

A Kinetic Study of the Thermoluminescence of Lithium Fluoride

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other of the tautomers is "frozen," and the selection rules for the particle on a circle particularly inapplicable.

COMPARISON WITH EXPERIMENT

The band maxima determined by Erdman and Corwin⁶ for a simple porphine, etioporphine II, and its dihydrochloride occur grouped about centers of gravity of 477 and 495 $m\mu$, respectively:

Free base	λ $\epsilon \times 10^{-4}$	622 0.480	595 0.195	572 0.621	532 0.850	498 1.37	397 15.7
Dihydrochloride	λ $\epsilon \times 10^{-4}$	598 0.680		555 1.54		415 18.1	

The predictions of the last section fit the observed data about as well as might be expected, considering the many approximations.

The hydrogenated porphines exhibit the behavior attributed to them in the previous section, in that the

center of gravity of their bands remains about the same, but the ϵ_{\max} of the long wave-length bands increase. The center of gravity for a bacteriochlorophyll that was studied by French⁹ is 549 $m\mu$. From the standpoint of the transition energy, a bacteriochlorophyll is most similar to the model substance, so that the approximate agreement of the calculated 615 $m\mu$ is gratifying.

ACKNOWLEDGMENT

The writer wishes to thank Dr. Frank M. Huennekens for calling his attention to the problem and for many stimulating discussions. He likewise extends thanks to Professors H. J. Dauben, Jr., and P. Rothmund for samples of porphines. Finally he would like to acknowledge a debt to the publications on benzene of Drs. A. L. Sklar and M. Goeppert-Mayer.

⁹ C. S. French, *J. Gen. Physiol.* **21**, 71 (1937).

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A Kinetic Study of the Thermoluminescence of Lithium Fluoride

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The isothermal decay of the thermoluminescence of single crystals of lithium fluoride activated by x-rays has been determined at various temperatures. The results are interpreted in terms of a simple reaction rate mechanism based on a picture of the thermoluminescent process similar to that of Johnson. The analysis of the isothermal decay studies is in agreement with the results of "glow curve" experiments on similar lithium fluoride samples where the intensity of luminescence is measured as the temperature of the crystal is heated at a constant rate.

Two principal types of electron traps in lithium fluoride are found to have trapping energies of 19,800 cal./mole and 45,300 cal./mole respectively.

INTRODUCTION

THIS paper describes an investigation of the thermoluminescence of single crystals of lithium fluoride activated by exposure to x-rays at room temperature. Studies have been made of the variation of luminescent intensity with time when the crystal is held at constant temperature and also when it is heated at a constant rate. The experimental data are analyzed from the standpoint of a simple reaction rate mechanism, and a method is developed for experimentally determining the energy of electron traps from the isothermal decay of the luminescent intensity.

It is found that in the lithium fluoride crystals investigated there are two principal types of electron traps having trapping energies of 19,800 cal./mole and 45,300 cal./mole respectively. A third type of trap of intermediate energy is indicated, but it is of secondary importance.

* Supported by the research committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

Johnson¹ has used the band theory of solids to develop a picture which qualitatively explains thermoluminescence in terms of the trapping of electrons which have been excited to the conduction band by the external radiation. These are subsequently released from the traps by energy transfer as the temperature of the crystal is raised. This type of model has been used by investigators for quantitative interpretation of their experimental results² in studies of the various phosphors.

The physical interpretation of electron traps has been discussed by several authors.³ They are usually associated with some type of distortion of the regular crystal lattice.

The earlier investigations of thermoluminescence

¹ R. P. Johnson, *J. Opt. Soc. Am.* **29**, 387 (1939).

² G. Fonda and F. Seitz, *Preparation and Characteristics of Solid Luminescent Materials* (John Wiley and Sons, Inc., New York, 1948); also, H. W. Leverenz, *Science* **109**, 183 (1949).

³ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940); I. Tamm, *Zeits. f. Physik* **76**, 849 (1932); L. Landau, *Physik. Zeits. Sowjetunion* **3**, 664 (1933); J. J. Markham and F. Seitz, *Phys. Rev.* **74**, 1014 (1948).

