf, J. Phys. Chem. Solids 24, 1687 (1963).

### C. The Effect of Heating Rate

In order to characterize a glow peak under various heating conditions, the variation of peak temperature with heating rate has been measured in detail. Typical results are shown in Fig. 2 for crystal No. 26.

Shown on Fig. 2 is an x-ray produced defect at 115°K. The experimental points are subject to a large error because of the overlap with the intense 133°K peak. The 158°K peak is present in the spectrum recorded after x irradiation but is inadequately resolved to be included in Fig. 2. The 158°K peak is resolved after populating with 2537 Å illumination.

There are significant differences in the positions of the glow maxima as a function of heating rate for the 194°K peak for the x-ray-excited, and optically-excited cases.

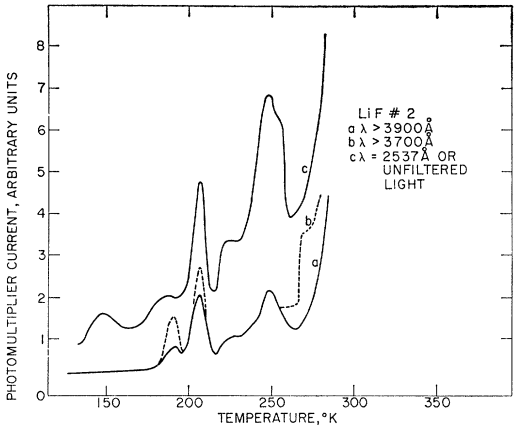

FIG. 4. Thermoluminescence obtained by gamma-ray irradiating a LiF crystal at 300°K, and then illuminating the sample, at 77°K, with the light from a low-pressure mercury lamp which was filtered, as indicated.

### D. Some Effects of Optical Re-excitation

The relative strength of the re-excited peaks depends on the intensity and wavelength of the exciting light. Figure 4 shows the thermoluminescence spectra of a room-temperature gamma-irradiated crystal (No. 2) which was then illuminated with unfiltered or filtered light at 77°K. A low-pressure mercury lamp either unfiltered or filtered by a 2537 Å interference filter produced curve c. Limiting the spectral range of the lamp changes the relative intensity of the peaks. Excitation with wavelengths longer than 3700 Å failed to produce the peak at 150°K. The spectra were reproducible.

### E. Irradiations Greater than $10^6$ R

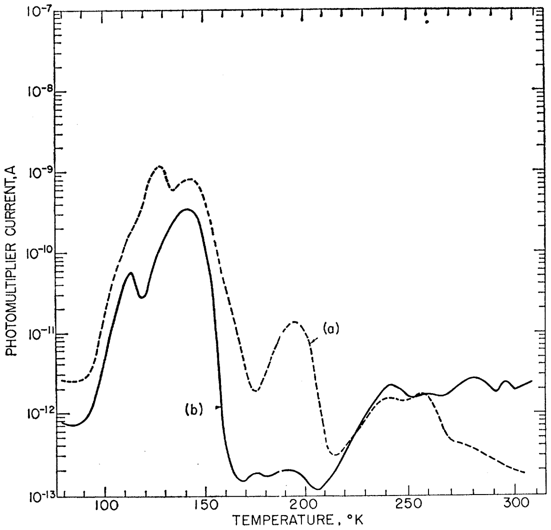

FIG. 5. Glow curves of LiF No. 30. Curve (a) was produced by an x irradiation at 80°K. The crystal was then given a $5\times10^6$ R gamma irradiation at 300°K, irradiated with x rays at 80°K and then curve (b) was obtained.

Irradiation of the order of $10^6$ R or more produces effects which are not generally seen at smaller doses. The thermoluminescence curve shapes obtained after x irradiation at 80°K are sensitive to the total concentration of defects in the crystal. These effects are demonstrated by the following sequence of experiments:

(I) Specimen 30 was x irradiated at 80°K and the thermoluminescence recorded between 80 and 300°K (see Fig. 5, curve a).

(II) The crystal was cooled to 80°K, re-excited with $F$-band light for 30 minutes and the thermoluminescence recorded between 80 and 300°K (see Fig. 6, curve a).

