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Space-Charge Effects in CsI Electroluminescence*

C. Paracchini

Istituto di Fisica, Università di Parma, Parma, Italy

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The photoemission at the metal-CsI crystal interface is examined at liquid-nitrogen temperature under square-wave excitation. The emission spectra of the initial flash and of the persistent luminescence are reported. The decays of the emissions just following the voltage application obey an inverse-power law. A qualitative interpretation of the initial brightness-wave behavior is obtained assuming the existence of traps with different capture cross sections. The brightness frequency dependence is interpreted assuming an exponential buildup of the space charge due to the injected carriers.

I. INTRODUCTION

The study of electroluminescence in alkali-halide crystals began a number of years ago,[1] but only recently has the effect been clearly identified and examined in several alkali halides.[2-4]

The light emission is generally observed at liquid-nitrogen and lower temperatures, where the intrinsic recombinations are radiative. An alternate electric excitation is needed for the persistence of the effect. The luminescence is easily detected by photomultipliers without any further amplification, if the amplitude of the applied fields is larger than 10^4 V/cm. However, no evidence of a threshold is obtained, and weaker light outputs are expected for lower excitation values.

The experimental results previously reported[2-4] show that the light emission is due to the radiative recombination of electrons in excitonic states with self-trapped holes. According to a model previously proposed,[3,4] the pairs are created by impact-ionization processes due to electrons accelerated in a high-field region, near the metal junction. Field or Schottky emission is responsible for electron injection from the negatively biased contact; Poole–Frenkel field-assisted thermal ionization generates the primary electrons at the field reversion.

Because it is easier to detect photons instead of the same number of electrons, light emission has been found useful for studying high-field electric effects in high-resistivity insulators, where direct current measurements are difficult to be obtained.[5]

In previously reported works[3,4] the observed luminescence was correlated with modern avalanche breakdown theories. This luminescent effect is also expected to be useful for the study of the space-charge formation following the injection and the trapping of carriers. Current measurements in these cases would be difficult to interpret, on account of the large polarization component; moreover, because of the sign inversion, a current time-integrated measurement should be impossible. This unfavorable experimental situation is avoided by observing light signals.

In the present work the effects of the injected space charge on the electroluminescence in CsI crystals are considered. The trapping and the release of electrons that play a role in the transient effects and in the brightness frequency dependence are examined. The study of these phenomena have been extensively performed on traditional electroluminescence cells,[1,6] but the results obtained have been hard to interpret, because of the difficulty of material purification and the existence of several recombination centers. Alkali halides are easily refined and, though the nature and the distribution of the trapping levels remain unknown in these cases also, the existence of a single radiative recombination process simplifies considerably the experimental situation.

Cesium iodide has been chosen for this work because it has the highest intrinsic luminescence efficiency among the alkali-halide crystals; with this salt a considerable effect is easily obtainable with lower values of the excitation voltage than needed for the other alkali halides. A high luminescent yield is particularly useful in the present work, where square-pulse excitations with low rise and fall times are needed and large amplitude pulses are then difficult to obtain.

II. EXPERIMENTAL

The samples were obtained from squared (1×1 cm) slices 0.3–0.1 mm thick. They were cut from CsI single crystals, supplied by Harshaw Chemical Company and Quartz and Silice. The slices were then made thinner and polished on wet paper. The specimens were placed between two copper electrodes. Thermal and electrical contacts were obtained by means of a thin indium disc on one side of the sample. The sample holder is then heated in vacuum up to 160 °C. The melted indium adheres to the crystal, assuring good thermal and electrical contact. The other side of the crystal is insulated from the electrode by means of thin (0.02

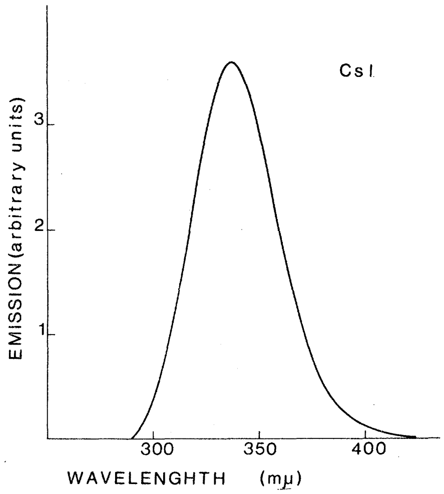

FIG. 1. Emission spectrum of the persistent component of electroluminescence obtained at liquid-nitrogen temperature with a CsI sample.