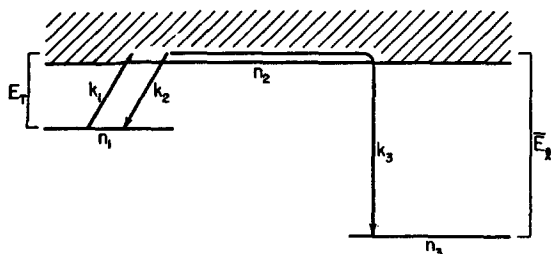


FIG. 1. Simplified energy level diagram illustrating the thermoluminescent process.

have been carried out along two major lines. One type of experiment is concerned with the functional form of the decay of the thermoluminescence with time when the crystal is held at an elevated temperature. Different analytical expressions have been derived to describe this decay based upon different assumptions. For example, Randall and Wilkins⁴ have shown that if the electrons which are released from the traps recombine directly with the parent ions the intensity of luminescence should decrease with time according to a first order expression of the type

$$I = I_0 \exp(-at). \quad (1)$$

The treatment of Randall and Wilkins has been extended by Garlick² to include the possibility of recapture of the released electrons by other empty electron traps. He has assumed first, that the number of electrons in the conduction band is small compared to the number trapped, and second that the capture cross section of empty traps for electrons is the same as that of the empty luminescent centers. This leads to the following time dependence of the luminescence:

$$I^{-1} = \left[\frac{N}{n_0^2 s} \exp(-E/RT) \right]^{\frac{1}{2}} + \left[\frac{s}{N} \exp(-E/RT) \right]^{\frac{1}{2}} t \quad (2)$$

where N is the total number of traps, n_0 is the initial number of trapped electrons, s is the frequency factor for the release of electrons from the traps, T is the absolute temperature, and E is the energy of the traps. At any fixed temperature this equation is of general form

$$I^{-1} = a + bt \quad (3)$$

which corresponds to the so-called "second-order" decay.

In practice the luminescent decays of most phosphors do not follow any simple functional form but are usually empirically fitted by some type of power law

$$I = I_0 t^{-n} \quad (4)$$

where n varies between 0.1 and 2.

However, in the present work the thermoluminescent decay of lithium fluoride has been resolved into two major components, each of which corresponds to a single type of trap decaying according to the second

order decay law. By choosing the proper temperature for the decay one or the other component can be made predominate, and its trapping energy can be determined.

The second type of experiment used in studies of thermoluminescence is concerned with the so-called "glow curves" first reported by Urbach.⁵ In this type of experiment the crystal is first irradiated and then heated so as to raise its temperature at a constant rate. The intensity of the luminescence is found to go through maxima which can be related to the various types of traps contributing to the luminescent process. Since the intensity decay of the industrial phosphors is usually complex this second type of experiment has found more general use. The thermoluminescent decay of lithium fluoride is of a sufficiently simple nature to permit analysis of both types of experiments from the standpoint of the second order decay law, Eq. (3).

This type of analysis when applied to the experimental data obtained for lithium fluoride crystals indicates that two major types of traps contribute to the thermoluminescence. These have trapping energies of 19,800 cal./mole and 45,300 cal./mole respectively. The same type of analysis is also applied to the results of "glow curve" experiments made with similar lithium fluoride crystals and it is found that the trapping energy for the higher energy traps as determined from the glow curve is in good agreement with that determined from isothermal decay. The lower trapping energy cannot be evaluated from the glow curve because of the composite nature of the decay in this region.

DEVELOPMENT OF EQUATIONS

When a crystal such as lithium fluoride is irradiated with x-rays, some of the electrons originally associated with ions in the crystal are excited to the conduction band where they are free to wander through the lattice. These excited electrons may encounter lattice imperfections such as negative ion vacancies or impurities where they are attracted and bound or "trapped" at ordinary temperatures.

