

Luminescence and Photoconductivity in Silver Halides*

G. C. SMITH†

Department of Engineering Physics, Cornell University, Ithaca, New York

(Received 12 May 1965)

Pulsed and steady-state luminescence and photoconductivity were measured in AgCl and AgBr at low temperatures using x-ray and uv excitation. The luminescence efficiency and electron range (*Schubweg*) are found to be competitive forms of response as functions of temperature. In AgCl at 4.2°K electron-hole pairs are captured (or formed) at a luminescence center in about 10^{-8} sec, thus accounting for the large decrease of electron range observed at low temperatures. A model is proposed in which an intrinsic luminescence center is represented by a shallow (0.05-eV) electron trap with a characteristic lifetime for radiative recombination after electron capture of about 25 μ sec. Similarity to the intrinsic luminescence of alkali halides is noted. Large dark currents of the order of mA and electroluminescence were observed in some crystals after pre-irradiation at 4.2°K.

I. INTRODUCTION

LUMINESCENCE is an important form of energy conversion in the silver halides at low temperatures; estimates for quantum efficiency of the order of 10% have been made.¹ In AgCl and AgBr broad blue-green emission bands are observed which seem to be characteristic of pure crystals.² Wiegand¹ measured the temperature dependence of the steady-state luminescence and photocurrent in AgCl. The luminescence was essentially constant below 50°K and was thermally quenched at higher temperatures with an activation energy of 0.05 eV. The photocurrent showed a maximum at about 50°K, with a sharp decrease at lower temperatures. Measurements of electron drift and Hall mobilities in the same temperature range show multiple-trapping effects,³ but their temperature dependence is not strong enough to account for the observed decrease,⁴ by several orders of magnitude, of the electron range. Ascribing this decrease to a drastically reduced electron lifetime—due to shallow traps—is a possible explanation for pulsed-photoconductivity measurements, but it leads to difficulties in the interpretation of high-intensity steady-state measurements such as were performed by Wiegand, since one would expect that finally all traps are filled, so that the free-electron concentration returns to the value observed at higher temperatures. Since this does not occur—indeed, one has difficulty maintaining a concentration sufficient for cyclotron-resonance measurements—one must postulate some relatively efficient form of electron-hole recombination which is active only at low temperatures. It is

the purpose of this paper to show that luminescence performs this function.

In pulse experiments above 80°K, Snavely⁵ observed that the luminescence efficiency is very low, of the order of 10^{-3} . In the present investigation it was attempted to elucidate further the relation between pulse and steady-state conditions by measurements to 4.2°K on the same crystals under otherwise identical conditions. Such measurements seem also of interest from a more general point of view, since highly efficient low-temperature luminescence has also been observed in alkali halides.⁶

II. EXPERIMENTAL PROCEDURES

Individually triggered uv and x-ray pulse excitations of 0.2- μ sec duration were used to create about 10^7 electron-hole pairs per pulse. The photocurrent and luminescence responses were displayed (and photographed) on an oscilloscope. Photocurrent pulses, either in the integrated form (e.g., Michel¹⁰) or in the direct, nonintegrated, form, were selected for display by a switching arrangement which changed the time constant of the detector circuit. For convenience of analysis the electric field was kept sufficiently low that the transit time was longer than the electron lifetime. In this mode of operation the integrated charge is proportional to the electron range, i.e., to the product of mobility, lifetime, and electric field. In the "direct" mode the rise time of the detecting equipment was less than 0.02 μ sec, so that the photocurrent decay times could be observed directly. The use of pulsed fields and the restriction to low total irradiation dosages prevented the buildup of internal polarization. It should be noted that both the x rays and uv light were absorbed in a layer of 10^{-3} cm, or less, while the sample thickness was a few mm.

The pulsed luminescence was observed by recording the light intensity falling upon a photomultiplier (EMI 9514B) as a function of time. As in the de-

* Based on a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree at Cornell University. This research was supported by the United States Atomic Energy Commission. Additional support was received from the Eastman Kodak Company and the Advanced Research Projects Agency.

† Present address: Institut für Polymere, Universität Marburg, Germany.

