Thermoluminescence and *F*-Centers. II. Experimental*

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(Received December 22, 1958)

The theoretical treatment developed in the previous paper is used to interpret experiments of thermoluminescence associated with the presence of *F*-centers in irradiated alkali halides. Some important features of the technique employed are discussed—in particular, the procedure used to establish the proper wavelength belonging to the light emitted in each glow peak.
The energy of activation and the probability factors of the phenomenon are determined, and it is shown that the second and third peak of thermoluminescence are probably due to direct radiative recombination of *F*-centers with V_2- and V_3-centers. On the contrary it is still uncertain whether the first peak is associated with V_1-centers or with Cu ion impurities in the NaCl lattice.

IN the preceding paper[1] a theory of thermoluminescence associated with the presence of *F*-centers in alkali halides was developed.[2] In the present paper the results of experiments on irradiated NaCl are discussed and interpreted on the basis of this theory.

1. EXPERIMENTAL EQUIPMENT

Detection of the thermoluminescence light was performed very simply through the use of RCA 1P21 or
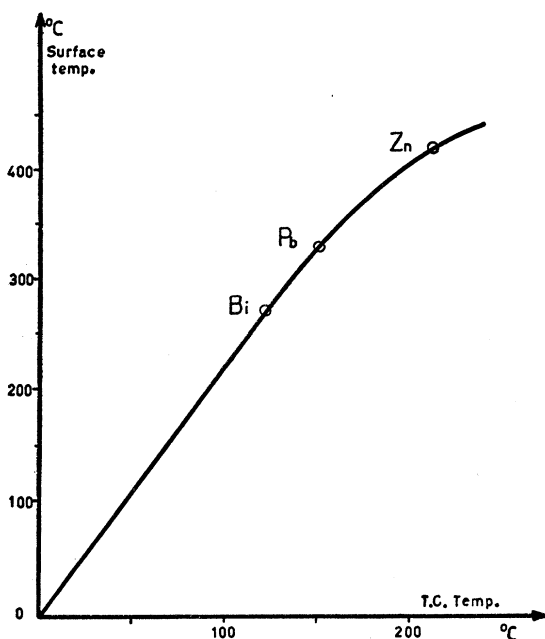

FIG. 1. Calibration curve of the oven temperature. Abscissas represent temperatures recorded by the thermocouple, while ordinates show the temperature of the emitting surface, obtained through the observation of the melting point of the metals indicated.

[1] Bonfiglioli, Brovetto, and Cortese, preceding paper [Phys. Rev. 114, 951 (1959)].
[2] The reader is referred to reference 1 for the equations and the meaning of the symbols, which appear in the following pages.

1P28 photomultipliers, recording directly the light spot of a galvanometer on a rotating drum equipped with a sheet of photographic paper.

The problem of constructing the oven was not trivial, and great care was devoted to obtaining reasonable temperature constancy throughout the sample. It is easy to show theoretically that rather small temperature gradients affect the shape of the glow curve tremendously.

After several attempts, the oven was finally built as a large plate of Cu (8-cm diameter), covered by a layer of evaporated Pt to avoid oxidation, with a small (0.8-cm diameter) well in the center and along the axis of the plate, to contain the specimen.
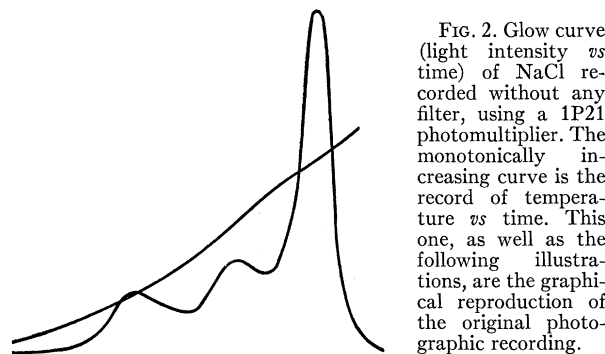

FIG. 2. Glow curve (light intensity *vs* time) of NaCl recorded without any filter, using a 1P21 photomultiplier. The monotonically increasing curve is the record of temperature *vs* time. This one, as well as the following illustrations, are the graphical reproduction of the original photographic recording.