(III) The crystal was exposed to a $5\times10^6$-R $Co^{60}$ irradiation at 300°K.

(IV) The thermoluminescence was recorded after x irradiation at 80°K (see Fig. 5b).

(V) Thermoluminescence was recorded after again cooling to 80°K and illuminating with $F$-band light for 30 min.

After gamma irradiation at room temperature, it is seen that the trapping levels at 158 and 194°K were reduced in intensity and additional weak structure appeared.

Experiments (I) and (II) could be carried out

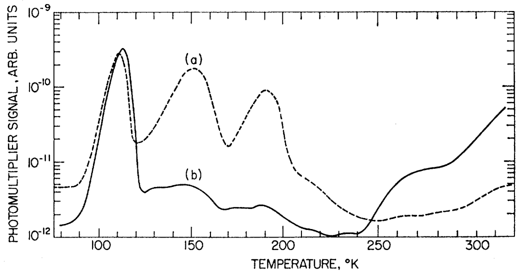

FIG. 6. Glow curves of LiF No. 30 obtained after illuminating with $F$-band light at 80°K, following the sequence described for Fig. 5.

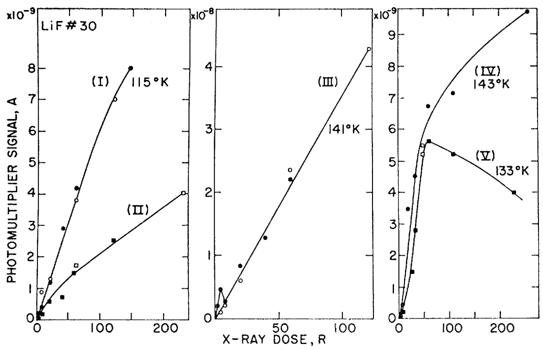

FIG. 7. Examples of glow curve intensity as a function of x irradiation dose at 80°K. (I) and (III) represent original crystal measured at 115°K and 141°K. (II), (IV), and (V) were obtained after the crystal had been irradiated with gamma rays for $5\times10^6$ R at 300°K. Solid points were obtained for increasing x-ray doses; open points were obtained after the maximum x irradiation.

repeatedly and in any sequence, giving reproducible thermoluminescence curves, provided that the same x-ray dose was used. An exception to this occurred initially at a dose of less than 10 R in the case of the 141°K glow maximum (see Fig. 7, III). It is apparent from the dose curve that an initial enhancement of the signal existed. The x-ray dose dependence of the glow peaks is shown in Fig. 7. The solid experimental points were obtained for successively increasing x-ray dose. The open points represent values obtained at a later time (i.e., after the maximum x irradiations).

## IV. ACTIVATION-ENERGY DETERMINATION

### A. Kinetics of the Thermoluminescence Process

Many methods for the analysis of glow peaks have been proposed. A summary and comparison of the methods was made by Nicholas and Woods.[13] One analysis due to Hoogenstraaten[16] points out that the activation energy can be obtained from a plot of $\ln(T_m^2/\beta)$ versus $1/T_m$, since these are related by the equation

$$\ln(T_m^2/\beta)=E/kT_m+\text{constant}, \tag{1}$$

where $T_m$ is the temperature of peak maximum, $\beta$ is the rate of rise of temperature, and $k$ is the Boltzmann constant. The expression (1) is insensitive to retrapping by the same shallow trap from which the charge was thermally released.[13]

The analysis is demonstrated in Fig. 8, which is constructed from the data of Fig. 2 for the glow peaks at 147, 158, and 194°K. The 194°K peak gives slightly different activation energies depending upon the method of excitation, namely, 0.31±0.01 eV and 0.34±0.01 eV for $F$-band and x-ray excitation, respectively.