mm) Teflon foil. In this way it is assured that the carriers injection from the metal into the insulator takes place only on one side of the sample. This asymmetrical geometry is necessary to show the different mechanisms which give rise to the electroluminescence.[3] The indium electrode is in thermal contact with a liquid-nitrogen reservoir, in order to make all the measurements at 78 °K. A Victoreen 7235 high-voltage triode is used to provide electric excitation by amplifying the signal obtained from waves or pulse generators. 50-μsec rise times and 10-μsec fall times are obtained in this way for 4-kV pulses.

The light emission is detected by a tri-alkali photomultiplier (EMI 9558 QA). A grating monochromator (Jarrel Ash 82400) is used to obtain the luminescence spectrum. Jena Glaswerk interferential filters and Wratten cutoff filters are also used to separate the intrinsic and the transient violet components of the initial flash. Further experimental details are described elsewhere.[3]

III. EMISSION SPECTRA

Two emissions have been observed when the electric stimulation is applied to the CsI crystals at liquid-nitrogen temperature. The first is a temporary flash, which appears during the first excitation cycles in a sample stored for a certain period of time at room temperature. This luminescence disappears after a few tens of milliseconds and it is restored only by heating the sample up to room temperature. Because of its short duration, the emission spectrum has been not obtained. However, by means of optical filters, it has been shown that this momentary emission lies in the violet-blue region.

The second component of the luminescence is persistent, as long as an alternate excitation is applied; its emission spectrum is shown in Fig. 1. Between 200 and 800 nm only one band with the peak at 345 nm is obtained. This emission is reported as due to the intrinsic luminescence in nominally pure CsI samples excited at 77 °K by ultraviolet or x radiation.[7] The half-width is 0.48 eV and it corresponds to that observed for the electron-hole radiative recombination at liquid-nitrogen temperature.

The spectrum assures then that self-trapped holes and electrons in excitonic states must be present in the zone of the sample where the light emission takes place. Further evidence of the nature of the luminescence is given by its sudden attenuation when the temperature of the crystal is increased over 90 °K.[8] These results confirm the analogous ones observed in other alkali-halide crystals.[3,4]

IV. INITIAL BRIGHTNESS WAVES

The brightness waves obtained with a square-wave excitation are shown in Fig. 2. The light is emitted only during and shortly after any variation of the externally applied field. If a constant voltage is added to the alternate excitation, no persistent change in the brightness waves is observed. Moreover, no light emission is obtained when only a constant electric field is applied to the crystal.

These results are justified considering the building up of space charges whose field reduces that externally applied. Space-charge creation can be accounted for by the trapping of the injected electrons. The formation of these space charges has two important consequences for the electroluminescence: The first is the formation of a potential barrier where the injected electrons are accele-

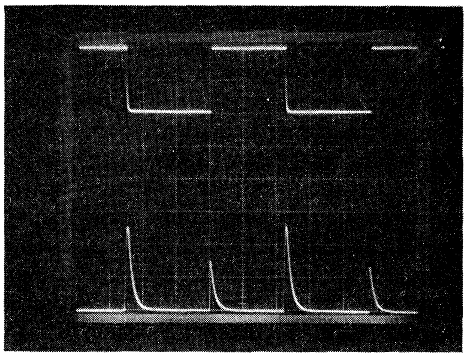

FIG. 2. Voltage and brightness waves obtained with square-wave excitation. Time scale 2 msec/division. Voltage amplitude 4 kV. Sample thickness 0.2 mm. Voltage polarity refers to the electrode in contact with the crystal.