Temperature was recorded by a Pt/Pt-Rh thermocouple located at a definite position, under the specimen, to be used in connection with a calibration curve. As a matter of fact we believed that no thermocouple located directly on the specimen could give a measure of the true temperature of the emitting surface. On the contrary we thought that it would have been wiser to make use of a calibration curve relating the temperature read by a thermocouple bound to a neighboring point with the true temperature of the emitting surface, as detected by the moment of melting of tiny pellets of pure metals lying on the specimen itself.

This was done, using Pb, Bi, Zn (in N_2 atmosphere to avoid oxidation) and merely looking at the formation of a droplet at the moment of melting.

Figure 1 shows our calibration curve (valid of course only for NaCl and for the actual value of the warming speed, namely $\beta \simeq 1°C/sec$). Temperatures of the light peak maxima obtained by this procedure always have been found to be in good agreement with the data in the literature.

A final point concerns the fidelity of response of the recording galvanometer towards the continuously growing signal. No difficulties arose from this cause, since it can be easily shown that, during the whole time interval, say t, for which $\beta t \ll T_0$, the response of the galvanometer is proportional to: $\exp[-E/k(T_0+\beta t)]$ that is, to the thermoluminescent light output. On the other hand, the relation $\beta t \ll T_0$ is in fact satisfied in all the experiments. Technically pure NaCl was used to prepare the polycrystalline powders used in the present experiments. Thorough purification was achieved by evaporation and supersaturation of the dissolved salt,
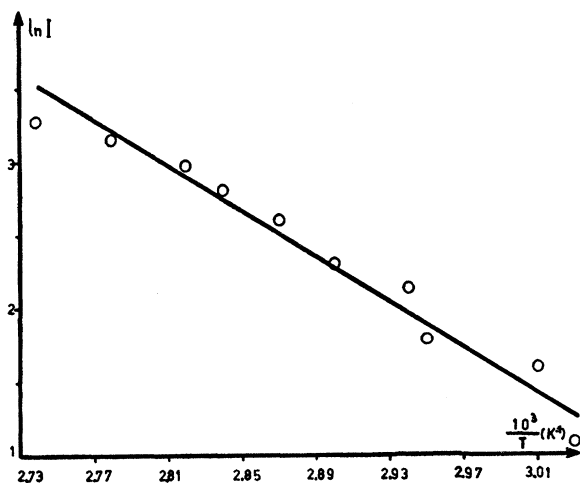

FIG. 3. Semilogarithmic plot of the light intensity *vs* $1/T$, for the initial rising part of a glow peak.

using polyethylene vessels (to avoid Si contamination) and de-ionized water ($\rho > 0.5 \times 10^6$ ohm cm). "Spectral purity" was achieved after three runs.

All the irradiations have been performed at room temperature using x-rays (35 kv-peak) from a glass windowed *W*-anode tube.

Invariably, we considered weak irradiations (giving a slightly yellow color, corresponding to approximately 10^{16} *F*-centers/cm^3).

2. EXPERIMENTS PERFORMED

The general features of the thermoluminescence of irradiated NaCl are well known, and we limit ourselves to considering in detail one definite run, chosen as an example among the great deal of records performed. The glow curve is shown in Fig. 2 as obtained from a 1P21 photomultiplier (spectral response *S*-4). Three

FIG. 4. Glow curve of NaCl recorded by a 1P21 photomultiplier through a 5-mm thick sheet of glass, showing that the first peak has been practically suppressed.

peaks of light appear, with the maxima at the respective temperatures: $T_{G1} = 382°K$, $T_{G2} = 495°K$, $T_{G3} = 589°K$. The second one is actually a rather poorly resolved doublet. The average value of β was around 1°C sec^{-1}.

According to the procedure already mentioned, the value of E has been measured in many cases for the first and third peak[3] and always there was found—within the experimental errors (about 0.1 ev)—a common value of 0.72 ev. Figure 3 shows an example of a semilogarithmic plot *vs* $1/T$.

At this point it is worthwhile to dwell on a very important subject: following our views, at each peak of thermoluminescence a different emission band must occur.