The shape of a single glow curve that is independent of other trapping processes depends upon the retrapping cross section, and in the case when no retrapping occurs the shape of the glow curve is given by first-order kinetics in the luminescence literature.[17]

$$I(T)=n_0S\exp\left(\frac{-E}{kT}\right)\exp\left\{\int_{T_0}^{T}\frac{-S}{\beta}\exp\left(\frac{-E}{kT}\right)dT\right\}. \tag{2}$$

When retrapping occurs (often referred to as second-order kinetics),

$$I(T)=\frac{n_0^2S\exp(-E/kT)}{m_r\left(1+\dfrac{n_0}{m_r}\displaystyle\int_{T_0}^{T}\frac{S}{\beta}\exp\left(\frac{-E}{kT}\right)dT\right)}, \tag{3}$$

where $I(T)$ is the luminescence intensity at temperature $T$, $n_0$ is the initial number of filled traps, $m_r$ is the total number of trapping states, and $S$ is the frequency factor. Expressions (2) and (3) have been evaluated by numerical integration and compared with experimental data. An example is shown in Fig. 9 for the 158°K peak. Comparison can be made only for completely resolved glow peaks.

An alternative analysis has been described by Kemmey, Townsend, and Levy[18] in which, at each temperature, the release (A) of carriers from centers is described by a simple Arrhenius equation and the rate of retrapping (B) of carriers and their redistribution between a number of trapping and recombination centers is calculated from the product of number of carriers, number of each type of unfilled trap, and the

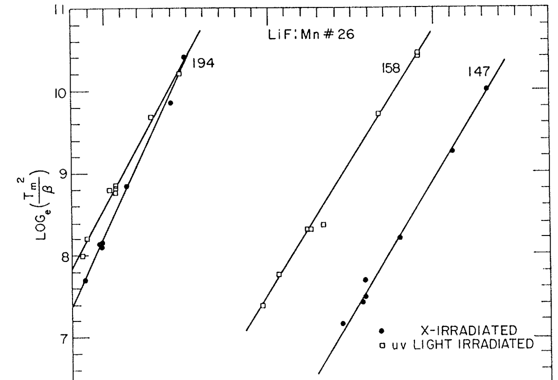

FIG. 8. Examples of activation energy determinations utilizing the equation

$$\ln(T_m^2/\beta)=E/kT_m+\text{constant}.$$

These symbols have the usual meaning and are defined in the text.

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[16] W. Hoogenstraaten, Philips Res. Rept. **13**, 515 (1958).

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[18] P. J. Kemmey, P. D. Townsend, and P. W. Levy, following paper, Phys. Rev. **155**, 917 (1967).

TABLE II. Activation energy of the major glow peaks. Glow-peak temperature measured at 6°K/min.

| Method of analysis / $T_m$ | 25.5 | 30 | 36.5 | 115 | 133 | 147 | 158 | 175 | 194 | 202 | 255 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Hoogenstraaten | 0.029 | 0.033 | 0.036 | 0.28 | 0.143 | 0.17 | 0.21 | 0.21 | 0.31 | | 0.59 |
| Slope of leading edge | | | | 0.25 | 0.26 | 0.19 | 0.28 | 0.21 | 0.54 | 0.43 | 0.73 |
| Isothermal decay | | | | 0.24 | 0.17 | 0.21 | 0.26 | 0.21 | | 0.40 | 0.76 |
| Numerical integration | | | | 0.319 | 0.26 | 0.28 | 0.25 | 0.23 | 0.53 | 0.46 | 0.82 |
| Frequency factor, $\text{sec}^{-1}$ | | | | $1.3\times10^{12}$ | $1\times10^{8}$ | $6.1\times10^{7}$ | $1.5\times10^{6}$ | | $4.3\times10^{12}$ | $3.9\times10^{12}$ | |
| $25kT$ (max) | 0.054 | 0.065 | 0.079 | 0.25 | 0.29 | 0.31 | 0.34 | 0.38 | 0.42 | 0.44 | 0.55 |
| Charge released | | | | $e^-$ | $h^+$ | $h^+$ | $e^-$ | $e^-$ | $e^-$ | | $e^-$ |
| Proposed defect model | | | | $H$ | $V_k$ | | | | $V_t$ | | |

capture cross section of the particular trap. These quantities (A) and (B) are calculated at each temperature by an iterative process. Quantities computed in this way are referred to in Table II as the result of numerical integration (row 4).