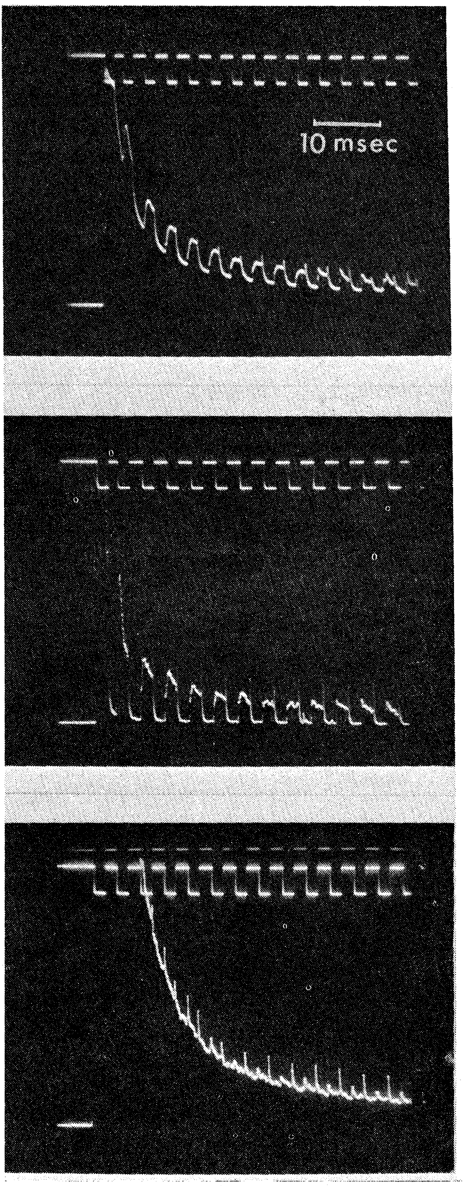

FIG. 3. Initial brightness waves obtained after storing the sample for several hours at room temperature. (a) Nonfiltered emission; (b) emission through 348-nm interferential filter (intrinsic luminescence); (c) emission through ultraviolet cutoff filter. Voltage amplitude 4 kV. Sample thickness 0.2 mm.

rated up to impact-ionization energies, and the second is the inhibition of further electron injection when the space-charge field balances that externally applied. Space-charge buildup takes place twice, as a consequence of different carrier transfers. The first happens before the application of any external voltage, when the electrodes are just applied to the insulator. Electrons are exchanged through the interface in order to keep vacuum and Fermi levels continuous across the junction; in this way a considerable distortion of the insulator conduction band can occur at the interface.[9] A considerable part of the voltage drop across the sample is then concentrated in this region.

The shape of the potential barrier in the depletion layer depends on the trap distribution in the insulating crystal. Thermoluminescence glow curves, obtained by heating the crystals after the electric excitation at 78 °K, show the existence of several electron traps at different energy depths. This fact suggests that the potential barrier formed at the metal-insulator junction should be of Rose's type.[10]

The second way of space-charge production takes place when a high-voltage bias is externally applied to the sample. Electrons are then injected from the cathode by means of field or Schottky emission. Passing through the depletion layer, electrons are accelerated up to ionizing energy and create pairs; some of these recombine radiatively giving rise to the luminescence. The injected electrons getting into the deep region of the crystal, where the electric field is low, are trapped and form a negative space charge, reducing the potential drop in the layer; the injection is then quenched and the luminescent effect drops.

Figures 3(a)–3(c) show the initial brightness waves obtained after a long period (several hours) of storage at room temperature. Figure 3(a) is the light response obtained in the entire sensitivity spectrum of the photomultiplier. Figures 3(b) and 3(c) are obtained with the same conditions as Fig. 3(a), but the light emission is filtered through an interferential filter at 348 nm and an ultraviolet cutoff filter, respectively. The comparison of the three photographs shows that during the initial-excitation cycles two intense and short light emissions take place: One is of intrinsic luminescence and is emitted only when the excitation voltage is on; the second emission is in the violet region and the output is persistent also while the externally applied field is off. It means that electrons are available for the recombination also when the injection is absent. This fact suggests that the electrons are captured in shallow levels from which they can escape spontaneously after some time. With this point of view one concludes that no V_k center is available in absence of applied field. It means that all the pairs formed during the avalanche process recombine within a very short period of time and no V_k center survives at the end of the electron injection.

Figure 4 shows the decay of light emission as obtained from Figs. 3(b) and 3(c); in both cases the instantaneous luminescence L decays with time according to an inverse power law $L = At^{-n}$. For intrinsic luminescence $n = 0.8$; for violet emission $n = 1.3$.