¹ D. A. Wiegand, Phys. Rev. **113**, 52 (1959).

² G. C. Farnell, P. C. Burton, and R. Hallama, Phil. Mag. **41**, 159, 545 (1960).

³ K. Kobayashi and F. C. Brown, Phys. Rev. **113**, 507 (1959).

⁴ R. Van Heyningen and F. C. Brown, Phys. Rev. **111**, 462 (1958).

⁵ B. B. Snavely, thesis, Cornell University, 1962 (unpublished); Phys. Status Solidi **9**, 709 (1965).

⁶ See M. N. Kabler, Phys. Rev. **136**, A1296 (1964).

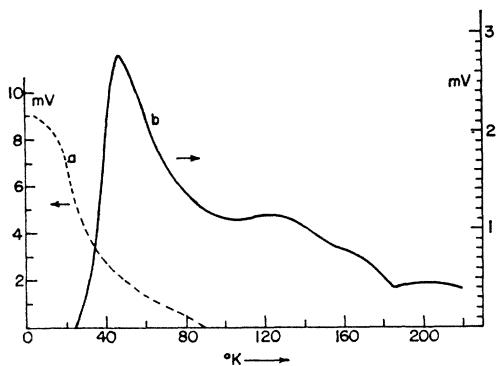


FIG. 1. Luminescence (a) and photocurrent (b) in chlorine annealed, zone refined AgCl; integrated values; pulsed uv excitation.

tection of pulsed photocurrent, alternative time constants in the detection system allowed the observation of either direct or integrated luminescence. Since a single excitation pulse results in a maximum of about 10^8 photoelectric events on the detecting photomultiplier, the direct mode of presentation yields a succession of "spikes," while the integrating mode converts each "spike" to a step in a monotonically increasing curve which exponentially approaches a constant value and from which the time constant of the luminescence decay can be determined. For purposes of analysis, the latter method proved more useful and the integrated luminescence pulse height was taken as a measure of the luminescence efficiency. Provision was also made for measuring the steady-state luminescence current from the photomultiplier by means of a picoammeter.

Samples a few mm thick and of 1–2 cm² area were cut from crystals of AgCl and AgBr.⁷ They were polished to an optical finish and annealed near the melting points in a quartz furnace. AgCl samples, some of which were from zone-refined ingots, were annealed in three different ways: (1) air annealed, (2) vacuum annealed, and (3) chlorine annealed. The only AgBr sample studied was air annealed. All operations were performed under photographic "safelights." An electrode of strips of Aquadag was painted on one surface of the crystal, and an 85% transparent gold mesh was pressed against the opposite surface by means of a sapphire disk. The sample, mounted on a suitable sample holder, together with electrode connections, temperature measuring devices, and a heater, was inserted into a helium cryostat which had Mylar-film windows to allow transmission of the weak (maximum 30kV) x-ray excitation. Four windows at right angles allowed for viewing and irradiating from different angles with respect to the direction of the applied fields and simultaneous irradiation with different sources. For further versatility, the sample holder could also be rotated. The x rays fell upon the sample surface coated

⁷ The author thanks F. Moser of the Kodak Research Laboratories for providing the crystals.

with Aquadag, while the luminescence was observed through the sample, the gold mesh, and a sapphire window on the opposite side. During experiments with uv light the excitation was usually directed through this same window and the luminescence was detected at right angles, appropriate filters being used to isolate spectral regions. The sample holder was sealed and partially evacuated during cooling to avoid sudden thermal changes in the sample. After transfer of helium to the cryostat, and slow cooling of the sample, the sample holder was filled with the heat-exchange gas to reach 4.2°K and ensure a uniform sample temperature.⁸

III. RESULTS

In general, measurements were made on freshly annealed samples. Repeated measurements without annealing or measurements on different similar samples showed slight variations from one run to the other, as has also been observed by other authors. They are caused by the high sensitivity of the electronic properties of the silver halides to past history. However, the general behavior is well reproducible. The figures represent typical results. Figure 1 shows the luminescence (integrated value) and photoconductivity (integrated pulse heights) as functions of temperature in chlorine annealed AgCl under pulsed uv excitation. The

