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Istituto di Fisica, Università di Messina

ac-dc Electroluminescence in ZnS (Powder and Single Crystal) [1]

By

A. CINGOLANI and A. LEVIALDI

The enhancement effect (E.E.) of ZnS is measured in a constant electric field superposed on an alternating field. Two cases are considered: a) a conventional sandwich-type electroluminescent (E.L.) ZnS (Mn, Cu, Cl) micropowder cell; b) a ZnS (Cu, Cl) single crystal ("gap") cell.
Capacity, current, and δ are simultaneously measured at different temperatures between 88 and 300 °K using frequencies in the range 6 to 20 kHz. The frequency corresponding to R_{max} is determined. The variation of R near R_{max} is found to be independet of tg δ. The value of the time constant of the E.L. cell is equal to half a period of the optimum applied frequency. The results are consistent with both the Fischer [1] model and the "impact-ionization" model.

Der Verstärkungseffekt (E.E.) im ZnS wurde in einem elektrischen Gleichfeld, das einem Wechselfeld überlagert war, untersucht. Die Untersuchungen wurden für folgende zwei Fälle durchgeführt: a) eine herkömmliche sandwichartige elektrolumineszierende (E.L.) ZnS (Mn, Cu, Cl)-Mikropulverzelle und b) eine ZnS (Cu, Cl)-Einkristallzelle (Spaltzelle).
Es wurden gleichzeitig Kapazität, Strom und tg δ bei verschiedenen Temperaturen zwischen 88 und 300 °K im Frequenzintervall zwischen 6 und 20 kHz gemessen. Die dem Wert von R_{max} entsprechende Frequenz wurde betimmt. Die Änderung von R in der Nähe von R_{max} ist unabhängig von tg δ. Der Wert der Zeitkonstante der E.L.-Zelle ist gleich der halben Periode der optimalen verwendeten Frequenz. Die Ergebnisse sind mit dem Fischer-Modell [1] und dem Stoßionisations-Modell im Einklang.

1. Introduction

A conventional electroluminescent (E. L.) cell [1] is a condenser with an E. L. microcrystalline powder embedded in a dielectric substance between the plates. If the dielectric has a conductivity comparable to that of the E. L. substance, one observes emission of light when a constant or an alternating electric field is applied.

As shown by Thornton [2], if the ac and dc fields are applied simultaneously, one observes an emission of light, the intensity of which is not necessarily equal to the sum of the two intensities obtainable with an ac or dc field.

One says that an "enhancement effect" (E.E.) exists if

$$R = \frac{B_t}{B_{ac} + B_{dc}} > 1 . \tag{1}$$

The brilliance B is the average intensity of the emitted light under stationary conditions. Similar effects can be obtained from electroluminescent single crystals.

Enhancement effects can be also produced by other means.

Destriau [3] and Marti [4] have examined the emission of light due to the action of X-rays superposed on that of an alternating field.

Gobrecht and Gumlich [5] report observations of emission due to ultraviolet
light and alternating field. Gobrecht, Gumlich [6] and Jaffe [7] used cathodic
rays and alternating fields. Mattler [8] examined E.E. due to the action of
α-particles and ac field, Gobrecht, Gumlich, Nelkowski, and Lacmann [9] have
examined the effect of infrared radiation superposed on X-rays and ac fields.
Kozine, Favorin, and Anasimova [10] have studied the pattern-deformation
of the brilliance wave when the cell is excited by ac and dc fields and its ampli-
tude is varied at constant frequency. A constant electric field polarizes the cell
or the single crystal, giving rise to memory effects that may last over many
hours [11, 12]. E.L. may be stored using a polarizing field and then abruptly
released by inverting the applied field or by applying alternating voltage.
It is impossible to establish a correlation between parameters measured at
different times, when changes in polarization or excitation have taken place.

In the present work we study, in E.L. cells and in single crystals, the E.E.
due to superposed constant and alternating fields because we consider the
understanding of this effect to be basically important for a consistent explana-
tion of E.L. We make simultaneous measurements of capacity (C), tg δ,
B (in ac, dc, and ac + dc), and current (I), at different voltages V_{ac} and V_{dc}.
The frequency ranges from 6 Hz to 20 kHz and the temperature from 88 to
300 °K.