The intrinsic emission is attributed to the recombination of pairs created by the impact-ioniza-

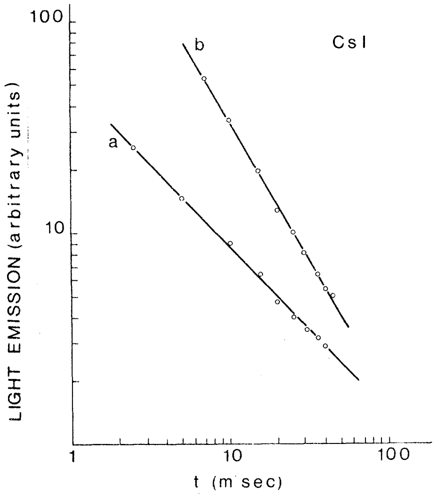

FIG. 4. Decay of the initial light emission obtained from the photographs of Fig. 3(b) (line a) and of Fig. 3(c) (line b).

tion process. The violet emission is on the contrary due to the recombination of free electrons with empty recombination centers which exist before any voltage bias. This luminescence vanishes after a few tens of milliseconds from the beginning of the excitation, and this fact assures that these centers are not ionized by the accelerated electrons.

Figure 5 shows the brightness waves obtained with the same stimulation as in Fig. 3, after the sample was excited by an electric field for several minutes at liquid-nitrogen temperature. No initial burst of light is obtained under these conditions and a buildup effect similar to that observed in other electroluminescence cells is evidenced.[1,6] No difference in the brightness waves is observed selecting the emission by filters. This assures that the luminescence is now only intrinsic, as evidenced also by Fig. 1. The recombination centers responsible for the violet emission are now completely filled and only a prolonged heating makes these centers again available. A more detailed knowledge of the involved recombination center is necessary to know the recombination process concerning the blue-violet emission and the kinetics of its emptying at room temperature.

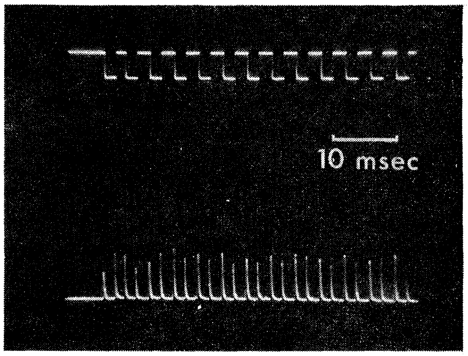

FIG. 5. Initial brightness waves obtained after the sample was excited with an electric field for several minutes at liquid-nitrogen temperature. The time scale and the conditions of the electric stimulation are the same as in Fig. 3. The sensitivity scale is five times larger than Fig. 3(a).

As far as the intrinsic luminescence emission is concerned, the results obtained can be explained by the existence of different trapping levels. Let us consider two main groups of traps with two different capture cross sections S_1 and S_2 ($S_1 > S_2$). The time one electron can spend in the conduction band before getting trapped is proportional to S^{-1}. On the other hand, the escape probability is directly proportional to S.[11]

When electrons are injected at low temperature for the first time, they find all the traps free to receive them, and they are preferably captured in S_1 traps. The filling of these traps takes place in a time t_1 during which the traps S_2 are practically empty. During this period of time the field attenuation by means of injected electrons is low and it is possible to observe luminescence.

When the external field is removed or inverted the electrons in S_1 traps will be easily freed; those in S_2 traps, on the contrary, will remain trapped and will reduce the injection of electron at the subsequent voltage pulse. The progressive filling of the S_2 traps will last until at every negative pulse all the injected electrons are captured practically only in S_1 traps. After that the brightness waves