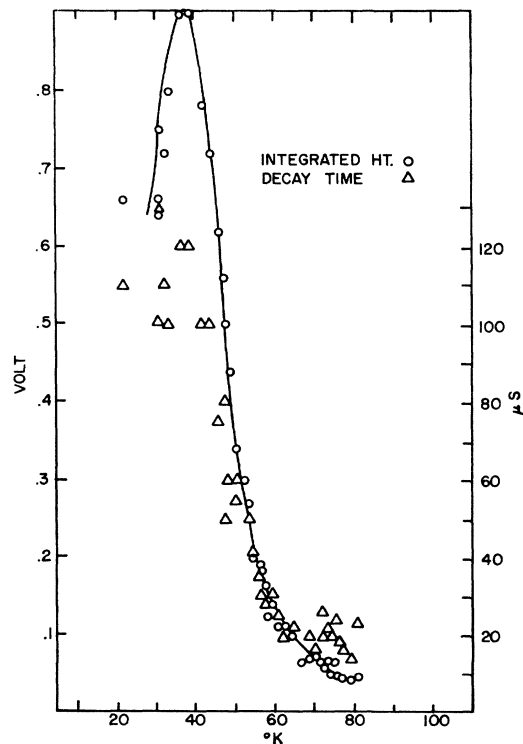


FIG. 2. Luminescence intensity (integrated value) and decay time in vacuum annealed AgCl; pulsed x-ray excitation.

⁸ For further details see G. C. Smith, thesis, Cornell University, 1965 (unpublished).

characteristic feature of these curves is the strong luminescence response at low temperatures, where the photocurrent pulses are very small or not observable. As the temperature increases, the luminescence decreases while the current pulses grow rapidly. Similar competitive responses are obtained with crystals which were not zone refined and with Ni-doped samples, and also with crystals annealed in air, in Cl_2 , or in vacuum, except that in the Ni-doped or vacuum-annealed crystals the photocurrents were smaller. After strong pre-irradiation with uv light at 4.2°K a weak luminescence was observed which decayed within a period of minutes. No other effects were observed, while pre-irradiation at 77°K had the usually observed effect of increasing markedly the electron lifetime.

In all these cases the luminescence decay is exponential; the decay times are approximately proportional to the integrated pulse heights as shown, e.g., in Fig. 2, indicating that the initial rate of luminescence is temperature-independent and that the decrease of efficiency at higher temperatures is associated with a decrease of decay time. In the temperature range where the luminescence decreases and the photocurrent increases, the photocurrent pulses exhibit a sharply decreasing decay time with increasing temperature. At higher temperatures, the photocurrent decay times are comparable to the $0.2\text{-}\mu\text{sec}$ duration of excitation (in the absence of pre-irradiation), while the integrated height shows an over-all gradual decrease, as might be expected from a monotonically decreasing mobility in this range.

The maximum energy conversion efficiency of AgCl as an x-ray scintillator is about 10%, or about 25 eV per luminescence photon, as determined by comparison with anthracene.⁹ This efficiency is comparable to that for the creation of free electrons measured by Michel¹⁰

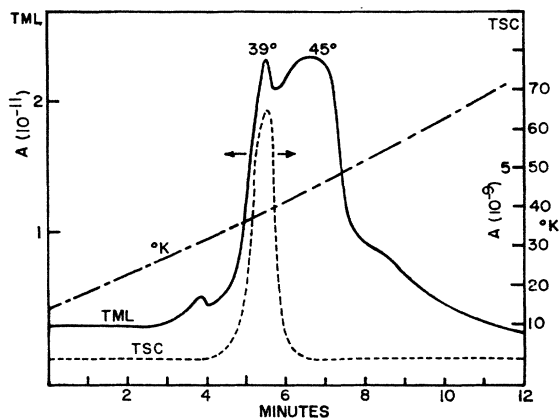


FIG. 3. Thermally stimulated currents (TSC) and thermoluminescence (TML) in chlorine-annealed AgCl; x-ray pre-irradiated; 100-V internal field.

