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Impact Ionization in Alkali Iodide Crystals*

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The electroluminescence near the metal-insulator contacts is examined in four alkali iodide crystals. The instantaneous light emission is studied as a function of the electric field and of the temperature. The results obtained are in agreement with a recent avalanche-multiplication theory. The observed effect supports the existence of impact-ionization processes in alkali halide crystals at low temperatures and the formation of potential barriers at the metal-insulator interface.

I. INTRODUCTION

The electroluminescence in alkali halide crystals has been recently reported in several works.[1-4] The effect is observed with alternate electric excitations and it is localized in thin regions of the sample near the metal contacts. In nominally pure crystals the electroluminescence is obtained at liquid-nitrogen or lower temperatures and the emission spectra assure that the observed light is due to the radiative recombination of electrons in excitonic states with self-trapped holes (V_k centers).

In semiconductors and in low-gap insulators electroluminescence was studied mainly for technological applications. In low-conductivity materials this phenomenon is especially useful as a tool for the study of the electrical properties under high electric fields. Transport and injection phenomena in semiconductors are, in fact, relatively well known, but the interpretation of the same effects in high-resistivity compounds is still incomplete and the proposed models are not throughout accepted.

Electric breakdown in insulators, for example, is a phenomenon still largely discussed, in spite of the large amount of work already done.[5] A large variety of mechanisms have been proposed for its interpretation: avalanche multiplication, electrode injection, internal field emission, space-charge phenomena, and so on. Impact ionization is the more widely accepted process, yet, on the ground of this hypothesis, several different models have been proposed for explaining the avalanche-starting event and the final mechanism leading to the sample disruption. At the moment the situation is still unclear; while most of the authors assumed that electric breakdown is connected with impact ionization, little experimental evidence is available proving the existence of carrier avalanche in insulators with extremely low conductivity. The study of electroluminescence has been helpful in these cases: Van Geel and others[6] ascribed the luminescence during the anodic oxidation of aluminium and tantalum to impact ionization. Cooper and Elliott have examined the light emitted from KBr crystals a few tens of nanoseconds before the sample collapse and deduced that the electric breakdown is initiated in the cathode region.[7] More recently Baessler and co-workers have evidenced impact ionization in Mylar films by means of photoemission under high electric fields.[8] Similar work was done by Hsu in anthracene crystals.[9]

The purpose of the present paper is to give some experimental evidence of the impact ionization in alkali halide crystals and to compare the obtained data with recent avalanche theories.

Among alkali halides the iodine salts have the highest intrinsic luminescence efficiency.[10] Moreover, in these compounds, the electron-hole recombination is radiative at liquid-nitrogen temperature, while for other alkali halides lower temperatures are required. These reasons suggest the choice of the iodides for studying electroluminescence in alkali halides.

II. EXPERIMENTAL

The samples were obtained from single-crystal lumps; KI was grown by the Kyropoulos method in our laboratory; all the other iodides were supplied by Harshaw Chemical Co.

Square (1×1 cm) slices 0.5–0.1 mm thick were obtained by cleaving and lapping. The samples were placed between two copper electrodes covered by thin indium foils. The thermal and the electrical contact was obtained by melting the indium foils under vacuum. Usually only one of the two electrodes was prepared in this way. The other was insulated by means of a thin Teflon foil (see Sec. III).

The dependence of the effect on the applied voltage was studied at liquid-nitrogen temperature. The temperature control between 80 and 20 °K was obtained using a Cryotip heat exchanger. The high-voltage electrical excitation was supplied by amplifying low-voltage waves or pulses with a step transformer or with a 7235 high-voltage triode. The light emission was detected by a trialkali photomultiplier, whose response was examined by an oscilloscope. A boxcar integrator was used to examine the brightness waves in detail and to select a part of the light signal. Other experimental details are described elsewhere.[2,4]

III. BRIGHTNESS WAVES

Light emission occurs only during the applied field variations and disappears rapidly with constant voltage; neither quantitative nor qualitative changes of the brightness waves are observed by adding a dc component to the ac one; with sinusoidal excitation, brightness waves are leading the voltage ones. These results suggest that the effect is contemporary to the emission of carriers from the electrode and it is quenched when the injected carriers create a space charge which reduces the externally applied field.