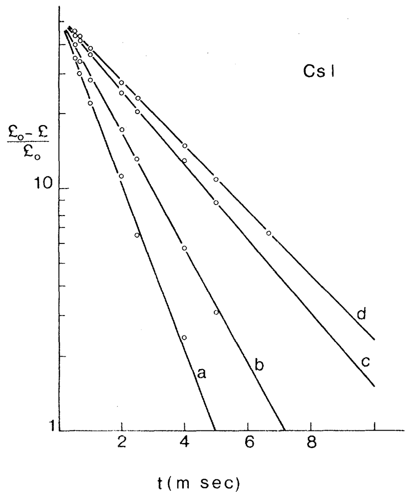

FIG. 6. Plot of $\mathcal{L}$, the light quantity emitted during one excitation cycle, vs t, the reciprocal of the electric stimulation frequency, Curves a, b, c, and d are obtained at about half-hour intervals. Square-wave voltage amplitude 2 kV.

will maintain their shapes (Fig. 2). While the filling of the S_2 traps is going on, the space charge created by the injected electrons will increase, and this fact explains the initial decrease of the light output.

V. BRIGHTNESS FREQUENCY RELATION

The brightness frequency relation has been extensively studied on various electroluminescence cells[1,6] and many of the results obtained can be accounted for on the basis of space-charge buildup. In the present case, the instantaneous light emission L is dependent both on the value of the applied field E and on its rate of change.[3] The study of the brightness frequency relation, intended as the study of the dependence of light emission on the excitation pulse duration, must be performed, in this case, with square-wave excitation, in order to avoid any effect related with the variation of dE/dt on the frequency.

It is supposed that the space-charge buildup is exponentially time dependent, after application of a voltage step,

$$q(t)=q_0\,(1-e^{-t/\tau}), \tag{1}$$

where q is the charge injected into the crystal from the beginning of the excitation.

The carriers created by impact ionization do not contribute to the space charge, because of the neutrality of their sum. Equation (1) has already been used in similar problems[12] and has been useful for interpreting the electroluminescence in alkali-halide crystals on the basis of impact ionization process.[3,4] Under the assumption of Eq. (1), the number of carriers forming the space charge increases with the period of the excitation wave. The number of electrons exchanged between the metal and the insulator is then higher at low frequency. These electrons give rise to the impact ionization; consequently the light output $\mathcal{L}$, integrated over one single excitation cycle, is expected to diminish at higher frequencies.

Typical experimental results, obtained on CsI samples at liquid-nitrogen temperature, in the frequency range between 100 and 2000 Hz are shown in Fig. 6. $\mathcal{L}$, the light emitted during one excitation cycle, is obtained by dividing the integrated light output B by the frequency ν.

The experimental points shown in Fig. 6 assure that the dependence of $\mathcal{L}$ on the excitation period $T=1/\nu$ is well fitted by the equation

$$\mathcal{L}=\mathcal{L}_0\,(1-m\,e^{-T/\tau}). \tag{2}$$

$\mathcal{L}_0$ and m are positive constants. The straight lines refer to successive measurements performed on the same crystal at intervals of about half an hour. The slope, which decreases progressively, proves that τ increases slowly in time. Equations (1) and (2) can be correlated under the following conditions.

(i) T in (2) is equal to t in (1). It is the time during which the carriers can be exchanged between the metal and the insulator.

(ii) $\mathcal{L}$ is proportional to q^m: $\mathcal{L}=aq^m$ with $a>0$. This second hypothesis is not demonstrated, but it seems reasonable, with $m>0$, because (a) $\mathcal{L}=0$ when $q=0$. No light emission is obtained without any injected charge. (b) $\mathcal{L}$ is monotonically increasing with q. This means that the number of radiative recombinations during one excitation cycle increases with the number of injected carriers.

With the substitution of $\mathcal{L}=aq^m$ into (1), one has $\mathcal{L}=aq_0^m(1-e^{-t/\tau})^m$, with $t>0$; thus $e^{-t/\tau}<1$. The factor within the parentheses can be expanded in a convergent binomial series, and neglecting the exponential terms with power higher than one, $\mathcal{L}=aq_0^m(1-me^{-t/\tau})$, which is equal to (2) with $\mathcal{L}_0=aq_0^m$. When $t\rightarrow 0$, $\mathcal{L}\rightarrow\mathcal{L}_0(1-m)$ which experimentally is found to be smaller than $\mathcal{L}_0$. This means that, in accordance with one of the preceding conditions, $m>0$. Moreover, $\mathcal{L}$ and $\mathcal{L}_0$ have the same algebrical sign; consequently, $1-m>0$ and $0<m<1$. When long excitation periods are used, $t\rightarrow\infty$ and $\mathcal{L}\rightarrow\mathcal{L}_0$ independently from the value of m.