⁹ F. D. Brooks, *Progr. Nucl. Phys.* **5**, 276 (1956); R. C. Sangster and J. W. Irvine, *J. Chem. Phys.* **24**, 670 (1956).

¹⁰ A. E. Michel, *Phys. Rev.* **121**, 968 (1961); thesis, Cornell University, 1960 (unpublished).

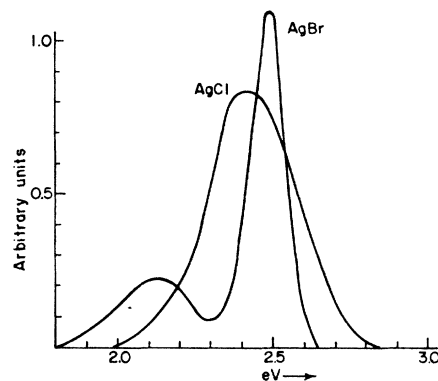


FIG. 4. Luminescence emission spectra of AgCl and AgBr; $T = 4.2^\circ\text{K}$; $3650\text{-}\text{\AA}$ excitation (steady state).

under similar circumstances, but lower than the value of 7.5 eV per electron determined from nuclear-counter-type experiments.¹¹

Results similar to those with x-ray excitation are obtained with pulsed uv excitation of the same intensity except for the details of the temperature dependence. However, the luminescence decay times at low temperatures do not exceed about $25\ \mu\text{sec}$, i.e., they are much shorter than those observed with x-ray excitation. Because of high local density of excitation along the path of an x-ray photon, and of the possibility of radiation damage and energy storage in higher excited states, the shorter lifetime observed with uv excitation should represent a more intrinsic property of the luminescence process.

In air annealed AgBr with x-ray or uv excitation, no luminescence pulses could be observed down to 4.2°K ; photoconductivity pulses remained larger than in AgCl at 4.2°K . At higher temperatures the photoconductivity response showed a temperature dependence similar to that observed by Snavely⁵ for vacuum annealed AgCl, except that the characteristic steep rise occurs at 180°K rather than at 220°K .

In AgCl thermoluminescence (TML) observed after pre-irradiation with x rays or uv at 4.2°K showed peaks at about 39 and 45°K as shown in Fig. 3. Simultaneously measured thermally stimulated currents (TSC) showed a peak coincident with the lower TML peak. These curves reflect the presence of traps with a thermal depth of the order of $0.1\ \text{eV}$ in a concentration exceeding $10^{18}\ \text{cm}^{-3}$. Simultaneous luminescence and photoconduction were observed upon illumination with near infrared light after pre-irradiation with uv at 4.2°K . Application of ac and dc potentials as low as 20 V after pre-irradiation yielded a transient luminescence. Assuming that electrons are the only mobile charge carriers—which is borne out by many experiments⁴—the inference may be drawn that conduction band electrons can participate in the luminescence at low temperatures.

¹¹ F. C. Brown, *Phys. Rev.* **97**, 355 (1955).

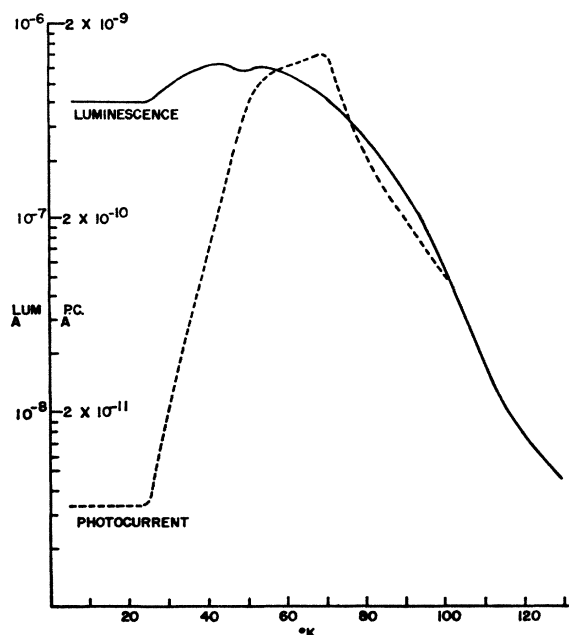


FIG. 5. Steady-state luminescence and photoconductivity in air annealed AgCl, etched in KCN; 3650-Å excitation; 10.5 V dc.