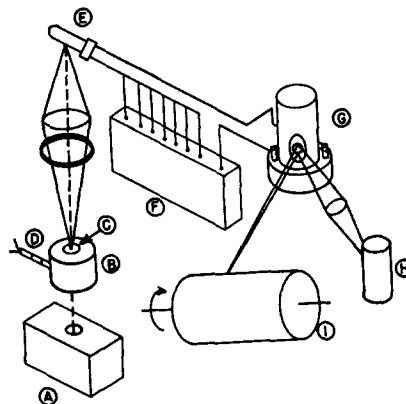


FIG. 2. Diagram of apparatus used to measure thermoluminescence. (A) Standardization lamp. (B) Furnace. (C) Sample. (D) Thermocouple. (E) Photo-multiplier tube. (F) Power supply. (G) Galvanometer. (H) Light source. (I) Rotating drum camera.

⁴ J. T. Randall and M. F. Wilkins, Proc. Roy. Soc. 184, 366 (1945).

⁵ F. Urbach, Wien. Ber. 139, 20, 354 (1930).

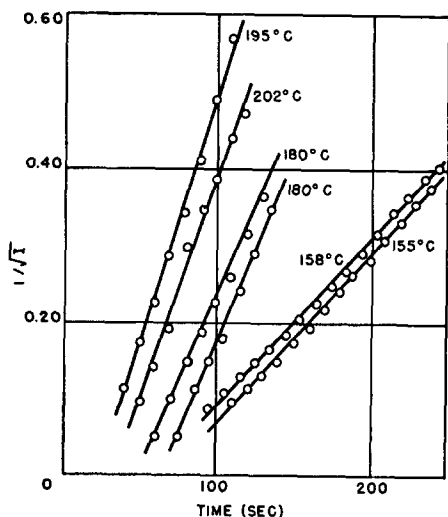


FIG. 3. Thermoluminescent decay of lithium fluoride at various temperatures.

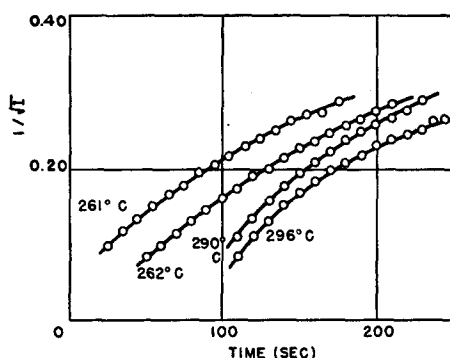


FIG. 4. Thermoluminescent decay of lithium fluoride at various temperatures.

As the temperature of the crystal is raised the probability is increased that a trapped electron will be released to the conduction band again by energy transfer. A released electron will remain in the conduction band until it encounters another trapping center and is retrapped or until it encounters and recombines with one of the ions which originally yielded electrons under the influence of the x-rays.

This second type of recombination results in the release of energy in the form of a quantum of light giving rise to the observed luminescence. A kinetic treatment of this process can be considered by referring to Fig. 1. n_1 represents the number of trapped electrons; n_2 , the number of electrons in the conduction band; and n_3 , the number of ionized ions with which electrons can recombine giving up quanta of light of average energy $\bar{E}_l = hc/\lambda$. Since the luminescence for lithium fluoride is predominantly blue, \bar{E}_l in this case will be of the order of 60,000 to 70,000 cal./mole.

In Fig. 1, the energy which a trapped electron must acquire in order to be excited back to the conduction band is represented by E_t .

If the crystal remains electrically neutral

$$n_1 + n_2 = n_3. \quad (5)$$

The situation as represented by Fig. 1 is analogous to the model used by Eyring in the development of the theory of absolute reaction rates for chemical reactions. Electrons which are trapped correspond to the initial state of the reaction; excitation to the conduction band corresponds to the formation of the activated complex; and electrons which have recombined with the parent ions correspond to the final state.