If a square voltage pulse is applied, the build up of the space charge is supposed to depend exponentially with time:

$$q = q_{0}(1 - e^{-t/\tau}); \qquad (1)$$

q is the charge injected from the contact into the insulator from the beginning of the excitation pulse up to the instant t. In Sec. VI it will be shown how the time constant τ can be evaluated by the phase angle between the brightness and the voltage waves. Formula (1) has been already successful to interprete the brightness-frequency relation in CsI electroluminescence.[4]

Figure 1 shows the brightness waves obtained from a KI sample with sinusoidal excitation at 80 ° K. The upper photograph shows the effect when both the electrodes are in contact with the crystal (two-electrodes configuration). The lower photo is obtained when only one electrode is in contact with the crystal (single-electrode configuration), the other being insulated by a thin insulating foil. In the first case the successive light peaks are similar, as one expects from the symmetry of the cell; little differences can be attributed, in this case, to accidental inequalities of the two contacts. When a single-electrode configuration is used, the light peaks appear alternatingly very different in shape and intensity. We distinguish in this case a "positive" light peak and a "negative" one, according to the algebrical sign of the electric field rate of change at their appearing. The applied-field signal is referred, in these cases, to the electrode in contact with the crystal. In Sec. V it will be shown that the two light peaks are due to different mechanisms; it is then necessary to study the two light peaks separately, in order to avoid the superposition of two different effects.

The present work deals mainly with the "negative" light peak, and the results presented in the following sections are obtained examining the behavior of the "negative" peak only. The single-electrode configuration is used throughout the work.

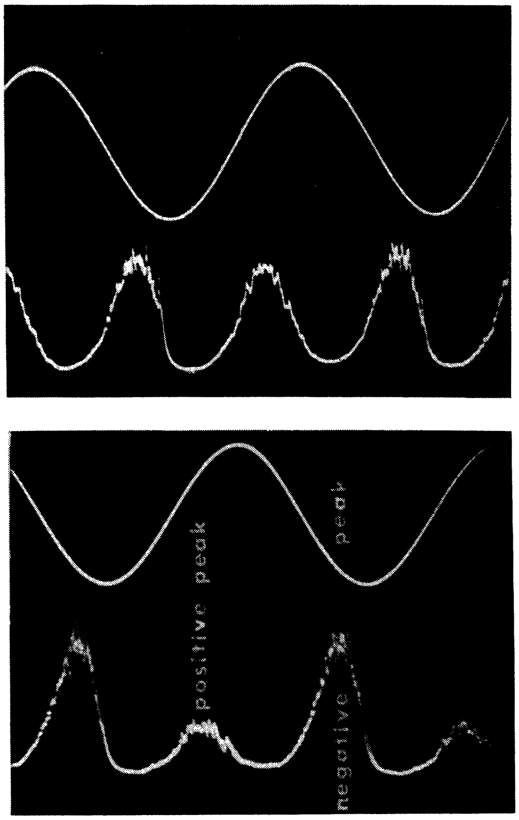

FIG. 1. Brightness waves obtained in a KI sample with sinusoidal excitation. The upper photo shows the light response with both the electrodes in contact with the crystal (two-electrode configuration). The lower photo shows the emission waves when only one electrode is in contact with the crystal (single-electrode configuration). In this last case the voltage is referred to the contact electrode. "Positive" and "negative" light peaks are here distinguished, according to the sign of the rate of change of the applied voltage.

IV. POSSIBLE MODELS

It has already been ascertained[2-4] that the spectrum of the electroluminescence, obtained from nominally pure alkali halides at liquid-nitrogen temperature, coincides with that of the intrinsic photoluminescence. The quenching of light emission at temperatures higher than that of the liquid nitrogen confirms that the observed luminescence is due to the radiative recombination of electrons with self-trapped holes.

By direct visula and photographic observations it was found that the light emission is localized in thin-crystal zones near the insulator-metal interfaces.[2]

These results show that the electric excitation generates electrons and V_k centers near the metal junction. Two mechanisms may be responsible for this: (i) single-carrier injection from the electrode, followed by impact ionization; (ii) double emission of electrons and holes from the opposite electrode.

In the following, two possible models based on each mechanism are presented. By using qualitative arguments a choice between the two is then proposed.

The first model requires that the injected carriers be accelerated up to high energies in order to produce free pairs by impact ionization. Because of the very low mobility of holes in alkali halide lattices, such a process must be due to accelerated electrons.