In AgBr similar TSC and TML peaks are obtained in the temperature range from 40–60°K.

The steady-state luminescence emission spectra of AgCl and AgBr (Fig. 4) were measured under steady state conditions at helium temperature using a cooled (80°K) RCA 7102 photomultiplier and a monochromator. The spectral response of the detection system was determined by calibration against a tungsten lamp assumed to radiate as a black body. The AgCl spectrum shows a single broad band at about 2.43 eV. No evidence of fine structure as reported by Vacek *et al.*¹² was observed. AgBr shows a narrower peak at 2.50 eV and a second, broader one at about 2.14 eV. These spectra are identical for both uv and x-ray excitation.

Representative steady-state luminescence and photo-current versus temperature curves are shown in Fig. 5 for an etched sample under very intense 3650 Å illumination. These curves are similar to those of Wiegand.¹ For low intensity 3650 Å excitation the luminescence falls to one-half of its maximum (low- T) value at ~60°K for AgCl and at ~15°K for AgBr. The detailed features of the temperature dependence are a function of intensity, type of excitation, and crystal preparation; this should be borne in mind when comparing results of different authors.

At 4.2°K the optical absorption and the steady state excitation spectra for luminescence and photoconductivity in AgCl show simultaneous increases with decreasing wave length at the absorption edge similar

¹² K. Vacek and J. Ringeissen, *J. Phys. Radium* **22**, 519 (1960).

to the photocurrent behavior observed by Brown¹³ and by Gordon.¹⁴

IV. MODEL FOR LUMINESCENCE

The results cited in the previous section may be interpreted in terms of a model, Fig. 6, in which the luminescence center is represented by a shallow electron trap. In addition, electrons are removed irreversibly from the conduction band by deep traps or nonradiative recombination centers. Defining the following quantities: w_1 = probability for capture by a luminescence center; w_2 = probability for radiative recombination at luminescence centers; w_3 = probability for thermal activation to the conduction band from a luminescence center; w_4 = probability for irreversible removal from the conduction band by nonradiative

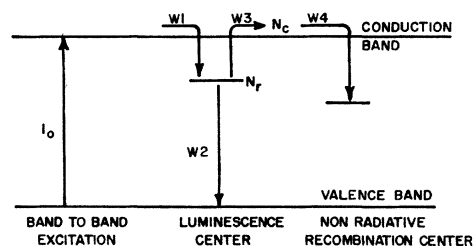


FIG. 6. Model for luminescence center.

processes; N_c = number of electrons in the conduction band; and N_r = number of electrons in luminescence centers, the steady-state luminescence efficiency is given by

$$(w_2 N_r / I_0) = [1 + (w_4 / w_1) + (w_3 w_4 / w_1 w_2)]^{-1}, \quad (1)$$

where I_0 is the rate of excitation; it is assumed that all processes are first order (e.g., that the number of traps is large compared to N_c). The only strongly temperature-dependent probability is w_3 , which is assumed to be determined by a thermally activated process according to: $w_3 = b_0 \exp(-E/kT)$, where b_0 is of the order of the lattice vibrational frequency and E is the trap depth. For $w_4 \ll w_1$, Eq. (1) reduces to the usual form for thermally quenched luminescence (e.g., Wiegand¹), but the pre-exponential factor has a different interpretation. The equilibrium free electron population is

$$N_c = (w_2 + w_3) / (w_1 w_2) I_0 [1 + (w_4 / w_1) + (w_3 w_4 / w_1 w_2)]^{-1}. \quad (2)$$

In order to obtain the temperature dependence of the steady state photocurrent per unit field, N_c must be multiplied by the mobility. Since N_c is the true free carrier concentration the Hall mobility has to be used and not the drift mobility, which differs widely from

¹³ F. C. Brown, *J. Phys. Chem.* **66**, 2368 (1962).