The experiment results obtained suggest that the number of pairs created by impact ionization during one excitation cycle is a power function of the number of electrons injected from the metal into the insulator during the same period of time. The exponent m is smaller than unity and its value is given by $m=1-[\mathcal{L}(t)-\mathcal{L}_*(t)]/\mathcal{L}_0\,e^{-t/\tau}$, where $\mathcal{L}_*(t)=\mathcal{L}_0\,(1-e^{-t/\tau})$. The results shown in Fig. 6 give $m\simeq 5$ for every straight line.

VI. CONCLUSION

The transient behavior of the initial brightness waves and the dependence of the light emission on the frequency of excitation for the photoemission obtained at the CsI-metal interface are interpreted on the basis of trapping mechanisms. Two radiative recombinations are involved at the beginning of the excitation; they decay with time according to an inverse-power law. One recombination gives out a blue-violet light and vanishes after few excitation cycles. The other luminescence is intrinsic and, after the initial burst, remains persistent as far as an alternate voltage is applied.

These results are qualitatively explained with the existence of traps with different capture sections. The brightness frequency relation is interpreted with the assumption of an exponentially time-increasing space-charge buildup. According to this model the light emitted during one excitation cycle, $\mathcal{L}$, depends on the injected charge q according to a power law $\mathcal{L}\sim q^m$ which gives a relation between q and the pairs of carriers created by impact-ionization process.

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Stress-Induced Dichroism and Energy Shifts in the *A*, *B*, and *C* Absorption Bands in KCl:Tl

A. M. Lemos and Carl Krolik
Adelphi University, Garden City, New York 11530

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The effects of uniaxial stress on the *A*, *B*, and *C* absorption bands of KCl:Tl are determined using a static and dynamic Jahn–Teller interaction. The uniaxial stress alters the local symmetry giving rise to preferred spacial directions which, in turn, causes dichroism in the observed absorption spectra. The dynamic interaction accounts for the "time-average" splitting of energy levels which manifests itself by causing shifts in the band peaks. A calculation of the polarization effects and the shifting of the energy levels is carried out for the cases of [001] and [110] uniaxial stress. This is accomplished by (a) determining the transition probabilities for transitions from the $6s^2$ ground state to the $6s6p$ excited state of Tl^+ in both $D_{4h}(001)$ and $D_{2h}(110)$ environments and (b) determining the excited-state eigenenergies in terms of the interaction modes characterized by the above symmetries. The results are shown to compare favorably with recent available experimental results. Several theoretical conclusions are reached which await experimental verification.

I. INTRODUCTION

When heavy-metal ions such as Tl^+, Pb^{++}, etc., are substitutionally deposited in alkali-halide crystals, new absorption bands appear, the *A*, *B*, *C*, and *D* bands. Since these crystals have cubic symmetry no dichroism is observed in these bands. However, when the crystal is stressed as shown in Fig. 1, the local symmetry is altered and both dichroism and shifts in the band peaks are observed.[1-3] We have made a calculation of the effects which [001] and [110] uniaxial stresses have on the *A*, *B*, and *C* bands in KCl: Tl. The calculation is a perturbation treatment based on the tight-binding model of the impurity center. In this model, the dominant electron-lattice interactions are assumed to take place within the cluster of ions defined by the impurity and its nearest neighbors. Spin-orbit, exchange, static, and dynamic electron-lattice interactions are included. This method of attack has proved successful in the analysis of the absorption and emission bands in KCl: Tl.[4-8] The essential difference between the stressed and unstressed crystal lies in the local symmetry. The change in symmetry causes a change in the static and dynamic electron-lattice interactions. This affects the splitting and mixing of the degenerate excited states. As a result, shifts in energy levels occur and transition prob-

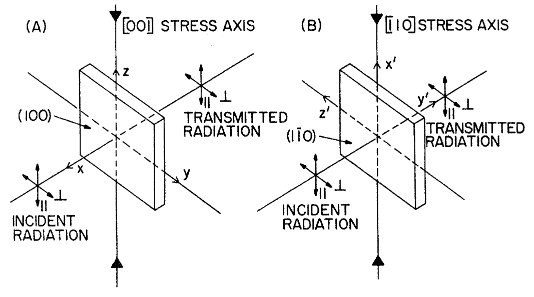

FIG. 1. Orientation of crystal axes with respect to incident radiation. (A) Configuration for [001] uniaxial stress; (B) configuration for [110] uniaxial stress.