If the applied potential drop is uniformly distributed over the whole sample thickness, the electric field is too low for generating impact ionizations. A high-field region is then required, as is confirmed by the fact that the luminescence is concentrated in thin zones near the metal contacts.[11] The pair production takes place where the electric field is higher: Electrons are pulled from valence into conduction band leaving free holes. These have a very short life in alkali halides and are very soon self-captured in the lattice, forming V_k centers. The electrons then recombine with the V_k centers and the pairs annihilate giving luminescence (negative light peak). The injected electrons then reach a low-field region where they are trapped (space-charge build up). At field reversal, the field ionization of the traps generates free electrons, which are accelerated back to the electrode, giving rise to a new avalanche and to the "positive" light peak.

According to this model, the number of pairs created in the unit time is equal to the impact ionization rate w multiplied by the free-electron density n. Supposing that the probability of the radiative recombination is field independent, the instantaneous light emission L is then proportional to the product nw. When electron injection takes place, n is proportional to the current injection j. At the field reversal, n depends in a similar way on the rate of the trap field ionization.

If a double-emission mechanism is involved, electrons and holes are injected at the same time from the opposite electrodes. When only one electrode is in contact with the crystal, electrons and holes are successively injected from the same contact, during the opposite excitation semicycles. In this case, during the electrons injection, part of them recombine with the V_k centers, formed in the previous semicycle, during the hole emission from the electrode. The remaining electrons are trapped (space-charge build up). These electrons are field ionized at the field reversal and they recombine with part of self-trapped holes, leaving others ready for the recombination with electrons in the following semicycle. According to this model the electroluminescence depends only on the injection currents, while in the former case, the impact-ionization contribution must be taken into account.

It is possible to choose one of the two aforementioned models, or at least to deduce which is prevailing, by studying how the brightness waves change in a temperature range, where the intrinsic luminescence efficiency remains constant.

The injection of carriers from a metal into an insulator is governed by Fowler-Nordheim or Schottky formulas[12]; field emission is essentially temperature independent, and Schottky injection increases exponentially with the temperature. Other possible injection mechanisms are intermediate between the two and their injection rate is again increasing with temperature. In any case the current injection does not decrease at higher temperatures.

Accordingly, if only double emission takes place, or if it is the main mechanism, electroluminescence should not increase at low temperature. On the contrary it is found that the brightness at 20 °K is about three times larger than at 80 °K (cf. Fig. 3). This result can be qualitatively explained considering a charge-multiplication mechanism. The impact ionization rate, in fact, decreases at higher temperatures, because of larger electron-phonon interaction. In the following sections it is shown that the impact-ionization model plays the predominant part in the effect. This conclusion is obtained by comparing the experimental results with those predicted by the avalanche-breakdown theory proposed by O'Dwyer.[13] He assumed that the hole mobility is much smaller than that of electrons, and only these carriers satisfy the continuity current condition. A further assumption requires that the collision ionizations are achieved only by the few electrons which are accelerated from thermal to ionizing energies without suffering any phonon collision. Under these conditions the mean rate of ionization per unit time is given by

$$w \sim F e^{-H/F}, \tag{2}$$

where H is independent from the internal local electric field F. H depends on the temperature T as

$$H \sim 1 + 2/(e^{\hbar\omega/kT} - 1) , \tag{3}$$

where ω is the longitudinal-optical-mode frequency. Figure 2 shows the computed values of w vs T for KI and CsI. The curves are obtained from (2) and (3), assuming all proportionality factors and the F value equal to unity. For KI, $\omega = 2.6 \times 10^{13}$ sec^{-1}, and for CsI, $\omega = 1.6 \times 10^{13}$ sec^{-1}.

V. TEMPERATURE DEPENDENCE

According to the impact-ionization model, the negative light peak is originated during the electron injection from the cathode. In this case the instantaneous light emission L is proportional to

