ISTITUTO ELETTROTECNICO NAZIONALE GALILEO FERRARIS

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TECHNICAL NOTE N.4.

CONTRACT: AF 61 (052) - 328

OBJECTIVE OF THE WORK: Study of electron traps in dielectrics by electroluminescence.

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TITLE: "Preliminary experiments on Electroluminescence of Zinc Sulfide."

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SUMMARY:

A short review of the literature on the subject of Electroluminescence (EL) is given. The analysis is limited to phosphors of (activated) Zinc Sulphide type and to so called "intrinsic" EL - that is to EL excited in condenser type cells, filled with powder phosphors embedded in a good dielectric medium.

A new technique is suggested for studying the behaviour of the EL. It consists of applying to the cells single transients of voltage (respectively rising or falling) with a constant rate of variation vs time. This, roughly speaking, allows to separate the effect of the electric field and of its time derivative, by changing independently the maximum voltage and its rate of variation. The circuits which have been used for this technique are described, as well as the (preliminary) results obtained with commercial EL cells. These results are of a rather good quantitiative character and look more suited to a physical investigation of the basic phenomena involved in EL than the results of the studies reported in the literature and obtained by conventional techniques.

Some final remarks are presented, concerned with technical improvements of the equipment and with further experiments we are planning on the subject dealt with in this Note.

1.- INTRODUCTION.

The phenomenon of the Electroluminescence (EL) has been known for quite a time (Destriau, 1936) and by consequence the literature on the subject is numerous[1]. The principal papers which have been considered are listed in footnote[2].

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(1) A complete bibliography on EL up to 1958 is given in:
H.F. Ivey, IRE Trans, Electron Devices, ED 6, 203.
A supplement to the above list appeared very recently in:
H.F. Ivey, Journ. Electrochem, Soc., 108, 590, 1961.

(2) a) P.Zalm, Philips Res. Rep. 11, 353 and 417, 1956
b) I.T. Steinberger, V. Bar, E.Alexander, Proc.Conf. Color Centers and Crystal Lum., Torino, Sept.1960, pg.210.
c) J.F. Waymouth, F.Bitter, Phys. Rev. 95, 941, 1960.
d) A.M. Bonch-Bruevich, O.S.Marenkov, URSS, Optics and Spech, 8, 449, 1960.
e) D. Curie, article in Progr. in Semic. 2, 251, Ed.Heywood and Co, London 1957.
f) P. Goldberg, Proc.Conf.Color Centers and Crystal Lumin. Torino, Sept.1960, pg.247.
g) W.W. Piper, F.E. Williams, Phys.Rev. 87, 151, 1952.
h) J.Lambe, C.C.Klick, article in Progr. in Semic., 3, 185, Ed. Heywood and Co. London 1958.
i) W.W. Piper, F.W. Williams, article in Solid State Physics, 6, 96, Ed. Acad.Press.New York, 1958.

The content of these paperswill be assumed as known and therefore we shall make free reference to them whenever necessary, for sake of brevity.

Let us remember firstly that several non identical species of EL are known, such as that associated with p-n junctions, or dc and ac EL in single crystals with ohmic contacts, or what has been sometimes called "intrinsic EL" (Destriau), where powder phosphors embedded in (practically) perfect dielectrics are used andno dc current can flow through the cell(x).

We shall focus our interest almost exclusively in this report, on the last case quoted, say "intrinsic EL" as presented by ZnS cells. This both because of the greater practical interest of this case, and because we felt as if this were the "purer" case to begin with. Moreover, the origin of the "primary" electrons causing the phenomenon is less clear in this case, as we shall show, as compared to dc EL. Last not least, condenser type cells are very easily available . As already pointed out, quite a lot of work has been performed on the phenomenology of the light emission associated with intrinsic EL, and the observations have been complemented and confronted with the results obtained with single crystals, or tricresylphosphate cells, exc. Moreover, even though by far the largest amount of work has dealt with sine wave excitation, square waves also have been used, or biased sine waves (i.e. sine + dc) and exponential waves from a capacitor - resistance circuit.

(x) This for example excludes in some way experiments with tricresylphosphate.

Some work has also been performed with non periodic excitation. The phosphors used has been almost always ZnS, with different activators and coactivators. Following Zalm[2a] the phosphors can be divided into two main groups:

a) with characteristic activators (such as ZnS (Cu,Cl). In this case ionization of centers takes place.

b) with fundamental activators (such as ZnS (Mn). In this case the centers are only excited.