The activation energy can be determined from the shape of the low-temperature wing of a glow peak. This is called "leading edge analysis," and is particularly useful in complex spectra with overlapping glow peaks. The leading edge of each peak may be measured in turn by careful annealing of the lower temperature peaks.[13]

### B. Isothermal-Decay Kinetics

Analyses based on the shape of a glow curve over a range of temperature may be perturbed by interfering effects such as overlapping peaks, changes in the quantum efficiency, or emission spectra of the luminescence. Some of these difficulties may be avoided by making measurements at constant temperature, i.e., under isothermal conditions. The study of isothermal decay in the range 105 to 150°K using crystal No. 30 showed that at least three untrapping processes occurred which produce luminescence. The crystal was irradiated at 80°K, quickly warmed to a specific temperature, and held there while the luminescence decay was measured. A logarithmic plot of this luminescence intensity versus time usually gives a decay which may be analyzed into the sum of sharply defined linear regions. It has been shown[17] that for first-order kinetics the decay is given by

$$I(T)=n_0S\exp(-E/kT)\exp[-St\exp(-E/kT)];\qquad(4)$$

$I(T)$, $n_0$, $E$, $S$, and $k$ were previously defined, and $t$ is time. Thus,

$$\ln I(T)=-St\exp(-E/kT)-E/kT+\ln(n_0S),\qquad(5)$$

and the slope $m$ of the $\ln I(T)$-versus-$t$ curve is

$$m_1=S\exp(-E/kT).\qquad(6)$$

Taking the slope at two temperatures $T_1$ and $T_2$ we can write

$$\ln(m_1/m_2)=(-E/k)(1/T_1-1/T_2),\qquad(7)$$

which is used to determine the activation energy $E$. The frequency factor $S$ may be found by substitution of (7) in Eq. (6).

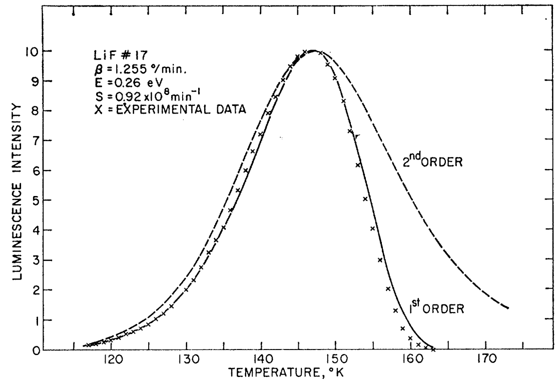

FIG. 9. A comparison of the experimental data for the 147°K peak with theoretical "first"- and "second"-order annealing kinetics.

It was found in LiF 30 that $\ln I(T)$ is not linear with time, but may be separated into three components each of which obeys Eq. (7) and has a different value of $m$. The lowest value of $m$ corresponds to the slope of the curve at large values of $t$. It is difficult, at the lower temperature, to analyze the data into the three stages because the fastest decaying component is also the smallest. The observed values of $m$ are shown in Fig. 10 as a function of $1/T$. The line (a) describes the luminescence associated with the highest temperature glow peak. Line (b) passes through the remaining points in the range 120 to 150° and is extended, as a dashed line, over the remainder of the temperature range. The activation energies marked "isothermal decay" in Table II were computed from these data.

The results from all the different methods are summarized in Table II, and it is seen that there is fair agreement among the different analyses. All the glow peaks are described by simple kinetics (i.e., no retrapping effects). There is a large spread in frequency factors from $10^6$ to $10^{12}$ $\text{sec}^{-1}$, which explains why some relatively deep trapping levels produce glow peaks at lower temperatures than shallower levels. For example, the 115°K peak has a depth of 0.32 eV and the 158°K peak is only 0.25 eV.