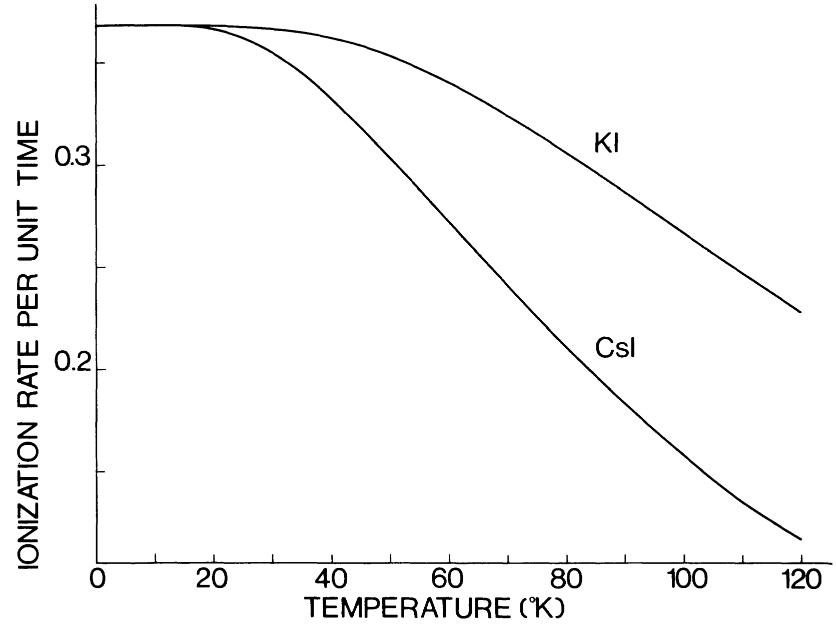

FIG. 2. Impact ionization rate vs temperature in KI and CsI, according to the used avalanche multiplication theory (Ref. 16). $w = \exp\{-1 - 2/(e^{\hbar\omega/kT} - 1)\}$ as obtained from formulas (2) and (3) in the text.

the product of the pair creation rate w with the free-electron density n. The ways they depend on the temperature and on the electric field are known from the already-mentioned theories of injection and of the charge multiplication processes. By comparing the electroluminescence emission with the theoretically predicted values, it is possible to have further information about the processes which take part in the phenomenon. The results presented in this section deal with KI and CsI, because, in these materials, the efficiency of the intrinsic luminescence is temperature independent between 20 and 80 °K. For this reason, they are particularly suitable for studying the dependence of the effect on the temperature in this range.

Figure 3 shows the brightness waves obtained from a KI sample with sinusoidal excitation at different temperatures. At 20 °K the area of the negative peak is nearly twice that at 80 °K. The area of the positive peak, on the contrary, is approximately the same in the two cases. This result shows that the two peaks have different origins and they must be examined separately. The light emitted during the electron injection, that is the area of the negative peak, is plotted in Fig. 4 as a function of H, the temperature-dependent parameter in O'Dwyer's theory. Both the results for KI and CsI show that the light emission is exponentially dependent on H, in agreement with the above-mentioned theory. The injection current must be, in these cases, temperature independent. Fowler-Nordheim emission is then the more probable injection process from the cathode into the crystal. Figure 3 shows, on the contrary, that the positive

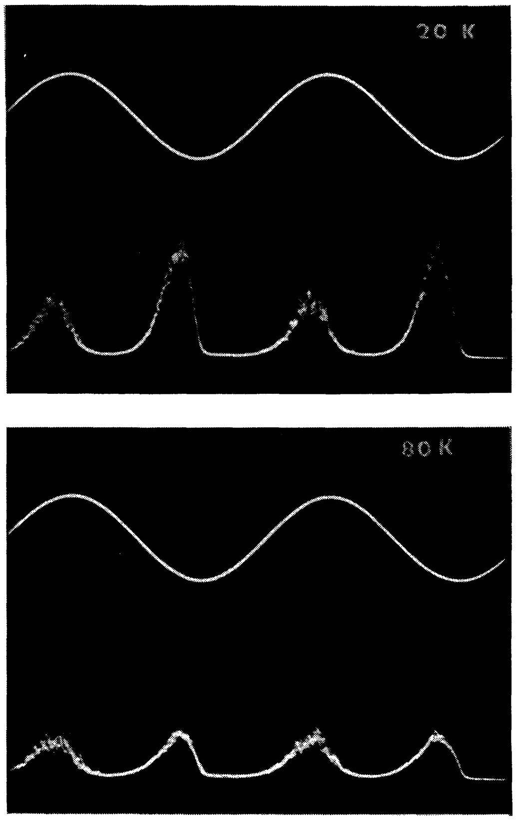

FIG. 3. Brightness waves obtained from a KI sample with "single-electrode configuration" at 20 °K (upper part) and at 80 °K (lower part). The "negative" peak increases at low temperature, the "positive" one remains approximately the same.