Following Eyring's development, we will assume that at a given temperature equilibrium exists between n_1 and n_2 , the molecule in the initial and in the activated states. This assumption of equilibrium becomes valid when n_2 is small compared to n_1 . Thus, if

$$K = n_2/n_1 \quad (6)$$

and

$$-dn_3/dt = k_3 n_2 n_3 \quad (7)$$

it follows from a simple kinetic treatment that

$$(1/n_3) - (1/n_3^0) = \left(\frac{K}{K+1} \right) k_3 t. \quad (8)$$

However, the intensity of thermoluminescence, I , is given by

$$I = \bar{E}_l (-dn_3/dt). \quad (9)$$

Where \bar{E}_l is the average energy involved in transition 3 and is not a sharp value because of the fact that the transition does not occur between sharp levels.

Combining Eqs. (6), (8), and (9) gives the intensity as a function of time as

$$I = \frac{\bar{E}_l k_3 [K/(K+1)]}{[k_3 [K/(K+1)] t + 1/n_3^0]^2}. \quad (10)$$

The variation of K with temperature is given by

$$K = K_0 \exp(-E_t/RT). \quad (11)$$

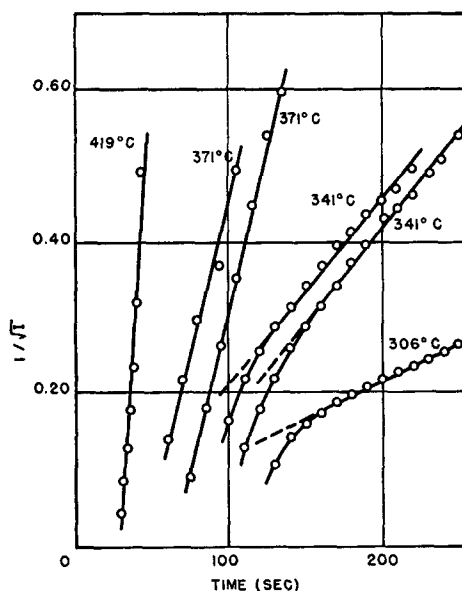


FIG. 5. Thermoluminescent decay of lithium fluoride at various temperatures.

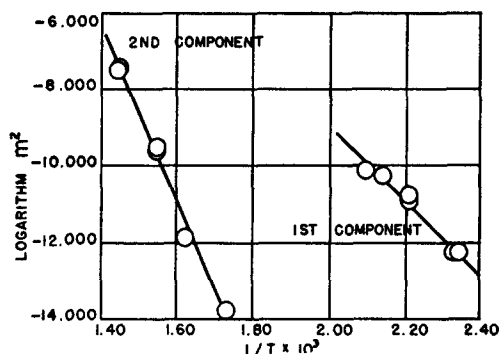


FIG. 6. Plot of $\ln m^2$ against $1/T$ for the two major components observed in the thermoluminescence of lithium fluoride. E for first component = 19,800 cal./mole. E for second component = 45,300 cal./mole.

Further, it will be noticed that K will be small compared to one and consequently

$$[K/(K+1)] \cong K. \quad (12)$$

Substituting Eqs. (11) and (12) into Eq. (5) and rearranging gives

$$I^{-1/2} = [(k_3/\bar{E}_1)K_0 \exp(-E_t/RT)]^{1/2} + [(1/n_3^0)[\bar{E}_1 k_3 K_0 \exp(-E_t/RT)]^{-1/2}] \quad (13)$$

which is essentially the same equation as that derived by Garlick.

According to Eq. (13), plots of $I^{-1/2}$ against t at a constant temperature should give a straight line having a slope given by

$$m_T = [(k_3/\bar{E}_1)K_0 \exp(-E_t/RT)]^{1/2}. \quad (14)$$

Determination of m_T at various temperatures makes it possible to evaluate E_t since from Eq. (14)

$$\ln(m_T^2) = -(E_t/R)(1/T) + (k_3/\bar{E}_1)K_0 \quad (15)$$

and a plot of $\ln(m_T^2)$ against $1/T$ should give a line of slope, $-E_t/R$.