Isothermal-decay analysis is the only method which is unaffected by the variation of luminescent quantum

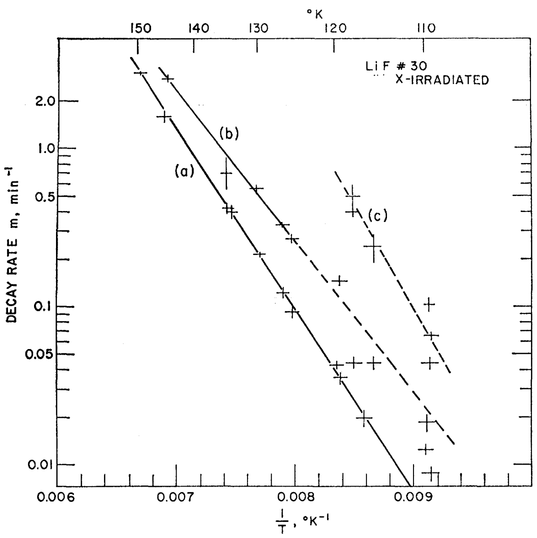

FIG. 10. Isothermal luminescence decay rates for LiF crystal No. 30 after x irradiation at 80°K. Lines (a), (b), and (c) are discussed in the text.

efficiency with temperature. The activation energy required to release a charge from a defect can be obtained from thermoluminescence measurements, but the analyses do not give any insight into the mechanism involved, or the condition (state) of the defect site remaining after the charge has been released. The energy of any optical transition associated with the defect should not be directly compared with the thermal activation energy for charge release.

## V. DISCUSSION

### A. Defects in Lithium Fluoride

Two principal facts emerge from both the data given above and previous work. First, the number and intensity of glow peaks varies greatly from sample to sample. Second, for each peak the activation energy and frequency factor obtained from the different experimental techniques are reasonably alike. One would like to decide which peaks are associated with intrinsic lattice defects and which are impurity related; also, to identify the defects involved and to determine how the impurities related to each glow peak are incorporated in the lattice. Other objectives are the determination of the sign of the trapped charge at each defect and the nature of the luminescence centers. For example, one wishes to determine whether the untrapped electrons interact with one type of luminescent center and holes with another.

Before discussing specific results, certain general conditions required for the observation of thermoluminescence will be described. The material must contain both traps which release charge as the temperature is raised, and must possess at least one type of luminescent center having the property that the product of the concentration and capture cross section is large compared with the sum of such products for nonradiative recombination processes. Thus, when glow peaks are not observed in a substance it may mean that there are insufficient luminescent centers even though the number of intrinsic defect related shallow traps are very large. In addition, a detectable fraction of the emitted photons must be transmitted through the crystal to the detector, which in this experiment is sensitive from 1.5 to 6.5 eV.

X irradiation produces free electrons and holes which may become trapped and give rise to characteristic glow peaks. If both types of traps exist then x irradiation will produce some glow peaks from hole untrapping and other peaks from electron untrapping. Illumination of LiF with light in the *F* absorption band (2537 Å) causes the release of electrons. These can fill electron-capturing defects, and subsequent heating will produce a glow curve typical of electron untrapping. Comparison of x-ray produced glow curves and glow curves produced by re-excitation with *F*-band light assist in distinguishing between electron and hole release. Some of the limitations of the method are

(i) Absorption bands associated with the hole centers may overlap the *F* band and the *F*-band illumination may release some holes. For example, the weak absorption band at 3400 Å has been identified as a hole center and has been shown to overlap the *F* band.[6,15,19]

(ii) It is impossible to repopulate a defect which is destroyed by heating. Thus the 115, 158, and 194°K glow peaks of Fig. 3 may be identified as electron traps and the remainder of the glow peaks are either hole centers or are due to defects which are removed during the first heating.

Two further types of experiment have been performed to distinguish between the electron and hole traps. (i) A crystal was both x irradiated at 80°K and exposed to *F* band light at 80°K before measuring the glow curve. The electrons released from the *F* centers may enhance the peaks from electron untrapping and reduce those from hole untrapping when the curve is compared with a glow curve obtained after x irradiation alone. Such an experiment resulted in a decrease of the 133 and 147°K glow peaks with respect to the other glow peaks. (ii) It is also possible to distinguish between different types of charge traps if one can alter the relative production rates or alter the concentration of luminescent recombination centers. Such changes may take place when one produces a powder sample from a single crystal, and therefore, the following experiment was performed. A single crystal was gamma-irradiated and the glow curve measured. The crystal was crushed and the powder was gamma-irradiated and the new glow curve measured. A comparison of the two curves

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[19] W. Kanzig, J. Phys. Chem. Solids **17**, 88 (1960).

showed that the peaks at 133 and 147°K were decreased relative to the other peaks in the powder.