In Section 2 we describe the experimental apparatus used in performing these
measurements.

In Section 3 we report our results.

In Section 4 we present the conclusions which may be drawn from the present
experiments and attempt a phenomenological interpretation.

2. Experimental Technique

Our E.L. cell is a "sandwich" prepared from ZnS (Mn, Cu, Cl) micropowder
embedded in epikote 812 (99% (volume) sulfide and 1% epikote), 0.01 cm thick,
placed between two SnO-treated, transparent, and conductive glass disks,
1 inch in diameter. We will refer to this as sample No. 1 (Fig. 1).

We have also used a ZnS (Cu, Cl) single crystal, metallized on one face so as
to leave a non-metallized slot 0.005 cm wide, i.e., a "gap" cell. We will call
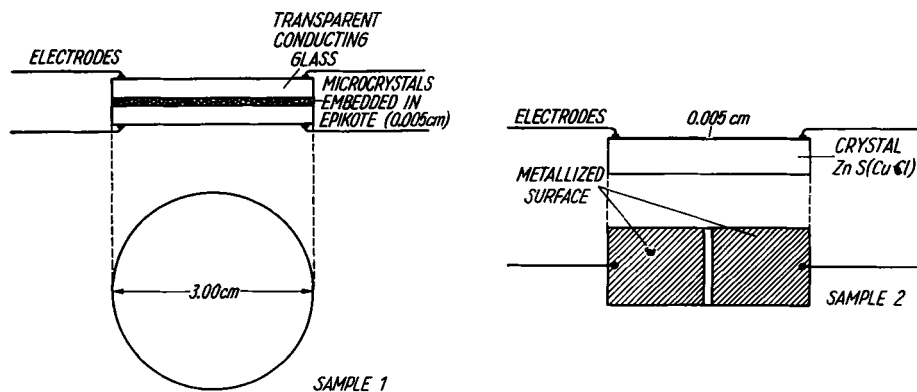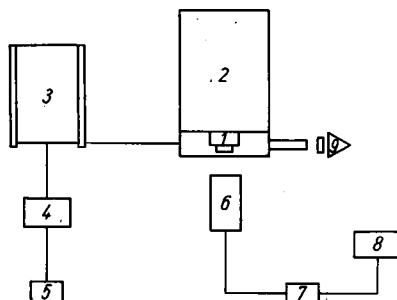this cell sample No. 2 (Fig. 1).

Fig. 1. Samples 1 and 2 used in the experiments

The E.L. powder and the cells were prepared in our laboratory. The single crystal was very kindly provided by Professor G. Bonfiglioli.

The E.L. cell is mounted in a cryostat in vacuum and can be connected to ac, dc or simultaneous ac and dc voltage. Light emission is measured by means of an EMI 8856B photomultiplier and the signal is amplified using a Keithley 603. A capacity bridge (General Radio type 1610) allows us to carry out the measurements of C, tg δ at all frequencies in the range from 30 Hz to 20 kHz.

The experimental arrangement is illustrated in Fig. 2

In attempting to measure the emission and R-value obtained at room temperature (RT) also at liquid nitrogen temperature (LNT), the necessary voltage became too high for our instrument. Therefore, we were not able to measure the corresponding values of C and tg δ. Ultimately, this limitation proved not essential, since a great number of curves reveal that the behaviour of the phenomenon is identical at high and low temperatures. It seems quite clear that the increase in the dc voltage and amplitude of the superposed ac voltage is equivalent to a rise in temperature. For example, the maximum of R at RT is obtained, at $V_{dc} = 80$ V and $V_{ac} = 35$ V, whereas at LNT the maximum is obtained at $V_{dc} = 300$ V and $V_{ac} = 150$ V.