EXPERIMENTAL DETERMINATION OF INTENSITY DECAY CURVES AT CONSTANT TEMPERATURE

Equations (13) and (15) were tested experimentally by observing the intensity decay of the thermoluminescence of lithium fluoride at various temperatures. The samples used in these experiments were in the form of plates one centimeter square and approximately two millimeters thick. These were cleaved from larger single crystals obtained from the Harshaw Chemical Company. The plates were exposed on both faces to 35-kilo-volt x-rays from a tube equipped with a copper target and an aluminum window. The exposure time for each face was two minutes and was carried out at room temperature.

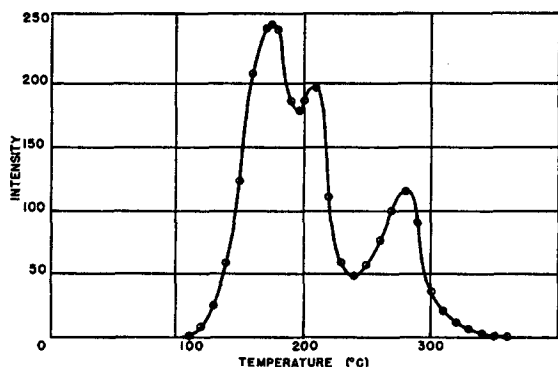


FIG. 7. Intensity temperature curve for lithium fluoride crystal. Rate of heating = 1.25°C/sec.

The apparatus used to measure the thermoluminescence is shown diagrammatically in Fig. 2. The irradiated sample was placed in a shallow Wood's metal bath on the face of the furnace. The light emitted was focused upon a photo-multiplier tube connected to a galvanometer, the deflection of which was recorded photographically on a drum camera rotating at a known speed.

Since the proportionality constant \bar{E}_1 appears in the expression for the slope, Eq. (14), it was necessary to standardize the recording circuit to the same relative value for all of the constant temperature decay studies. This was accomplished by means of the standardization lamp shown.

The spectral distribution of the luminescence was not determined in these experiments. However, it was visually examined and found to be of a light blue color. No apparent change in spectral distribution occurred during the course of the intensity decay.

The decay of the thermoluminescence of lithium fluoride with time is shown in Figs. 3, 4, and 5 for various temperatures. The decay is plotted in the form of $I^{-1/2}$ against time as indicated by Eq. (15).

For the temperature range between 150°C and 200°C the data follow straight lines as required by the equations. However, between 260°C and 290°C the data show pronounced curvature. At 304°C and 340°C the curvature appears in the initial portion of the decay but with additional time the data again become linear. At 370°C and at 420°C there is no further evidence of curvature.

This behavior can be explained on the basis of two luminescent processes one of which has a low trapping energy and the other, a higher trapping energy. At the lower temperatures only the low energy process contributes to the luminescence. As the temperature of the decay is increased the low energy process occurs more rapidly until at the high temperatures the high energy process is the only one which is left to give a measurable decay after the initial warm up period of the crystal.

In between these two temperature regions of low and high activation decay there is a region in which both processes contribute to the luminescence and thus the data cannot be represented by a simple $I^{-1/2}$ function.

According to Eq. (15) it is possible to determine the trapping energy from the plots of $I^{-1/2}$ against time at various temperatures. It has been shown that a plot of the logarithms of the squares of the slopes should also result in a straight line, the slope of which is $-E/R$.

Such plots were made for the two groups of straight lines obtained and shown in Fig. 6. The trapping energies corresponding to the two groups of lines are determined to be 19,800 cal./mole and 45,300 cal./mole from these plots.

GLOW CURVE EXPERIMENTS WITH IRRADIATED LITHIUM FLUORIDE

A second type of phenomena associated with thermoluminescence is the so-called "glow curves" of Randall and Wilkins which were first used by Urbach in studies on some of the alkali halides.

In this type of experiment the irradiated crystal is heated at a constant rate and the intensity of luminescence is observed to go through maxima which are related to the trapping energies contributing to the thermoluminescence. To describe this process, I is given by

$$I = -\bar{E}_l dn_3/dt \quad (16)$$

and the time variable is replaced by the temperature giving

$$I = -\bar{E}_l r dn_3/dT \quad (17)$$

where r is the rate of heating of the crystal.