Various qualitative results and sometimes quantitative relations (such as the brillance/voltage dependence): $B = a \exp(-b/V^{\lambda})$; $1/2 < \lambda < 1$; a,b constants) for sine wave excitation have been deduced from the experiments. The point of view which, as a consequence of the phenomenologicel survey, is generally accepted, is that intrinsic EL is basically nothing else than an "internal cathodoluminescence"(x). This means that, in both phenomena, one has to do with electrons (perhaps holes) traveling into the conduction band and causing light emission by collision with luminescent center which may be excited or ionized and subsequently return to their fundamental state by emitting radiation (and eventually phonons).

This process is sometimes referred to respectively an "impact excitation" or "ionization" and it is accepted as the basic mechanism of intrinsic EL by, foe example, Destriau, Curie,

(x) This statement, however, does not mean at all that there is complete agreement on this point, but just that there is a certain majority in favour of this assumption than of others. Cfr. e.g. the criticism by Steinberger and coworkers (2b). As a matter of fact, the whole field is still rather badly understood.

Piper and Williams and Zalm. Of course, between El and cathodoluminescence there is an obvious difference, as to the origin of the electrons travelling and colliding. But the fundamental similarity of the subsequent process - whatever its mechanism might be - is strongly suggested by the great similarity of the spectra emitted in EL or in cathodo, or photoluminescence of ZnS.

As a matter of fact (cfr.e.g. 3), there is no obvious agreement even as to certain details of the photoluminescence mechanism in ZnS phosphors. Nevertheless, we shall assume, as working hypothesis, that intrinsic EL is basically nothing else than the same luminescence which can be excited with cathode rays or photons. It takes however origin through a peculiar mechanism about which several hypothesis have been suggested. For example, Zalm[2a] assumed injection of carriers through a surface barrier at the contact phosphor/conducting phase; Piper and Williams[2g] and Curie[2c] consider field ionization of some suitable donor centers localized in the barrier.

Actually, Zalm seems to have investigated the question in great detail: he states - but to our best knowledge nobody successively confirmed this point of view in a sure manner - that intrinsic EL depends on the presence of a conducting phase of any kind (metallic, such as Ag,Al, or semiconducting such as Cu_2S) on the surface of the ZnS grains.

Some experimental evidences of this fact are offered

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(3) D.Curie, Proc.Conf.Color Centers and Crystals Lumin.Torino, Sept. 1960, pg.199.

in the paper[2a]. The reasonable suggestion is then made that the conducting surface phase may act as a couple of electrodes, injecting carriers into the phosphor.

More precisely, a double layer originates at the contact , which even though locally bends upward the bottom of the conduction band nevertheless depresses the whole potential of the crystal , so that a net lowering occurs of the value of the surface step. Moreover ,at some distance from the surface the bottom of the c.b. may become lower than the Fermi level provided a sufficient electric field is applied. In such a way electrons are able to tunnel into the phosphor. Piper and Williams[2g], on the other hand ,assumed that primary electrons initiating ionization of luminescent centers come from a limited number of donors levels in ZnS , which should be ionized by direct action of the electric field.

Actually , Zalm observes that the probability of such a process is strongly field dependent and if the field is high enough for ionizing donors of a given depth, all the donors should be immediately exhausted in a but slightly stronger field. In this way, the number of excitations should depend only on the instantaneous field and not on the time for which it is applied - that is to say not from the frequency of the (sinusoidal) voltage. This is actually contradicted by the experiment. These are the grounds on which the Zalm's criticism is founded which look rather reasonable indeed. Nevertheless , we do not feel that the question can be considered as settled by these simple reasonings , and will therefore assume that at present both the injection mechanism and that of field ioniza-

tion are still "a priori" possibilities, which, moreover, pose a problem still awaiting definite solution.