Actually, previous investigators[4] had verified that NaCl thermoluminescent light consists of three bands with their maxima located, respectively, at 3620, 4180/4320 (doublet), and 5250 A, but it was unknown whether or not the spectral composition of one peak differed from that of another. Therefore, we investigated this point, which is additionally important in determining the p_i values, as discussed previously. Actually, the areas of each peak have to be corrected for the spectral response of the phototube, in order to become proportional to the quantities N_{0i}.

Taking for granted the wavelengths from reference (4), we limited ourselves to searching for a correlation between the peaks and the wavelengths.

Measurements have been taken through filters of different transmission characteristics. One without filter is shown in Fig. 2, while Fig. 4 shows the curve obtained through a thick sheet of common glass, very absorbing for ultraviolet. Since the first peak is practically suppressed, we can conclude that it is ultraviolet, that is to say, it belongs to the 3620 A band.

For the other recordings (Fig. 5) use has been made of a GAB interferential filter, set at 0°, 10°, 20°, 30°, 40°, corresponding to various transmitted wavelengths, between 5215 A and 4760 A. What is actually observed is a progressive diminishing of the area of the third peak towards that of the second. Figure 6 shows the ratio σ_3/σ_2 of these areas *vs* the filter passing wavelength, λ_m. This ratio is manifestly a monotonically increasing function of λ_m within the interval considered. This

[3] An accurate determination of E from the second peak proved practically impossible, because it is exceedingly difficult to bleach out the first peak without affecting too much the intensity of the second one—as already experienced by other workers.

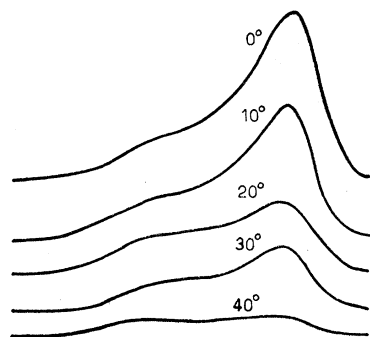[4] J. J. Hill and P. Schwed, J. Chem. Phys. **23**, 652 (1955).

FIG. 5. Series of glow curves of NaCl recorded by a 1P21 photomultiplier, while the interference filter quoted in the text was interposed and set at the different angles indicated in the figure.

circumstance permits the assignment of an emission band to each thermoluminescence peak.

In fact, it is possible to show (see the Appendix) with sufficient accuracy, that the ratio σ_3/σ_2 (vs λ_m) can be monotonic or can alternatively present only one maximum or one minimum, for a definite wavelength (say, λ_m^*). Furthermore, if the wavelengths of the (center of the) emission band of the second and third peak, respectively, are called λ_2 and λ_3, it happens that, according to the behavior of σ_3/σ_2, the following inequalities hold:

σ_3/σ_2 behavior	Inequalities	
monotonically increasing	$\lambda_2 < \lambda_3$,	(1)
monotonically decreasing	$\lambda_3 < \lambda_2$,	(2)
one maximum $\Big\{$	$\lambda_2 < \lambda_3 < \lambda_m^*$,	(3)
	$\lambda_m^* < \lambda_3 < \lambda_2$,	(4)
one minimum $\Big\{$	$\lambda_m^* < \lambda_2 < \lambda_3$,	(5)
	$\lambda_3 < \lambda_2 < \lambda_m^*$.	(6)

These inequalities solve our problem. In fact, by observing that the actual σ_3/σ_2 curve is monotically
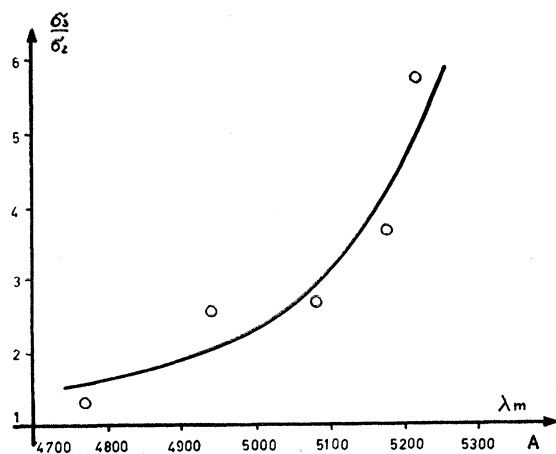

FIG. 6. Curve showing the ratio of the areas of the third peak to the second one, $versus$ the passing wavelength of the filter. This curve has been obtained using the glow curves of Fig. 5.

increasing within the interval investigated, and remembering that the actual values of λ_2 and λ_3 are 4180/4320 A, and 5250 A, we conclude that the only acceptable inequalities are (1), (3), and (5). That is to say: $\lambda_2 = 4180/4320$ A, $\lambda_3 = 5250$ A.