Integration of Eq. (12) gives

$$\int_T^\infty I dT = \bar{E}_l r n_3. \quad (18)$$

Using this expression for n_3 in the kinetic treatment, and again introducing the temperature dependence of K gives

$$I^{1/2} = [(kK_0)/(\bar{E}_l r^2)]^{1/2} \exp[-E_t/(2RT)] \int_T^\infty I dT. \quad (19)$$

The condition at the maximum can be described by setting the derivative of Eq. (19) equal to zero. This resulting expression can then be solved for E_t giving

$$E_t = 2RT_m^2 I_m \left[\int_{T_m}^\infty I dT \right]^{-1} \quad (20)$$

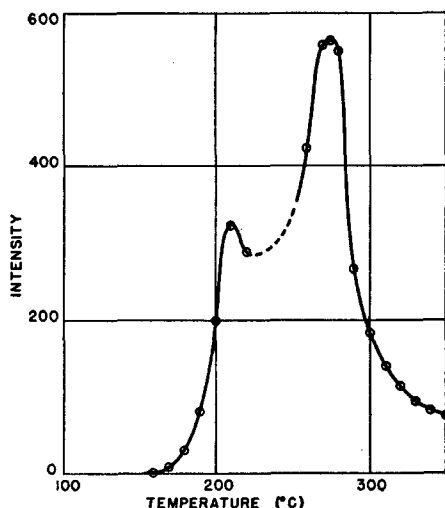


FIG. 8. Intensity temperature curve for lithium fluoride crystal annealed at 150°C after x-ray exposure.

TABLE I.

Rate of heating (°C/sec.)	T_{max} (°K)	I_{max}	$\int_{T_m}^\infty I dT$	E_t (cal./mole)
1.25	551	116	3040	45,800
1.26	534	116	3248	40,300
0.25	525	6.0	136	48,000
Average 43,700				

where the subscript m indicates the quantity at the intensity maximum.

Equation (20) indicates that we may evaluate E_t directly from the glow curve if $I_m T_m$ and $\int_{T_m}^\infty I dT$ can be determined.

Glow curves were obtained for the irradiated lithium fluoride crystals using the same apparatus, the temperature of the Woods metal both being measured at specified time intervals. These data allow one to plot the intensity as a function of temperature and a typical curve is shown in Fig. 7. It will be seen that there are two major peaks corresponding to the two major trapping energies observed in the previous experiments. In addition there is a small secondary peak which is too small to be detected by the constant temperature decay method.

The peak which occurs at the higher temperature is sufficiently isolated so that its corresponding trapping energy can be determined by using Eq. (20). The following table summarizes the results of measurements on several similar curves:

It should be noted in Table I that the value of E is relatively independent of the rate of heating used in the determination of the glow curve. This, of course, is in line with Eq. (20) which does not include the rate of heating.

The average value of 43,700 cal./mole for the second peak is in good agreement with the value of 45,300 cal./mole determined for the higher trapping energy by the constant temperature decay method.

MISCELLANEOUS EXPERIMENTS

1. Effect of Annealing

Crystals of lithium fluoride were exposed to x-rays in the manner described above and then placed in an oven

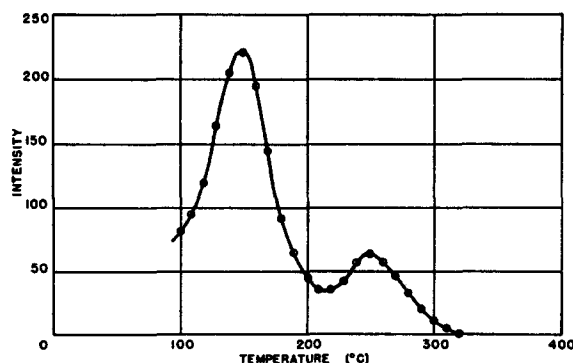


FIG. 9. Intensity temperature curve for lithium fluoride fused and ground.