Before describing the results as a whole, we wish to summarize the measurements carried out in our experiment: For samples 1 and 2 we verified that the rate of increase of lg B_{ac} as a function of $1/\sqrt{V_{ac}}$ and that of lg B_{dc} as a function of $1/\sqrt{V_{dc}}$ are straight lines, which confirms the findings of most authors. We measured the rate of increase of

$$B_{ac} \text{ as a function of } \nu \text{ for } V_{ac} = \text{const},$$
$$B_t \text{ as a function of } \nu \text{ for } V_{ac} = \text{const},$$
$$R \text{ as a function of } \nu \text{ for } V_{ac} = \text{const},$$
$$\text{tg } \delta \text{ as a function of } \nu \text{ for } V_{ac} = \text{const},$$
$$C \text{ as a function of } \nu \text{ for } V_{ac} = \text{const},$$
$$B_t - B_{dc} \text{ as a function of } 1/\sqrt{V_{ac}}$$

at different temperatures.

We further measured the rate of increase of C and of tg δ at RT and LNT at frequencies ranging from 30 Hz to 20 kHz in a condenser identical with sample 1 but prepared only from epikote 812.

We also prepared an E.L. gap-type cell (sample 3) with four electrodes in which the tip of electrode 1 is 1.3 mm away from that of electrode 3, and that of electrode 4 is 1.3 mm away from that of electrode 2. In the center of these four electrodes we placed a mixture of ZnS (Mn, Cu, Cl) and epikote 812 (same proportion as that used in sample 1). This device was set up in order to measure
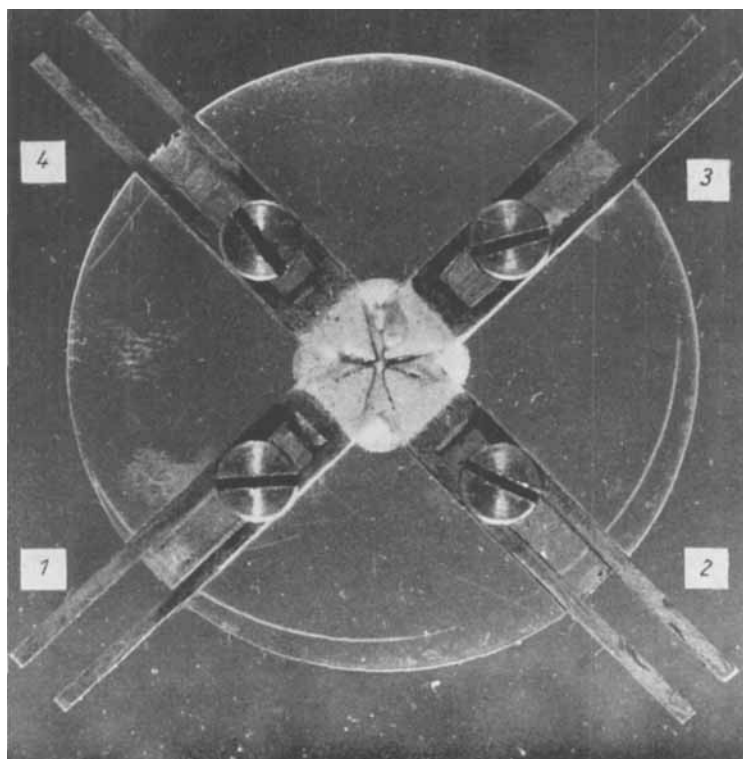
Fig. 3. Sample 3 with crossed electrodes

E.E. with superposed ac and dc voltages as well as with ac and dc voltages perpendicular to each other (Fig. 3).

3. Experimental Results

In our experiments with fixed values of V_{ac}, we measured R as a function of frequency using different values of V_{dc}. We observe that R increases at first at frequencies from 6 to 20 Hz, remains constant up to 30 Hz, then decreases
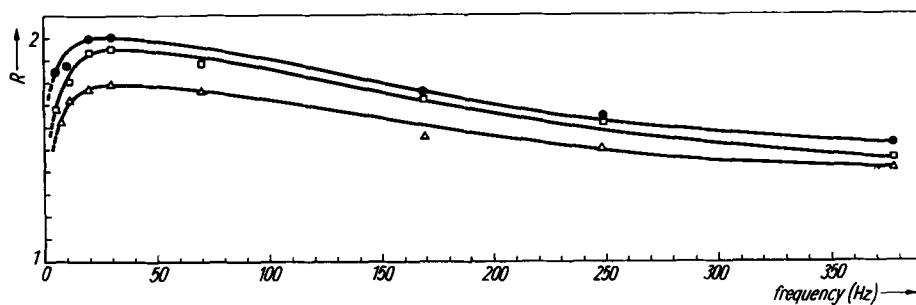

Fig. 4. Plot of R versus excitation frequency (sample 1)
● : $V_{dc} = 80$ V,   □ : $V_{dc} = 100$ V; $V_{ac} = 35$ V,   △ : $V_{dc} = 120$ V

asymptotically and attains the value $R = 1$ when the frequency is sufficiently increased.