All the above experiments lead to the conclusion that the glow peaks at 133 and 147°K are due to hole release. It is probable that the glow peaks at 47, 115, 158, 175, 194, 225, and 225°K are due to electron release. No conclusions may be drawn for the other glow peaks. This information is summarized in Table II.

It should also be possible to distinguish between the electron and hole traps from a measurement of the emission spectrum from each glow peak, because the charges of each sign should be trapped by a separate set of luminescent sites. Measurements of the wavelength dependence of the emission were not conclusive, since at present only the most intense peaks are bright enough to make a spectral measurement.

Often it is incorrectly assumed that a sufficiently long irradiation will completely fill all of the electron and hole traps. Complete filling can occur when certain conditions are fulfilled, for example, when a filled trap cannot be emptied by recombination with a carrier of opposite sign. If a trap has an unusually large trapping cross section it may be rapidly filled while all the other traps remain relatively empty. Inspection of Table I shows that the glow peak at 68°K is detectable only after *F*-light excitation. This would occur if the 68°K peak results from electron release from a trap which has a large recombination cross section when electron occupied. During the x irradiation, both electrons and holes are available, so that a negligible number of the traps are populated. However, during optical excitation the defect will acquire electrons since these are the only available charges.

It is useful to compare the thermoluminescent data with other reported annealing studies of defects in lithium fluoride. Specific models of defects in LiF have been derived from ESR data by Kanzig and coworkers.[19,20] Kanzig performed isochronal anneals with an anneal period of 30 min. Thus for each defect the temperature of the maximum rate of annealing corresponds to a thermoluminescence peak obtained at a very low heating rate. Thus his temperatures are lower than the temperature quoted for a 6°K/min heating rate.

The results summarized in Table II show that the peak at 115°K is due to electron untrapping, the peak temperature is impurity sensitive, and varies in magnitude from sample to sample. The *H* center measured by Kanzig is an $F_2^-$ molecular ion substituting for a $F^-$ ion, with the molecule aligned along $\langle 110\rangle$. It is batch sensitive and anneals at 110°K by the release of an electron. In addition, Hayes and Wilkens found the annealing temperature varied in LiF doped with different concentrations of Ni.[21] It is therefore probable that the 115°K glow peak is associated with the annealing of an *H* center.

The most intense ESR spectrum comes from the $V_K$ center which is identified as a "self-trapped hole." It is common to all LiF crystals and anneals rapidly at 130°K. The glow peaks at 133 or 147°K might therefore be connected with this defect, since both are very intense and appear to be from hole traps. The 147°K peak occurred in more samples than the 133°K peak but the 133°K peak is stronger in divalently doped crystals. It is known that in KCl the addition of divalent cations produces a strong $V_K$ center. By analogy this suggests that in LiF the 133°K glow peak occurs when a hole is released from a $V_K$ center.

Kanzig has also observed a center called the "$V_t$" center which thermally anneals near 190°K and a "$V_F$" center which anneals below 230°K. Neither is completely understood, but both are hole traps. Their decay mechanism is uncertain and Kanzig suggests that both involve multiple lattice defects. Thus the 194°K glow peak may be associated with the $V_t$ center since it anneals at a similar temperature. As was mentioned above, this glow peak is found only when the 133°K glow peak (assigned above as the $V_K$ center) is observed. Kanzig observed an increase in $V_t$ centers during the annealing of the $V_K$ centers. Therefore, the $V_t$ center and the 194°K glow peak may arise from the same defect. It is conceivable that a complex center will produce a hole-like *g* value in the ESR measurement but decay by the release of an electron.

If the $V_F$ center is related to either the 225 or 255°K glow peak there must be consistent behavior between the ESR and glow peak data. Four defects ($H$, $V_K$, $V_t$, $V_F$) are produced at 80°K by x-ray irradiation but none of their ESR signals are produced at irradiation temperatures above 185°K. However both the 225 and 255°K glow peaks are produced at all temperatures up to 220°K, an example of this is shown in Table I for crystal No. 21. Neither of the glow peaks and the $V_F$ ESR signal are therefore related.