¹⁴ A. M. Gordon, *Phys. Rev.* **122**, 748 (1961).

the Hall mobility^{3,15} at temperatures near and below the transition from dominantly photoconductive to dominantly luminescence response ($\sim 60^\circ\text{K}$ in AgCl; $\sim 15^\circ\text{K}$ in AgBr). This difference reflects, at least in part, the multiple trapping in the luminescence centers. From pulse experiments in AgCl a set of parameters can be determined: $w_1=10^8$, $w_2=4\times 10^4$, $w_3=10^{13}$ $\exp(-0.05/kT)$, and $w_4=10^7$. Curves representing Eqs. (1) and (2) and the photocurrent are plotted in Fig. 7 for this choice of parameters. For the same model the integrated luminescence and photocurrents in the case of pulsed excitation turn out to be proportional to the steady state values in the approximation justified by the numerical values given above. While these calculated curves reproduce the general behavior of the observed curves, it is clear that this model represents only a first approximation in the luminescence-photocurrent relationship. In particular, the effects of other shallow traps, such as those observed in TSC and TML measurements, and other very shallow traps, have been ignored. The role of possible hole transport has been neglected (see also Wiegand¹).

With high-intensity steady-state excitation the probability for loss of a conduction-band electron by non-radiative processes w_4 is much smaller than for pulsed excitation, since some of the deep traps which determine

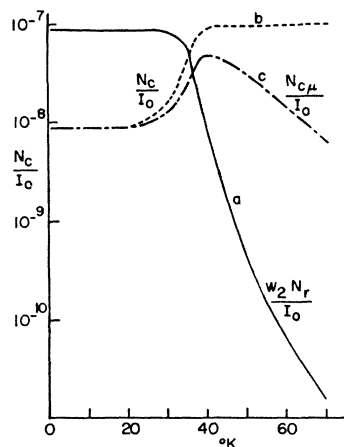


FIG. 7. (a) Calculated luminescence efficiency, (b) free-electron concentration, and (c) photoconductivity; integrated values; pulsed excitation (for values of parameters see text).

w_4 in the low intensity measurements have been filled during irradiation. The decrease of w_4 moves the onset of the luminescence decrease to higher temperatures (because of the increased recapture of electrons at the luminescence center) and increases the ratio of photocurrents at high and low temperatures in agreement with observations. Figure 8 represents the calculated curves with the same parameters as in Fig. 7, but with $w_4=10^5$ instead of 10^7 .

Since variations of crystal treatment did not cause substantial differences in the luminescence behavior, it

appears that the luminescence center is intrinsic, i.e., not associated with impurities. The high luminescence efficiency requires high capture probability of both electron and hole. Viewed in this way, it seems likely that the hole trap responsible for the short hole lifetimes usually observed^{4,15} may be identical with the luminescence center. The nature of the recombination center is not clear. Wiegand¹ suggested that it is a silver ion vacancy. After capture of a hole, such a center would, however, presumably be electrically neutral, hence would not seem able to compete for electrons with other traps in the manner required for the highly efficient radiative recombination. Since the temperature dependence of the luminescence and some other features are similar to what has been observed in some alkali halides (see Kabler, Ref. 6), it is also possible that the center is a self-trapped hole, a V_k center, as is the case in the alkali halides. However, attempts to find an optical absorption band characteristic of such a center were unsuccessful. While simultaneous TML and TSC experiments suggest that free carriers participate in the luminescence, they do not preclude the possibility that excitons,¹⁶ rather than free carriers, are formed by the exciting radiation with subsequent radiative recombination.