3. DETERMINATION OF p_i

The procedure used to get the p_i values is as follows: first, a complete record of the entire glow pattern is taken, without any filter. The peaks are graphically isolated, assuming that each rising part is an exponential ($e^{-E/kT}$) and their areas measured (in arbitrary units).

Now these areas are to be corrected and their sum normalized to one: that is to say they have to be divided, respectively, by the corresponding ordinates of the curve of spectral response of the phototube [called $i(\lambda)$ in the Appendix]. Table I gives the results for the curve of Fig. 2.

Now Eqs. (16) and (17) of reference (1) have to be used with $h = 3$. Let us point out that our crystals appear always practically colorless after the emission of the third peak of light; this means, as already observed, $n_f \simeq 0$.

It is possible now to get the values of N_{0i}, n_{0i}, as quantities proportional to n_{01}.

Using now the experimental values of E and of the $T_{G,i}$ and Eqs. (11) and (14) of reference (1), we obtain the ratios:

$$p_1 : p_2 : p_3 = 5.03 \times 10^3 : 1.73 \times 10^1 : 1.$$

Through one optical absorption measurement and using Smakula's formula, n_{01} has been determined in the case examined, obtaining $n_{01} \simeq 10^{16}$ cm^{-3}. It then follows that

$$p_1 = 2.10^{-8} \text{ cm}^3 \text{ sec}^{-1},$$
$$p_2 = 9.10^{-11} \text{ cm}^3 \text{ sec}^{-1},$$
$$p_3 = 5.10^{-12} \text{ cm}^3 \text{ sec}^{-1}.$$

with an accuracy which is less than for their ratios.

4. IDENTIFICATION OF L_i-CENTERS

In Sec. 4 of reference 1 some implications have been developed, which the proposed mechanism of F-center thermoluminescence contains, regarding the position of the ground level of L_i-centers within the forbidden band. It is now possible to show how those statements actually agree with experiment.

The first idea which occurs is that L_i-centers are merely the various kinds of V-centers which are introduced in the lattice together with F-centers by irradiation, and whose relative abundance is actually strongly dependent, as it is well known, upon the thermal history of the crystal.

The absorption wavelengths of V_1-, V_2-, and V_3-centers in NaCl, determined by Casler, Pringsheim, and Yuster[5]

[5] Castler, Pringsheim, and Yuster, J. Chem. Phys. 18, 1564 (1950).

Table I. Normalized corrected areas of the peaks.	
First peak	$A_1 = 0.088$
Second peak	$A_2 = 0.145$
Third peak	$A_3 = 0.767$

Table II. Energy gap as sum of emitted and absorbed photons.

i	(a)			i	(b)
	1	2	3		1
$h\nu_{T,i}$	3.425	2.966/2.870	2.362	$h\nu_{T,i}$	3.425
$h\nu^{V}_{i}$	3.594	5.570	5.904	$h\nu_{Cu}$	4.864
ϵ	7.019	8.536/8.440	8.266	ϵ	8.289

are, respectively: 3450 A; 2226 A; 2100 A. It is however to be pointed out that a private communication by Professor Pringsheim—whose kindness is gratefully acknowledged—informed us that the value 3450 A is probably unreliable. Using the data just quoted, we obtain, through Eq. (19) of reference (1), the values of ϵ shown in Table II(a). Actually the value obtained from the second peak of light (doublet) is very near to that obtained from the third peak. On the contrary the value obtained from the first peak sensibly deviates, which may not be significant, for the reason mentioned. In addition it should be remarked that V_1-centers can be seen only at low temperatures.[5] As a consequence, the identification of L_2- and L_3-centers with V_2- and V_3-centers[6] appears confirmed, while the same cannot be stated for L_1- and V_1-centers. A possible interesting alternative has been suggested to the writers by Klick,[7] who pointed out that small impurities of Cu in NaCl (as low as 4×10^{-8}) give rise to an absorption band at 2550 A. Moreover our NaCl contained Cu impurities, nonentirely eliminated during the purification which only reached spectral purity level.