Measurements were made with crystals containing Mg, Mn, Ce, Zr, and Ti to determine if these impurities produce specific glow peaks. Of these elements only Mg produces additional peaks and, as was previously found by Schulman, the Mg related peaks occur near 482°K. The entire group of peaks from 430–490°K appears to be related to the Mg. Even in the heavily magnesium doped crystals the intensity of the glow peaks is relatively low. Johnston[22] has shown that 100 ppm is the maximum amount of Mg that will remain dispersed in LiF; greater doping merely produces colloidal metal aggregates.

### B. Comparison with other Alkali Halides

If the thermoluminescence processes observed in LiF are related to intrinsic LiF defects, then the other

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[20] W. Kanzig and T. O. Woodruff, J. Phys. Chem. Solids **5**, 268 (1958).

[21] W. Hayes and J. Wilkens, Proc. Roy. Soc. (London) **A281**, 340 (1964).

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TABLE III. Glow peaks and annealing stages in the alkali halides.

| Crystal | Anneal temperature | Defect | Comment | Reference |
|---|---|---|---|---|
| LiF | 115 | $H$ center | | Present work |
| | 133 | $V_K$ center | | |
| | 194 | $V_t$ center | | |
| | 47,68,158,175,225,255 | | electron untrapping glow peaks. | |
| | 133,147 | | hole untrapping glow peaks. | |
| LiF | 115 | $H$ center | ESR | 19 |
| | 130 | $V_K$ center | ESR | 19 |
| | 180 | $V_t$ center | ESR | 19 |
| | 230 | $V_F$ center | ESR | 19 |
| NaCl | 66 | | electron release | 7 |
| | 155 and 170 | | release different type of charge | 27 |
| KCl | 56 | $H$ center | ESR | 20 |
| | 56 | $H$ center | optical absorption | 25 |
| | 128 | $V_1$ center | optical absorption | 26,28 |
| | 130 | $V_K$ center | ESR | 20,28 |
| | 150–175 | $F'$ center | optical absorption: N.B. the higher temperature annealing occurs in impure samples. | 26,29 |
| | 125,250,390 | | release one type of charge | 30 |
| | 145,280,315,415,480 | | release the other type of charge | 30 |
| KBr | 54 | $H$ center | ESR | 20 |
| | 120 | $V_1$ center | optical absorption | 26,29 |
| | 143 | $F'$ center | optical absorption | 26,29 |
| | 225 | $V_4$ center | optical absorption | 26 |
| | 246 | $V_4$ center | optical absorption | 26 |

alkali halides may show analogous glow peaks. Such a correlation is well known in the case of optical absorption bands.[23,24] The thermoluminescence from several alkali halides has been measured at a constant heating rate of 6°K/min. The temperature of the largest glow peaks is summarized in Fig. 11 as a function of the lattice parameter. Results obtained by other authors at similar heating rates are included. However, it is not useful to include data obtained at vastly different heating rates. The over-all thermoluminescence curves obtained in the different alkali halides are similar.[10]

In some cases the thermoluminescence can be associated with the annealing of specific defects which have been identified by ESR, etc. Table III shows the annealing temperature related to specific defects. This provides a basis for a comparison of glow peaks in several alkali halides. The annealing stages in KCl, KBr, and LiF on the line labeled A in Fig. 11 are all correlated with the bleaching of $H$ centers.[19,20,25] In addition the glow peak for NaCl on line A is related to electron release[7] which is consistent with the $H$-center annealing as observed in LiF.