V. LARGE CURRENTS AND ELECTRO-LUMINESCENCE

In air annealed AgCl and AgBr after strong pre-irradiation at 4.2°K (i.e., under conditions of long lifetime), dark currents were observed which, upon raising the temperature, assumed values of the order of mA if ac or dc voltages in excess of 20–50V, a kind of breakdown voltage, were applied. These currents were

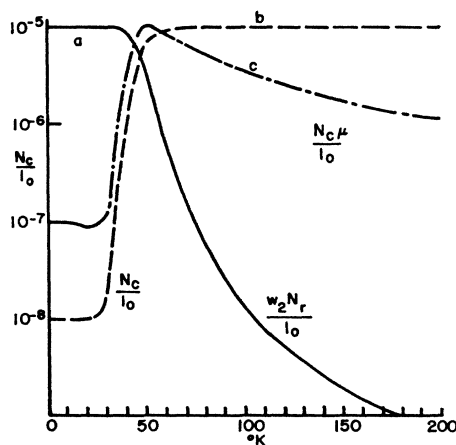


FIG. 8. (a) Calculated luminescence efficiency, (b) free-electron concentration, and (c) photoconductivity; steady-state excitation (for values of parameters see text).

¹⁵ F. C. Brown and K. Kobayashi, *J. Phys. Chem. Solids* **8**, 300 (1959) and D. C. Burnam, F. C. Brown, and R. S. Knox, *Phys. Rev.* **119**, 1560 (1961).

¹⁶ F. C. Brown, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Plenum Press, Inc., New York, 1963), p. 349.

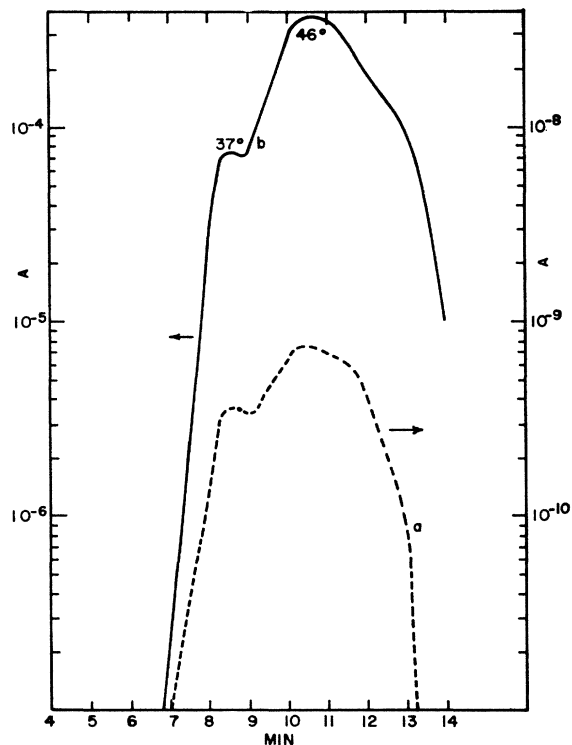


FIG. 9. (a) Electroluminescence and (b) dark currents in zone refined, air annealed AgCl after heavy uv pre-irradiation at 4.2°K; 10 V dc.

accompanied by electroluminescence which seemed to have the normal spectrum according to rough measurements using filters. Figure 9 shows this behavior in AgCl with a constant heating rate of 5°/min. The peak

temperatures correlate well with those observed in normal TSC and TML experiments. From the current, (i.e., the free-carrier concentration) and the luminescence intensity one can estimate the probability for radiative recombination, which turns out to be several orders of magnitude smaller than in the normal pulse experiments. A reduction of the heating rate by an order of magnitude gave a comparable reduction in the value of peak current. These observations suggest that emission from traps was a controlling factor. In order to explain the high currents, it is then necessary to postulate very long electron lifetimes and carrier injection at the electrodes. It is suggested that the "breakdown" behavior is associated with the impact ionization of traps by "hot" electrons.¹⁷ Such electrons may have a much smaller capture probability at the luminescence center, thus accounting for the low radiative recombination probability. Another possible explanation is unavailability of holes needed for recombination: Though the concentration of free electrons (and thus the current) has been enhanced very much by the breakdown process, the concentration of holes, thermally released from traps, is not much larger than under normal conditions.

ACKNOWLEDGMENTS

The author is indebted to Professor H. S. Sack for his advice and constant interest in this work. Professor H. Mahr generously contributed from his experience with similar measurements in the alkali halides. Discussions with B. Snavely, A. Ballonoff, and R. Laibowitz are gratefully acknowledged.

¹⁷ D. Martz and F. Garcia-Moliner, *J. Phys. Chem. Solids* **26**, 551 (1965).