If one makes use of the fact just quoted, a value of ϵ which fits very well with the others two is obtained, as shown by Table II(b).

This result seems to indicate that Cu can actually play a role in our thermoluminescence, but regarding this point, it must be emphasized that such an hypothesis results in peculiar implications concerning the charge of the Cu ion in the lattice. It is probably not useful to dwell further on this topic, since it has not yet been sufficiently investigated experimentally.

Finally, with regard to the value of ϵ, it may be noted that it is near to, but less than, the value of the fundamental absorption for NaCl, which is 9.7 ev,[8] corresponding to 1280 A.

5. CONCLUSIONS

In conclusion, it appears that thermoluminescence is a very valuable tool for the study of lattice imperfections and that other problems in this area might utilize this technique. However, it should be emphasized that, for such purposes, several experimental improve-

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[6] It is understood that what we call here V_2- and V_3-centers are merely those which cause the absorption bands of reference 5: as a matter of fact, the ideas about the structure of V-centers are still far from definite.

[7] We desire to express to Dr. Klick our grateful appreciation for the attention paid to our work and for this valuable suggestion.

[8] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), p. 508.

ments are necessary in comparison with the usual simpler procedures. First of all, spectral analysis of the emitted light must be correlated with the different glow peaks; the absorption spectrum must be explored in a fairly large range and with the highest attainable sensitivity. Finally, the proper kinetics and order of the process have to be taken into account in order to interpret experimental results, eventually searching in a preliminary way, for a direct confirmation of both.

The writers hope to be able in near future to investigate the many points which the present analysis has not yet treated in a satisfactory manner.

APPENDIX—BEHAVIOR OF σ_3/σ_2 vs λ_m

Let us consider first the current response of the ensemble filter plus phototube, vs the wavelength of the incoming light.

Let us indicate with $i(\lambda)$ the current of the photomultiplier when its cathode is illuminated by a source which emits a number ϕ of photons per unit time, of wavelength λ (ϕ is a constant versus λ; $[\phi] = \sec^{-1}$), under the identical conditions as the specimen. Let us also call $\tau(\lambda_m, \lambda)$ the curve of transmission of the filter, where λ_m stands for the wavelength of greatest transmission. We can assume with good accuracy

$$\tau(\lambda_m, \lambda) = a \exp\left[-\left(\frac{\lambda - \lambda_m}{\Lambda} \right)^2 \right], \qquad (1)$$

where Λ is related to the width of the passing band. It is easy to show that the wavelength corresponding to the maximum of response for the ensemble filter plus phototube, differs from λ_m by the amount

$$\Delta\lambda_m = -\frac{1}{2}\Lambda^2 \left(\frac{d \ln i}{d\lambda} \right)_{\lambda = \lambda_m}. \qquad (2)$$

For our very selective filter we find $\Delta\lambda_m$ smaller than 10 A, which is completely negligible. This remark is very important, since the total response of the ensemble, that is the current of the phototube with the filter before it, under the flux ϕ, can then be written as

$$j(\lambda_m, \lambda) = i(\lambda_m)\tau(\lambda_m, \lambda). \qquad (3)$$

Let us now assume, for the spectrum of the photons emitted during the ith peak at the time t, a Gaussian

shape, say,

$$\Psi_i(\lambda,t) = A_i \exp\left[-\left(\frac{\lambda-\lambda_i}{\Theta_i}\right)^2\right], \qquad (4)$$

where λ_i stands for the center of the emitted band, Θ_i is related to its width, and A_i is a function of t which can be determined by considering that:

$$\int_0^\infty \Psi_i(\lambda,t)d\lambda = -\frac{dN_i}{dt}. \qquad (5)$$

Equation (4) is sufficiently accurate, considering the purpose of our calculation, which deals with inequalities.