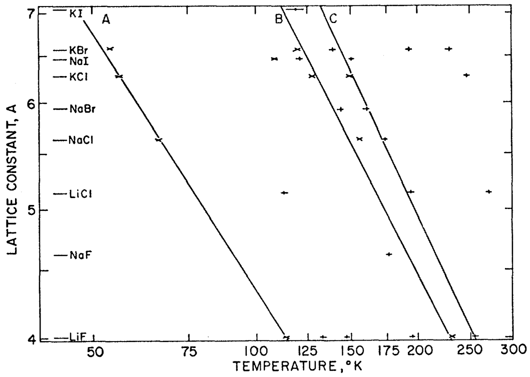

FIG. 11. A summary of the intense glow peaks and annealing stages observed in the alkali halides. Plus (+) measurements were obtained by the present authors, $x$ measurements by other authors. Lines A, B, and C are discussed in the text.

The justification for lines B and C in Fig. 11 is as follows: The glow peaks plotted are the two strongest peaks observed, in most samples, in each of the alkali halides. In KCl and KBr the $F'$ centers[26] anneal at temperatures near line C. Other glow peaks along this line are reported to be associated with release of electrons. ESR and optical absorption measurements have shown that the annealing stages of hole defects in LiF, KCl, and KBr [20,26–30] lie close to line B. Measurements of the emission spectra[27] of the glow peaks in NaCl and KCl show that the peaks can be divided into two groups. One group of peaks produces an emission spectrum which has the strongest glow peak at a temperature near line B. The other group of glow peaks has a peak which occurs near line C. It is possible that the two emission curves result from different types of

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charge release. It is therefore probable that line B indicates the temperature of a hole release and line C indicates the temperature at which an electron is released in the various alkali halides. A more detailed discussion of the defects associated with lines B and C in Fig. 11 would be too speculative to include at the present time.

## VI. SUMMARY

The glow-curve measurements from a variety of LiF samples have been described. These have been used to determine the activation energies and pre-exponential (frequency) factors describing the untrapping processes for the majority of the glow peaks. In many cases it has been determined if a particular glow peak is related to electron or hole release.

An attempt has been made to relate specific peaks to charge release from known defect centers. The peak at 115°K ($E=0.32$ eV) is associated with the $H$ center; the peak at 133°K ($E=0.26$ eV) has been attributed to the $V_K$ center and the 194°K ($E=0.53$ eV) peak to the $V_t$ center. Despite the similarity of the annealing temperature for the $V_F$ center with the glow peak at 225 or 255°K, the glow peaks arise from different defects.

Finally, the annealing temperatures associated with a variety of processes, observed for different alkali halides, have been compared. Trends, similar to the Ivey-Mollwo relation, are observed and indicated that the annealing temperatures associated with a variety of processes can be correlated with the lattice parameter.

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# Numerical Analysis of Charge-Redistribution Processes Involving Trapping Centers*

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(Received 1 September 1966)

A method for calculating charge-transfer processes in solids has been developed which is particularly suited for use with a computer. In this instance it has been applied to the computation of thermoluminescent glow curves. The concentrations of all defects in the crystal, which enter into the calculations, and all normal lattice sites in the host crystal are specified. Also, the initial electron, hole, and exciton, i.e., excited-state, populations are specified. The computation proceeds in arbitrarily small time steps. During each step the concentrations of trapped charge, the carrier concentrations, the radiative relaxations of excited centers, etc. are adjusted in accord with the physical processes involved. The temperature is fixed during each computational time increment, but may be made an arbitrary function of time. When used to analyze experimental data, some initial conditions usually are fixed and a process of successive approximations is used to determine the remaining parameters, e.g., activation energies and preexponential factors. The method is designed to analyze data in cases which cannot be described by tractable analytical expressions or when a closed expression cannot be applied readily. It has been used for analyses of measurements of thermoluminescence in lithium fluoride by Townsend, Clark, and Levy. As an example, the analysis of one of their glow peaks is included.

THERMOLUMINESCENCE is a useful tool for studying the nature, thermal stability, concentrations, etc., of shallow-electron and hole-trapping centers in luminescent materials. The thermoluminescent process involves the thermal release of trapped charges, the possible retrapping of these charges in the original or in other traps, and their ultimate trapping by recombination and/or luminescent centers. Recombination may or may not involve the emission of light. Experimental results are usually presented as light intensity as a function of temperature or time. Curves of such results are referred to as thermoluminescence spectra or glow curves.

In a few cases the equations describing the physical processes which give rise to the glow curves can be

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