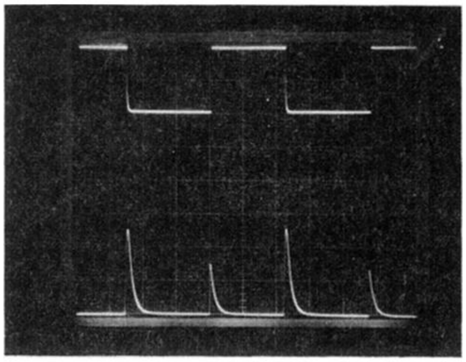

FIG. 2. Voltage and brightness waves obtained with square-wave excitation. Time scale 2 msec/division. Voltage amplitude 4 kV. Sample thickness 0.2 mm. Voltage polarity refers to the electrode in contact with the crystal.

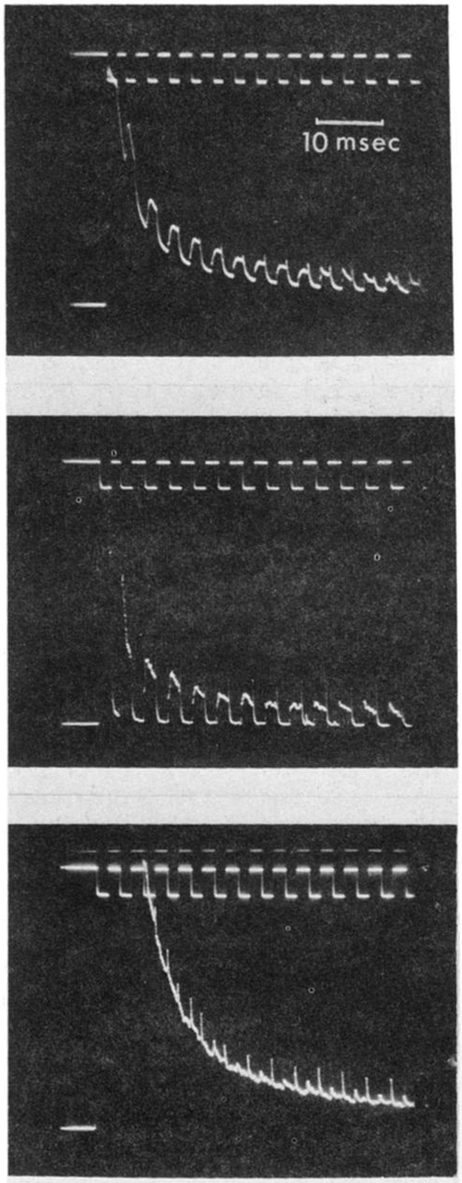

FIG. 3. Initial brightness waves obtained after storing the sample for several hours at room temperature. (a) Nonfiltered emission; (b) emission through 348-nm interferential filter (intrinsic luminescence); (c) emission through ultraviolet cutoff filter. Voltage amplitude 4 kV. Sample thickness 0.2 mm.

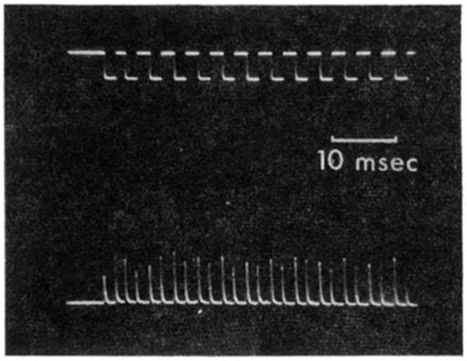

FIG. 5. Initial brightness waves obtained after the sample was excited with an electric field for several minutes at liquid-nitrogen temperature. The time scale and the conditions of the electric stimulation are the same as in Fig. 3. The sensitivity scale is five times larger than Fig. 3(a).