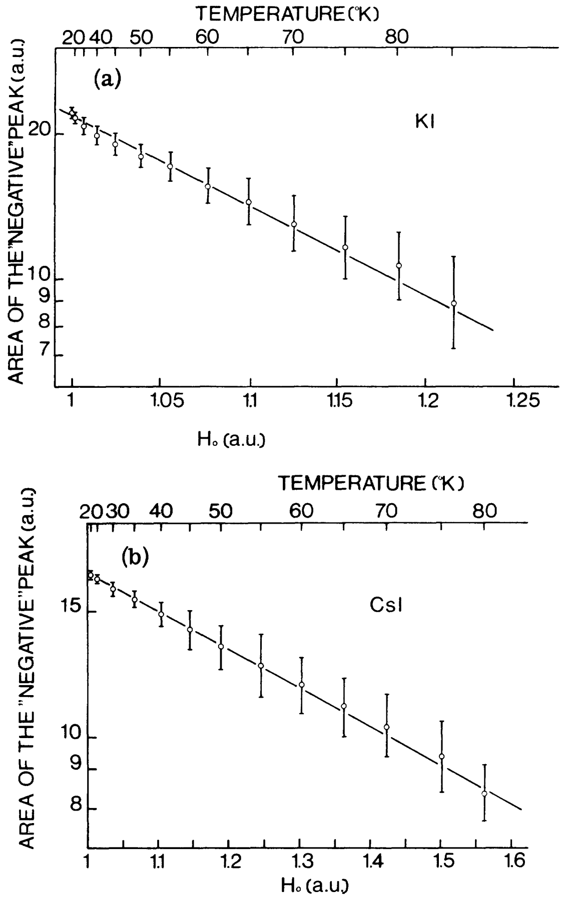

FIG. 4. (a) Plot of the "negative" peak area vs $H_0 = 1 + 2/(e^{\omega/kT} - 1)$ for a KI sample. (b) Plot of the "negative" peak area vs H_0 for a CsI sample.

light peak remains approximately the same between 20 and 80 °K. A lower free-electron density must be now available at lower temperatures, as it is expected supposing that the trapped electrons are ionized through field-assisted thermal ionization (Poole-Frenkel effect).

VI. VOLTAGE DEPENDENCE

In Sec. V it was found that tunnel injection is responsible for the electron emission from the cathode. Impact ionization produces pairs which recombine giving out light. This model is confirmed by studying the dependence of the light emission on the electric field. The light emitted during the electron injection from the cathode is proportional to jw (Sec. IV), where j is the injection current and w is the impact-ionization rate. According to Fowler and Nordheim, the tunnel emission current is $j \sim F^2 e^{-a/F}$, where F is the electric field; then with the use of (2), the field dependence of the instantaneous light emission L is

$$L \sim jw \sim F^3 e^{-b/F} \,, \qquad (4)$$

a and b indicate field-independent parameters. Formula (4) is valid under the assumption that the number of pairs which recombine radiatively is proportional to that of the created pairs.

The internal electric field F and the externally applied field E are related through the type of the potential barrier formed at the metal-insulator interface, and through the growing of the injected space charge with time.

Traditionally the barriers at the metal-insulator interface are either parabolic (Mott-Schottky type) or exponential (Rose type), depending on the ratio between trapped- and free-carrier densities and on the trap energy distribution.[14] In alkali halides, the concentration of free carriers in respect to the trapped ones is very low, moreover several traps at different depths are existing in the forbidden gap. The presence of these trapping levels can be easily evidenced by thermoluminescence glow curves, obtained by heating the samples to room temperature, after they have been excited with electric field at 80 °K. Under such conditions, the potential barrier which more probably takes place at the junction is an exponential one (Rose-type barrier), where the maximum field intensity is proportional to the potential drop across the crystal. It is supposed that the avalanche process is mainly restricted in the region of the barrier, where the field has its highest value, in order to have a proportionality link between E and F.

Owing to the space charge created by the injected electrons, the local field F decreases in time in respect to E. As already mentioned in Sec. III, the building up of the space-charge field takes place exponentially in time with a constant τ. The values of τ do not depend only on the electric intrinsic characteristics of the used material, but also on the energetic trap distribution and on their cross capture section. It is then necessary to know the value of τ for every examined crystal. Anyway, as will be explained in the following, a very precise value of τ is not required for the present measurements, when τ varies in the range of milliseconds. At present τ is evaluated by means of the phase shift between brightness and voltage waves using a sinusoidal excitation.