In Fig. 4 where the frequency is raised only up to 20 Hz we show three curves obtained from sample 2 with the same value of $V_{ac} = 35\,V$ and three different values of V_{ac}, viz. 80, 100, and 120 V. We also observe that the maximum and the general features do not change. These characteristics are temperature-independent.

It is well known that when a cell or a single crystal is excited by a dc voltage, polarization occurs. The decrease of light in time is the effect of increasing polarization.

Polarization can be cancelled by superposing an adequate alternating field or by inverting the polarity of applied voltage. The depolarization time of the cell can be measured: it is the time necessary to reduce the light intensity to half its value after the exciting constant field is switched off.

We observe that in our samples the depolarization time is 0.3×10^{-2} s. This value is approximately equal to the time during which the total applied field decreases, if we use the frequency corresponding to R_{max} (30 Hz).

Fig. 5a shows the decrease of the imaginary part of the dielectric onstant ε'' of sample 1 which occurs as frequency ν rises beyond 30 Hz. We observe that $\varepsilon'' = \sigma/\nu$ where σ is the conductivity-constant. This means that only free carriers are involved in the process and not dipolar terms. Consequently, the capacity diminishes with increasing ν (Fig. 5b).
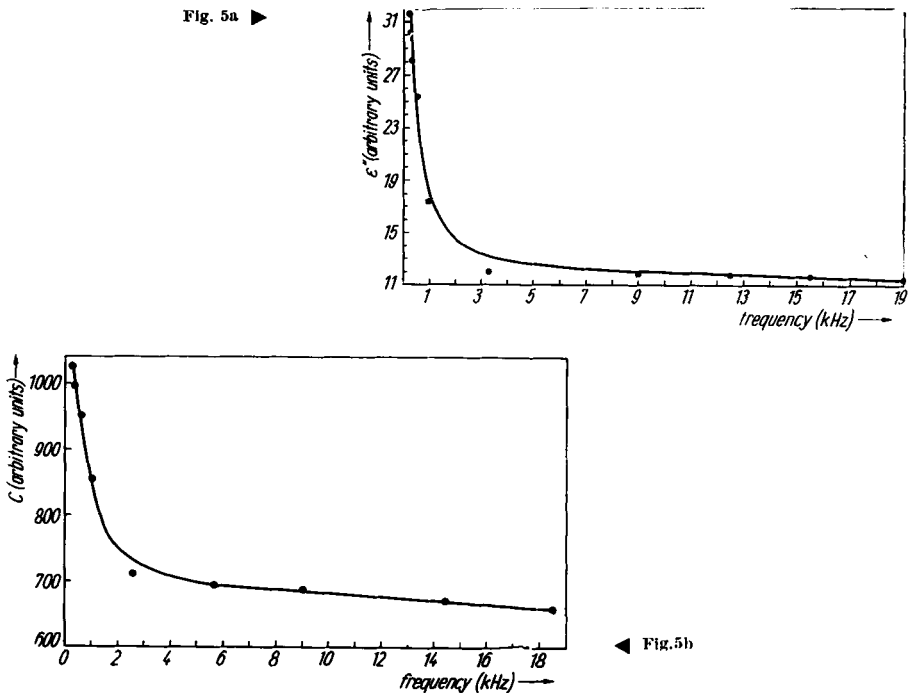
Fig. 5a ▶