held at 150°C for a period of five minutes. From a consideration of Fig. 6 it will be seen that the low energy traps are unstable at this temperature whereas the higher energy traps are still stable. Consequently, one might expect to be able to selectively empty the low energy traps and, if the retrapping concept of the simple model is correct, to increase the number in the higher energy traps. An intensity-temperature curve for a crystal treated in this manner is shown in Fig. 8, plotted on the same relative intensity scale as Fig. 7. The peak ordinarily occurring at 150°C corresponding to low energy trapping has been removed. However, the secondary peak and the high energy peak are still present. It will be noticed that the intensity of the high energy peak is increased by this treatment which can be interpreted to mean that more electrons are in the higher energy traps. These additional electrons can be accounted for on the basis of the simple model used in this paper by assuming that some of the electrons which were removed from the low energy traps were recaptured by the traps which were still stable.

2. Effect of Fusion

Experiments were run to determine the effect of fusion upon the characteristic glow curve of lithium fluoride. Some of the same crystalline material used in the above experiment was fused in a platinum crucible and cooled rapidly by pouring out on a clean platinum plate. The solid button was then ground in an agate mortar. Copper foil squares, one centimeter on a side were coated on one side with glyptol and a layer of the ground sample was pressed on top of this. These samples were then exposed to x-rays and glow curves were run in the manner described above. A typical curve is shown in Fig. 9. It will be seen that the two major peaks corresponding to the two major trapping energies are both present in about the same relation as for the single

crystal samples. However, there is no evidence of the smaller secondary peak which appears for the single crystals on the high temperature side of the first peak. This suggests that this secondary peak is due to the presence of a volatile impurity such as one of the components of air in the original samples. The fusion and quick chilling removed the volatile component without noticeably affecting the other types of traps.

CONCLUSIONS

The kinetic equations derived from the simple reaction rate mechanism are adequate to describe the thermoluminescence of lithium fluoride as a function of time and temperature. Two major types of traps and one secondary type of trap have been found in lithium fluoride by constant temperature decay studies and by glow curve experiments. In the case where the trapping energy could be determined by both methods the values so obtained were in substantial agreement.

The observed effect of annealing at a temperature where the low energy trap alone is unstable can also be explained on the basis of the simplified model.

Fusion of the crystal and subsequent quick chilling of the melt removes the secondary traps but does not affect the two major traps. This indicates that the secondary traps may be due to volatile impurities, possibly one of the components of air.

Further experiments on the cause of these traps and on the general effects of impurities in the thermoluminescent process in alkali halides will be reported in a subsequent paper.

The author would like to acknowledge gratefully the advice and counsel of Professor Farrington Daniels during the course of this work. He would also like to acknowledge the assistance of Mr. Donald Saunders in taking the experimental data. He wishes to thank Professor Joseph Hirschfelder for helpful comments during the preparation of the manuscript.

Electrochemical Thermodynamics and Kinetics of Hydrogen Overvoltage

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Department of Chemistry, University of Oregon, Eugene, Oregon

(Received March 15, 1949)

The problem of hydrogen overvoltage is attacked by a method making systematic use of chemical and electrochemical potentials. More precise formulas are thereby obtained than in previous theories and a more definite interpretation of the transfer coefficient of Erdey-Grúz and Volmer is arrived at. The Tafel empirical equation is discussed and the existence, in some cases, of several Tafel regions is considered. Activation free energies, energies, and entropies for the discharge process are calculated and the mechanism involving formation of atomic hydrogen is shown to be entirely plausible.

INTRODUCTION

IN spite of the large amount of experimental and theoretical work which has accumulated in the field of hydrogen overvoltage, confusion and disagreement are still prevailing, as is characteristically shown by the

papers presented at the General Discussion on Electrode Processes held by the Faraday Society.¹ Very

¹ Faraday Society Discussion, I (1947). See the papers on hydrogen overvoltage in Part II, pp. 50-126, and their discussion, pp. 127-141.