After t' from the beginning of excitation, the maximum field in the barrier $F(t')$ is related to the applied voltage $E(t)$ by the following formula:

$$F(t') \sim \int_0^{t'} \frac{dE(t)}{dt} e^{-(t-t')/\tau} dt \,; \qquad (5)$$

if $E(t) = \sin\omega t$, one has $dF/dt = 0$ when

$$\frac{\omega}{t_m} \sin\omega t_m - \omega^2 \cos\omega t_m + \frac{1}{\tau^2} e^{-t_m/\tau} = 0. \qquad (6)$$

The value of t_m in (6) is that in correspondence to the maximum light output. Being the effect monoton-

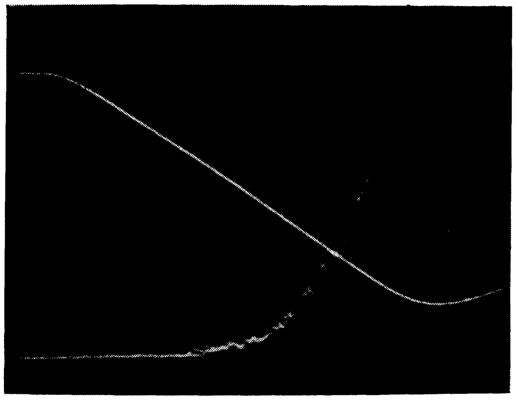

FIG. 5. Light response obtained from a RbI crystal with a negative ramp excitation at 80 °K. The voltage polarity is referred to the electrode in contact with the crystal (sample thickness: 0.45 mm, 0.1 msec/div, 1 kV/div).

ically increasing with the excitation, t_m also gives the time when F is maximum. The values of t_m can be obtained from photographs like those shown in Figs. 1 and 3; t_m, substituted in (6) with the proper ω, gives τ. Because of the uncertainty of t_m, τ can be obtained, with such measurements, only in the range of few milliseconds. For the three examined crystals τ is found to be 2–3.5 msec for NaI and RbI and 1.5–2.5 msec for KI.

When a ramp is used, $E = at$ and (5) becomes

$$F(t) \sim E(t)\,(\tau/t)\,(1 - e^{-t/\tau}) = a\tau(1 - e^{-t/\tau}), \qquad (7)$$

which gives the time-dependent relation between F and E, under the assumption that E and F are proportional in time-independent conditions.

Figure 5 shows the light emission obtained when a negative bias, linearly increasing with time, is applied to the electrode in contact with the sample. The values of $E(t)$ obtained from the photograph are corrected through the (7), in order to have $F(t)$. The light emitted at a certain instant is then correlated with the corresponding value of F.

Figure 6 show $\ln(L/F^3)$ vs $1/F$ for two types of crystals examined, NaI and RbI. These results are obtained with the applied voltage varying between 2 and 5 kV, the light-emission measurements spread correspondingly over two decades; in Fig. 6 the ordinate data appear much contracted because of the division by F^3.

The alignment of the experimental points assures that the expression (4) satisfactorily represents the increase of luminescence, while the electrode in contact with the crystals is acting as a cathode.

In Fig. 6 the vertical segments show the random errors of the light emission. The horizontal segments show the values of F obtained from E with range of E, ΔF does not change very much. This the two extreme values of τ indicated above. These segments show systematic errors and are drawn with hyphened lines.