Performing the integration of Eq. (5), $\Psi_i(\lambda,t)$ becomes

$$\Psi_i(\lambda,t) = -\frac{dN_i}{dt} \exp\left[-\left(\frac{\lambda-\lambda_i}{\Theta_i}\right)^2\right]\Big/ \pi^{\frac{1}{2}}\Theta_i. \qquad (6)$$

It has been assumed, in an approximate way, that the spectral composition of the glow light remains constant during the whole emission of the peak, that is to say λ_i and Θ_i do not depend upon t (that is upon T). The current of the photomultiplier at the time t, due to the photons belonging to the whole emission band considered, is obviously

$$I(\lambda_m,t) = \frac{i(\lambda_m)}{\phi} \int_0^\infty \tau(\lambda_m,\lambda)\Psi_i(\lambda,t)d\lambda. \qquad (7)$$

The area of the peak will then be given by

$$\sigma_i(\lambda_m) = \int_{t_0}^{t_1} I(\lambda_m,t)dt$$

$$= \frac{i(\lambda_m)N_{i0}}{\phi\Theta_i\pi^{\frac{1}{2}}} \int_0^\infty \tau(\lambda_m,\lambda) \exp\left[-\left(\frac{\lambda-\lambda_i}{\Theta_i}\right)^2\right]d\lambda. \qquad (8)$$

Use of Eq. (4) yields

$$\sigma_i(\lambda_m) = \frac{N_{i0}i(\lambda_m)}{\phi}a\frac{\Lambda}{(\Lambda^2+\Theta_i^2)^{\frac{1}{2}}}\exp\left[-\frac{(\lambda_m-\lambda_i)^2}{\Lambda^2+\Theta_i^2}\right]. \qquad (9)$$

Now we consider the ratio $\sigma_3(\lambda_m)/\sigma_2(\lambda_m)$ with which we are concerned. We have

$$\frac{\sigma_3(\lambda_m)}{\sigma_2(\lambda_m)} = \frac{N_{03}}{N_{02}}\left(\frac{\Lambda^2+\Theta_2^2}{\Lambda^2+\Theta_3^2}\right)^{\frac{1}{2}}$$

$$\times\exp\left[\frac{(\lambda_m-\lambda_2)^2}{\Lambda^2+\Theta_2^2}-\frac{(\lambda_m-\lambda_3)^2}{\Lambda^2+\Theta_3^2}\right]. \qquad (10)$$

The behavior of this function of λ_m is still a quadratic exponential, that is to say, only one maximum or one minimum can appear. In the particular case $\Theta_2=\Theta_3$, the quadratic term vanish and the curve becomes a purely exponential one, increasing or decreasing according to the case that $\lambda_2<\lambda_3$ or $\lambda_3<\lambda_2$, respectively. If $\Theta_2<\Theta_3$, a minimum occurs; a maximum, if $\Theta_3<\Theta_2$. By straightforward procedure, it can be found that the minimum or the maximum takes place at a value of λ_m, say λ_m^*, which verifies the following equations:

$$\lambda_3-\lambda_m^* = \frac{\Lambda^2+\Theta_3^2}{\Theta_3^2-\Theta_2^2}(\lambda_3-\lambda_2), \qquad (11)$$

$$\lambda_2-\lambda_m^* = \frac{\Lambda^2+\Theta_2^2}{\Theta_3^2-\Theta_2^2}(\lambda_3-\lambda_2). \qquad (12)$$

Now from Eqs. (11), (12) it follows that

$$\text{for}\quad \Theta_2<\Theta_3\quad\text{or}\quad \begin{cases}\lambda_m^*<\lambda_2<\lambda_3\\ \lambda_3<\lambda_2<\lambda_m^*\end{cases}, \qquad (13)$$

$$\text{for}\quad \Theta_3<\Theta_2\quad\text{or}\quad \begin{cases}\lambda_2<\lambda_3<\lambda_m^*\\ \lambda_m^*<\lambda_3<\lambda_2\end{cases}, \qquad (14)$$

which are the inequalities quoted in the text.