DELAYED LUMINESCENCE IN ALKALI HALIDES UNDER F BLEACHING[†]

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Samples of NaF, LiF, NaCl and KCl were x-irradiated (40 KeV - 20 mA) at 300°K for a few seconds to 20 minutes. The luminescence spectrum of these samples under F bleaching was studied with controlled time delay between bleaching and emission. The "delayed luminescence" (D.L.) of NaF and LiF gave spectra centered near 580 mμ with half-width close to 60 mμ. For KCl, the spectrum peaked at 420 mμ with half-width of 74 mμ. The corresponding spectrum of NaCl was not successfully resolved. The growth and decay of the D.L. for NaF are characterized by the activation energy: $.014 \pm .002$ eV and $.024 \pm .002$ eV. The effects of temperature are also investigated. Comparative analysis of the data appear to favor a model based on the recombination between a vacancy-pair with "hole",¹ and the electron released from an F center under F bleaching.

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¹ F. Seitz, Revs. Mod. Phys. 18, 384 (1946) and 26, 7 (1954).

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It has been known that F light bleaching of F centers results in the destruction of F centers, and the formation of F aggregate centers, such as M centers. We would like to present experimental evidences favoring the recombination between trapped holes and electrons from F centers, also take place under F bleach. Experimentally, we control the time lapse between F bleaching and the luminescence that is detected. We call this D.L. in contrast to the ordinary luminescence that is detected while the F bleach is in progress.

May 1 have Slide 1

This illustrates the experimental setup. The time delay control device is a pair of synchronized choppers. When light is shining on the sample, no D.L. is detected, and while D.L. is being recorded, no light is falling on the sample. Time delay is optimized to be .09 sec. Otherwise, the set-up is a conventional luminescence set-up.

May 1 have Slide 2

Two groups of samples are employed. Each group has a common halogen. Under F light excitation, normal luminescence characteristic of F, M and F_3^+ centers are observed. These are compared with D. L. The peak of D. L. cannot be associated with any one of the direct luminescence, except in the case of NaF, where the peak of D. L. is very close to that of F_3^+ center. If this is true also for LiF we should expect the peak of D.L. of LiF to be near 540 mu. However, as evident from this table, this is not the case. We also note that the peak of D. L. from NaF and LiF are the same. The implication is that D. L. is characteristic of common halogen ion. This is inconsistent with the D.L. of KCl and NaCl. The reason that D.L. of NaCl could not be successfully resolved is probably because of the closeness of F band and D.L. peak. We also would like to draw attention to anti-Stoke shift observed in the case of KCl.

In order to examine possible role of V_2 centers, intensity of D.L. is studied as a function of X irradiation time and F bleaching time. The slide presents the results for KCl as an example. D. L. and V_2 centers show saturation after 10 min. of irradiation time. Upon continuous F bleaching, D.L. and F concentration decrease together with time, while V_2 concentration remains constant. This is an indication that V_2 centers are not involved in the mechanism of D.L.

May I have Slide 4

In the case of LiF, only gamma irradiated and later annealed samples render D. L. It is generally believed that a substantial concentration of vacancy pairs are formed in this kind of sample. We speculate that samples emitting D. L. contain vacancy pairs.

May I have Slide 5

With the apparatus arrangement as shown earlier, we recorded photographically the growth of D. L. curves as soon as the shutter is opened, and the decay of D.L. when the shutter is closed. From such curves, growth and decay time constant above 77°K are evaluated. Time constant is plotted against inverse absolute temperature. There are two components of time constant. One is temperature dependent, and the other is temperature independent. The former implies migration of some defect centers, while the latter suggests tunnelling process. From the temperature dependent part, activation energy is calculated. The activation energy for growth period is smaller than the activation energy for decay process. We interpret that during the growth period, recombinations take place between nearest centers first, and during decay period, recombinations between further away centers are in effect.

We can speculate on a possible mechanism of D.L. in the following way. F light ionizes F centers as well as produces excitons, possibly $V_k + e$ model excitons. A hole formed near a vacancy pair is immediately captured by the vacancy pair to form Seitz H center. The H center in turn recombines with a wandering electron and emits luminescence even after the removal of exciting light. This corresponds to the temperature dependent part. As for tunnelling process, we modify the first equation by (B). The kinetic equations are derived assuming the wandering electron to be migrating defect, leading to the concept of τ_g and τ_d . Their predictions appear to be consistent with the data shown in the preceding slide.

TABLE OF ABSORPTION AND EMISSION BANDS

SLIDE 2

SAMPLE	ABSORPTION ^(a) BAND		DELAYED LUMINESCENCE		DIRECT LUMINESCENCE		
	F(mμ)	V ₂ (mμ)	PEAK (mμ)	H.W. (mμ)	F(mμ)	M(mμ)	F ₃ ⁺ (mμ)
NaF	341	—	580	60	LNT ₇₈₅ ^(β)	653 ^(β)	LHeT ₅₇₅ ^(γ)
LiF	250	—	580	90	—	670 ^(δ)	540 ^(δ)
NaCl	458	223	—	—	LNT ₁₁₂₀ ^(ε)	1070 ^(ε)	—
KCl	556	230	420	75	LNT ₁₀₁₀ ^(ζ)	1080 ^(η)	—

(a) J. H. SCHULMAN AND W. D. COMPTON, "COLOR CENTERS IN SOLIDS", PAGE 29,
(PERGAMON PRESS INC. N.Y. 1962).

(β) P. PODINI, PHYS. REV. 141, 572 (1966)

(γ) L. F. STILE AND D. B. FITCHEN, PHYS. REV. LETTER VOL 17, NO 13, (1966)

(δ) Y. FARGE, G. TOULOUSE AND M. LAMBERT, J. PHYS. (PARIS) 27, 287 (1966)

(ε) TH. P. J. BOTDEN, C. Z. VAN DOORN, AND Y. HAVEN, PHILLIPS RES. REPTS. 9, 469 (1954)

(ζ) F. LUTY AND W. KUHNERT, PHYS. STAT. SOL. 14, 157 (1966)

(η) C. J. DELBECQ, Z. PHYSIK 171, 560 (1963)

Na F

 τ (sec.)

GROWTH

DECAY

 $1/^\circ\text{K} \times 10^{-3}$

τ (SEC.)

KCl

TABLE OF ACTIVATION ENERGY

SAMPLE	ACTIVATION ENERGY (eV)	MIGRATION ENERGY (eV)
NaF	$.014 \pm .002$	$.024 \pm .002$
LiF	—	—
NaCl	—	—
KCl	—	$.33 \pm .01$

SUGGESTED MECHANISM FOR D.L.

B) FOR NaF NEAR LNT, LiF AND KCl

1) REPLACED BY

4) REPLACED BY

GROWTH TIME CONSTANT (τ_g)

$$I(t) \propto [H_s][e^-]$$

$$\frac{d[e^-]}{dt} = k_1 - k_2[e^-]$$

$$[e^-] = [e^-]_{\infty} (1 - e^{-t/\tau_g})$$

$$I(t) = I(\infty)(1 - e^{-t/\tau_g})$$

DECAY TIME CONSTANT (τ_d)

$$\int I(t) dt \propto [H_s]$$

$$I(t) \propto \frac{d[H_s]}{dt}$$

$$\frac{dH(t)}{dt} \propto [H(t)]$$

$$[H_s(t)] \propto [H_s(0)] e^{-t/\tau_d}$$

$$I(t) = I(0) e^{-t/\tau_d}$$