It is important to note that, in the examined

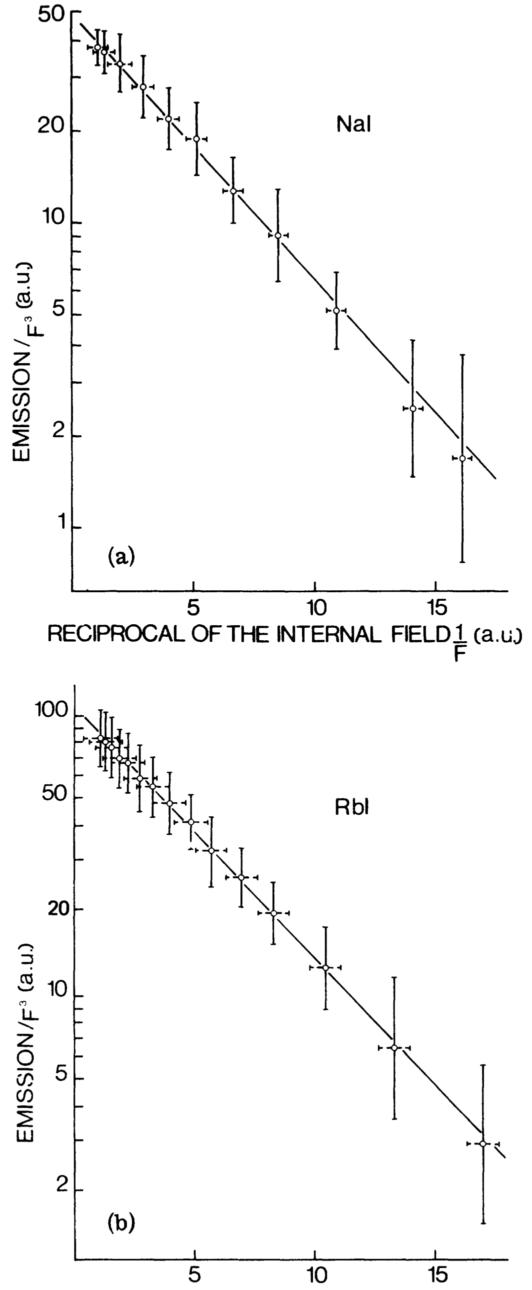

FIG. 6. (a) Plot of $\ln(L/F^3)$ vs $1/F$ for a NaI sample. The vertical errors are due to the randomly scattered measurements of the light emission. The horizontal hyphened segments show the systematic errors in the evaluation of F from E through formula (7). (b) Plot of $\ln(L/F^3)$ vs $1/F$ for a RbI sample. The vertical and the horizontal errors have the meaning of Fig. 6(a).

fact assures that the obtained alignment is not compromised by an error of τ in the range of milliseconds.

VII. CONCLUSIONS

The electroluminescence in some alkali iodide crystals has been interpreted according to an impact-ionization model. The dependence of the photoemission on the temperature and on the electric field is explained, with the mentioned mechanism, under the following assumptions:

(a) Potential barriers are formed at the metal-insulator interface. The maximum field in the barrier is proportional to the applied voltage (Rose-type barrier).

(b) Fowler-Nordheim tunnel injection is responsible for the electron emission from the negatively biased electrode.

Moreover, the brightness waves of the electroluminescence at different temperatures suggest that (i) hole injection from the metal into the crystals is negligible or nonexistant; (ii) trapped electrons can be freed by means of field-assisted thermal ionization.

The obtained results show the possibility of studying the injection and transport processes in low-conductivity insulating crystals by observing the photoemission under high electric fields.

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[11] The formation of space-charge layers near the junction with a metal is commonly assumed in semiconductors, but it is a still discussed problem in wide-gap and high-resistivity insulators (Ref. 12); the study of electroluminescence should be a useful way to investigate this problem.

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Magneto-optical Study of a Charge-Transfer Band in Vanadium-Doped MgO[†]

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A study of the magnetic circular dichroism and optical absorption associated with a band at 5.15 eV in vanadium-doped MgO is presented. The band is assigned to an electron transition from an orbital predominantly on the oxygen ligands of the V^{3+} ion to an orbital predominantly on the V^{3+} ion. Theory for the magnetic circular dichroism originating from the orbitally degenerate ground state is proposed, and the result of an analysis is found to be consistent with the presence of a dynamical Jahn-Teller effect in the ground state. A classification of the excited-state symmetry is made which implies a reversal from the conventional ordering of the πt_{1u} and πt_{2u} ligand-orbital energy levels.

I. INTRODUCTION

The magnetic circular dichroism (MCD) of a charge-transfer band associated with the V^{3+} ion in MgO is of interest for several reasons. The non-Kramers ground state of the V^{3+} ion is expected to be Jahn-Teller active in cubic MgO and there may be a modification of the ground-state magnetic properties by the electron-lattice interaction. However, these magnetic properties are not easily studied. The ion is undetected in MgO by electron paramagnetic resonance even though the less stable V^{2+} ion is commonly seen. The magnetic circular dichroism is, nevertheless, applicable to an investigation of the magnetic properties.