◀ Fig.5b

Fig. 5. a) Imaginary part of the dielectric constant ε'' versus excitation frequency (sample 1), b) Capacity versus excitation frequency (sample 1)
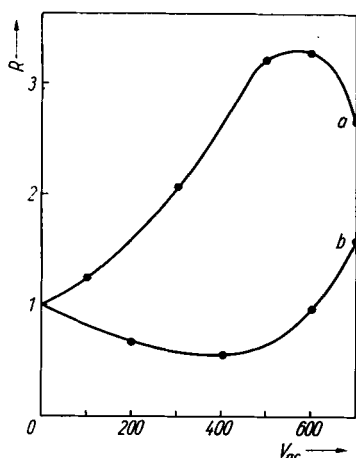
Fig. 6. Plot of R versus V_{ac} with a) $V_{dc} = 800$ V (sample 2), b) $V_{dc} = 400$ V (sample 2)

Now, if we analyze the variation of R due to changes in V_{ac} or V_{dc} near the value of R_{max} for a given frequency, we observe that tg δ remains constant.

We also note that the emission spectrum remains unchanged and does not depend on the kind of excitation (ac, dc or ac + dc). It was checked that the dielectric characteristics of epikote do not substantially affect the behaviour of ZnS.

As noticed by Thornton [2] the brightness wave has the same frequency as the alternating field when R has its maximum.

In order to demonstrate that E.E. requires the two fields to be oriented to one another in a particular way, we used a cell with four electrodes in form of a cross (Fig. 3). This allowed us to show that only when the alternating amplitude is superposed on the value of the dc voltage does one obtain an E.E. whereas if the two fields (direct and variable) are perpendicular to each other, $R = 1$.

For ac alone we verified the Lehman [13] relations between ε', ε'', and V_{ac}.

In the experiments carried out with a single crystal (sample 2) we observe the same behaviour as with sample 1. The only difference is that with sample 2 we also observe a "quenching" which means that $R \leq 1$, as is shown in Fig. 6.

4. Conclusions and Discussion

The various theories proposed so far for the interpretation of electroluminescence are phenomenological and qualitative. The fluid state of this problem is obvious from the fact that an entirely new point of view was proposed only two years ago by Fischer [14], 26 years after the discovery of E.L.

A previous model, proposed by Curie [15] in 1953, was based on the assumption that electrons are accelerated in Schottky barriers. The local high electric field produces hot electrons which are capable, in an avalanche process, of ionizing luminescent centres (impact-ionization model).

A second model assumes that the minority carriers are injected in a p–n junction (injection minority carriers). This model was proposed by Destriau [12].

The variation of light emission intensity (brilliance wave) has a frequency twice that of the exciting alternating electric field. This is considered as a proof that barriers exist. In fact, in each half period only the barriers in one direction are effective. If current is rectified, the frequency of the brilliance wave is halved.

In the model suggested by Fischer the author essentially assumes the existence of a conductive metallic line joining two semiconducting regions. At the interfaces semiconductor–metal–semiconductor, Schottky barriers are formed. When a potential drop occurs between the two endpoints of the chain, the metal injects holes into the negative semiconductor and electrons into the positive semiconductor. These holes and electrons are captured by hole traps (luminescent centres

that are thereby ionized) and electron traps, respectively. Charge compensation requires that there be as many donor states as there are ionized states (acceptor states). If polarity is inverted, thereby inverting the poles of the metallic line, the electrons recombine with the holes in the recombination centres, and this leads to the emission of light. During the inversion two space charges are set up, one of holes and one of electrons. In the presence of a drift current, the two space charges are maintained permanently, but part of the positive space charge is neutralized by the injected electrons, thus producing an emission from the cathode.

We will now examine our results in some detail, taking into account the existence of Schottky barriers.

The fact that the frequency of the brilliance wave (light intensity variation) is halved for R_{max} becoming equal to the frequency of electric excitation, shows that constant voltage polarizes the system, keeping the barriers in one direction quite inactive while only those in the opposite direction are active.