The optical aspects of the study are also of interest and the study of a charge-transfer band is

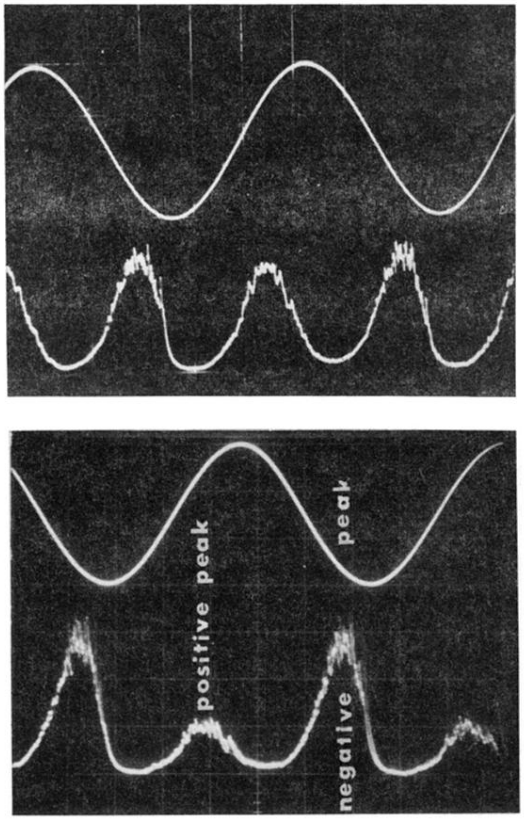

FIG. 1. Brightness waves obtained in a KI sample with sinusoidal excitation. The upper photo shows the light response with both the electrodes in contact with the crystal (two-electrode configuration). The lower photo shows the emission waves when only one electrode is in contact with the crystal (single-electrode configuration). In this last case the voltage is referred to the contact electrode. "Positive" and "negative" light peaks are here distinguished, according to the sign of the rate of change of the applied voltage.

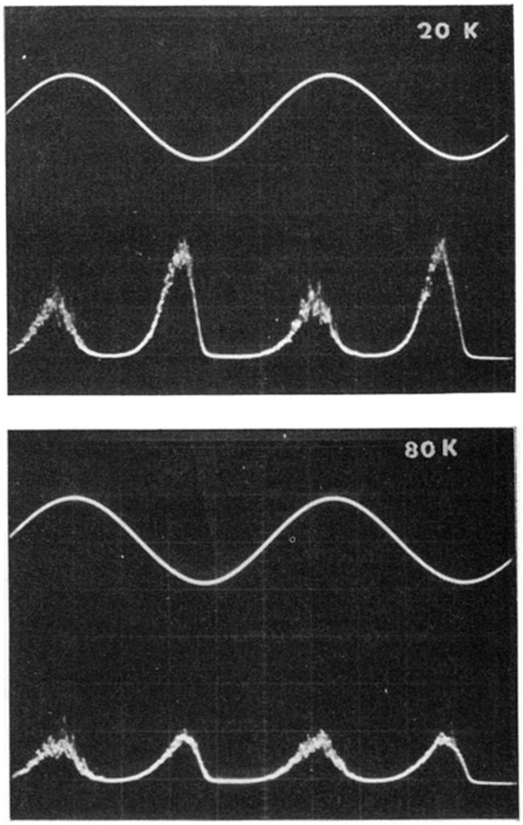

FIG. 3. Brightness waves obtained from a KI sample with "single-electrode configuration" at 20 °K (upper part) and at 80 °K (lower part). The "negative" peak increases at low temperature, the "positive" one remains approximately the same.

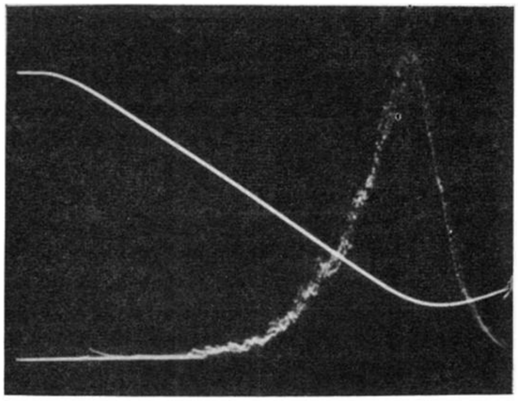

FIG. 5. Light response obtained from a RbI crystal with a negative ramp excitation at 80 °K. The voltage polarity is referred to the electrode in contact with the crystal (sample thickness: 0.45 mm, 0.1 msec/div, 1 kV/div).