When we obtain values not too close to R_{max} for which R decreases with increasing B_{ac}, we find that tg δ increases: we are therefore dealing with normal intrinsic E.L. which depends only on V_{ac}. However, as soon as R is close to the value for R_{max} (which can vary from 1.5 to 2.5), V_{ac} may be varied without causing any change in tg δ, i.e., we encounter a new mechanism here, in which brightness does not increase with increasing carrier concentration but rather with increasing proportion of radiatively recombining carriers. The fact that R has a maximum at frequencies between 20 and 30 Hz and that this frequency is the same as that necessary to depolarize the system, and is identical to that found by Gobrecht et al. [9] for other types of E.E. and for a different sample of ZnS shows that the delay cannot be attributed to the interjacent dielectric (epikote). This result is further borne out by the measurements made on single crystals and those carried out on pure epikote. The fact that tg δ remains constant for varying frequencies as the alternating voltage is varied in the region near R_{max} appears to be a most important point, since it shows that the number of radiative recombinations (i.e., R) can vary greatly even though the number of free electrons present in the crystal remains constant.

The brilliance wave in ac alone shows a difference between its minimum and maximum values depending on the excitation frequency. Specifically, for a frequency equal to 600 Hz the minimum value of B_{ac} is equal to 1/2 the maximum value of B_{ac}. This means that the half time or mean life time is $\tau = 4 \times 10^{-4}$ s; this corresponds to a trap at 0.3 eV, as can be deduced from

$$1/\tau = p = s \cdot e^{-w/kT} ,\qquad (2)$$

where

p is the probability per second to release an electron,

w is the depth of the trap in eV,

s is a constant $= 10^9$ s^{-1},

T is the absolute temperature,

k is the Boltzmann constant.

If we measure the time needed to halve B_{dc} we find $\tau' = 3 \times 10^{-2}$ s. To account for this difference of two orders of magnitude between τ and τ' we notice again that whereas the position of R_{max} depends slightly or not at all on the temperature, the afterglow curve (which we measure for varying frequencies) depends strongly on the temperature according to (2).

The value τ' is the condenser time constant of the E.L. cell, i.e. the product of the electrical resistance of the dielectric by condenser capacity.

The dielectric in sample 1 is the microcrystalline powder embedded in epikote and in sample 2, the single crystal.

In Fischer's model the maximum number of recombinations depends on the following situation: •

1. A maximum number of electron traps must be occupied so that, by charge compensation, an identical number of holes can be trapped, i.e., a large number of luminescent centres must be ionized.

2. During every variation of the field a sufficient number of electrons the applied constant electric field must be available, comparable to the number of ionized centres (acceptor-traps). The interval during which the half-cycle of alternating voltage diminishes the applied constant electric field must be equal to the value of the condenser time constant, i.e., $\tau' = 3 \times 10^{-2}$ s.

It is possible to explain the experimental results using the models of "impact ionization" or "bipolar field emission"(Fischer). The expression for E.L. brightness in the impact-ionization model is

$$B = I_d\, N\, M\, P\,, \qquad (3\,a)$$

where

I_d is the reverse diffusion current across the Schottky barrier,

N is the probability of ionization by collision for an electron within the barrier,

M is a factor for avalanche multiplication,

P is the probability of radiative recombination.

The expression for E.L. brightness in "bipolar field emission" is

$$B = I_F\, P\,, \qquad (3\,b)$$

where

I_F is the current field emission given by the Fowler-Nordheim equation.

From the terms of expression (3a) one finds the empiric law

$$B = a\, e^{-b/\sqrt{V}} \qquad (4)$$

that can also be obtained using the Fischer model [14] in which ionization by collision is not a fundamental factor, as is the case when using the Fowler-Nordheim expression for field emission. If in equation (1) we substitute for the values B_{ac}, B_{dc}, and B_t those obtained from equations (3a) and (3b) in which the corresponding values for the current I have been used, we find, in the region near R_{max}, an estimated value always lower than 1, whereas experimentally $R_{max} > 1$. The scheme involving a simple superposition of the effects, with no interaction, is thus insufficient to explain the experimental results. We must therefore assume that, besides the diffusing electrons, there is also a space charge which is dissipated, whose constituents are used in radiative recombinations when the constant electric field is superposed on the alternating field (ac + dc).

To conclude, we may say that essentially dc gives rise to a space charge and ac modulates it. The expression for this space charge, valid for internal fields greater than 1.7×10^5 V/cm, has been calculated by Kroemer [16]:

$$\varrho = e\, E\, I_d\, S\,, \qquad (5)$$

where

ϱ means density of the space charge,

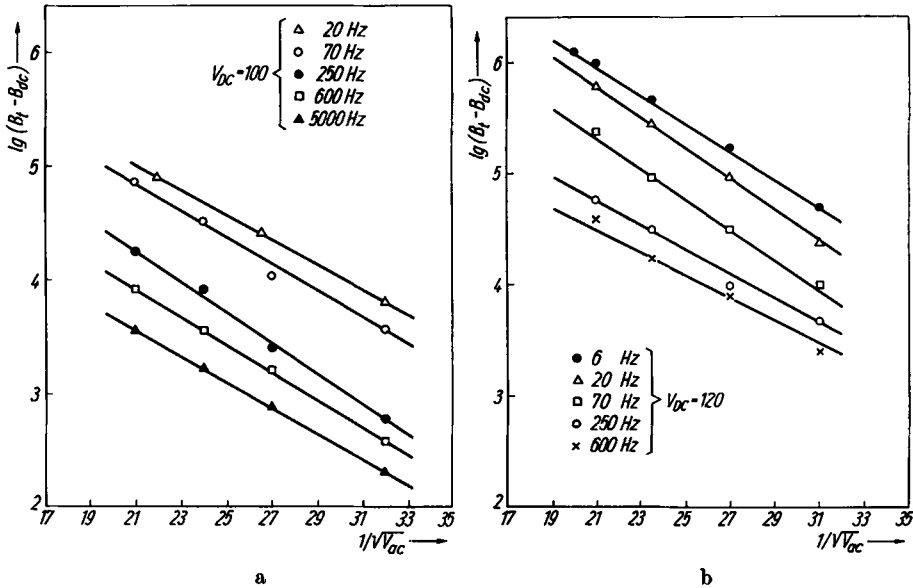e electron charge,

E internal electric field,

Fig. 7. a) E.E. of sample 1, at different frequencies, versus $V_{ac}^{-1/2}$; $V_{dc} = 100$ V, b) E.E. of sample 1, at different frequencies, versus $V_{ac}^{-1/2}$; $V_{dc} = 120$ V

I_d diffusion current in the impact-ionization model or field-emission current in Fischer's model,

$$S = \frac{10}{3} \frac{h}{a} \frac{K\,T}{(K\,\theta_D)^2} \frac{\lambda}{2\,F} \quad \text{viscous damping coefficient}$$

(λ is the mean free path between successive collisions, F the width of the conduction band, θ_D the Debye temperature, a the lattice constant).

To satisfy our model, we must replace the term I_d in equation (3a) or I_F in equation (3b) by a total I_t due to two contributions (diffusion current and space charge current) i.e.,

$$B_t = I_d\left(1 + \frac{E\,S}{t}\right)NMP\,, \tag{6a}$$

$$\text{or} \quad B_t = I_F\left(1 + \frac{E\,S}{t}\right)P\,. \tag{6b}$$

If we write

$$I_d\,N\,P\,M = B_{dc}\,,$$

$$I_d\,N\,M\,P\frac{E\,S}{t} = B \qquad \text{for the impact-ionization model}$$

and

$$I_F\,P = B_{dc}\,.$$

$$I_F\,\frac{E\,S}{t}\,P = B_{ac} \qquad \text{for Fischer's model}$$

we find the general expression

$$B_t - B_{dc} = A\,e^{-b/\sqrt{V_{ac}}} \tag{7}$$

as observed (Fig. 7) near R_{max}. This equation is the relation governing normal E.L., with different constants. The same result has been found by Marti [3] for the case of E.E. with X-rays and V_{ac}.

We also obtain a direct confirmation of Thornton's interpretation [2] that E.E. is due to the modulation of a space charge, by means of a cell with four electrodes. In this experiment, in fact, E.E. can be observed only when the superposed fields are parallel. It is also established that R_{max} depends quite critically on frequency.

The mechanism of E.E. can be interpreted phenomenologically as follows: A part of the electrons are trapped and a part form a space charge. The time constant of the condenser is the diffusion time of the electrons.

As the frequency increases, the space charge, formed by dc, cannot re-diffuse and the light output decreases.

It is difficult, in this stage, to decide if Fischer's mechanism is the only one present.

The variation of the wave pattern confirms the importance of the space charge in E.E.

Acknowledgements

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