Both these ideas about the first among the three steps necessary to produce EL (namely, injection by conducting surface phase or field excitation of donors) seem besides to agree with an experimental feature well established and quoted by several Authors - we mean the fact that, at least if the excitation voltage is not too high (Cfr.Zalm[2a]), the light comes out from the side of the cell which at the time considered is cathodic. Another experiment worth of mention which can be related to the question of the polarity of the emitting regions is described in the paper by Waymouth and Bitter[2c], whereby the behaviour of single grains of the EL phosphor is investigated. The Authors discovered that the luminescent spots of a given grain bright or alternatively remain dark according to the circumstance that the local electric field is parallel or antiparallel to a given direction of reference . This, we think, points out directly that the active regions have a "vectorial" character and therefore are very likely to consist of double layers.

This same paper is also perhaps the most complete and quantitative about a further feature, worth of mention: that of the so called frozen polarization of the EL cells. The phenomenon of the frozen polarization (FP) of electroluminophors is so well known (but rather badly understood) that literature speaks well of "photoelectrets" and that it forms the basis of some commercial system for storing images to be reproduced at a sug

cessive time[4].

The consequences of the FP are manyfold and rather complicated: some of them, which - as we shall see - can be brought to light in a particularly striking way by our technique of single transients, are quite impressive. For example, it turns out that two successive light pulses may have a ratio of heights 1: 1 or up to about 1:100 depending on the time separating the second from the first pulse. It is not worth to dwell any more on the description of these phenomena. We limit ourselves to point out that a strong correlation seems to exist between the value of the FP and the light output of which the EL cell is capable at that very moment. As we said, an account of these experimental facts is given - among others - in the paper of Waymouth and Bitter already quoted.

On the other hand, very little appears established as to the mechanism by which FP takes place and influences the light output - and this point of course will receive our attention in next future.

2.- EXPERIMENTAL.

Basically, the technique we used was the following: the electroluminescent cells(x) (Westinghouse Rayscent Panels

(4) Cfr. article by H.Kallman and J.Rennert, in Proceeding Symp. on Solid State phenomena and Electric circuits, pag.325, Polytechnic of Brooklyn April 1957.

(x) The characteristics of the panels, as kindly communicated to us by the Research Laboratories of the Westinghouse Electric Corporation are the following:
Phosphor: ZnS (predominantly cubic phase) activator and coactivator: Cu and Cl in the mole percentages indicated:

	Cu	Cl
Blue	0.6(0.03)	0.14 (0.10)
Green	0.6(0.1)	0.34 (0.16)

The numbers in parenthesis refer to the % retained in the finished phosphor, after firing and washing - while the other numbers represent additions prior to firing. The phosphors are produced according to US Patent 2,874,128 Febr.1959 (A.Watchell).

"green" or "blue", 2" X 2" sized) undergo single voltage transients, where voltage increases (or decreases) at a strictly constant rate vs time, from zero (respectively from V max) to V max (respectively to zero volt). The value of V max could be varied from about 120 Volt (the treshold for a detectable light output under our conditions) up to 220 V; and the rate of rise (or of descent) of the voltage from about 10 V/msec up to 1000 V/msec. This is accomplished by the circuitry shown in fig.5. Positions A of the switch correspond to voltage rise, and positions B to descent. Capacitors C_1.....C_8 provide changing the rise or descent rates, while potentiometer P changes the value of Vmax, fixing the cutting value of diode D. The constant rate of charging of the capacitors is ensured by the boot - strap circuit BS. Valves V_1 act as trigger forming circuit, to trigger the time axis of the cathode ray tube. Valve V_2 acts as an electronic switch: the voltage transient wanted begins when the manually operated mechanical switch S disconnects the grid of V_2 from the ground. A cathode ray Oscillograph (Dual beam Tektronix oscilloscope model 516) has its A channel connected to the terminals of the electroluminescent cell, while the time basis is actuated by the triggering pulse from V_1. A camera records the transient. To the B channel of the same oscilloscope goes the other variable to be recorded sinchronously with the voltage transient. In our experiments this second variable was the light output of the cell. It is to be remarked that the bipolar switch connected to the cell serves to exchange between each other its cathodic and anodic faces so as to have the side facing the phototube always of the same polarity. This remark

is important for the reasons explained in Introduction paragraph.

When recording light pulses, the cell was viewed by a RCA photomultiplier Mod. 6810 A (14 dynodes) equipped with a low-noise medium gain voltage divider, and energized by a (P-10, Italelettronica) stabilized supply operated normally at 2000 V. When operating with such high-gain tubes and fairly long light pulses (10^{-4} - 10^{-3} sec) care must be exercised to avoid saturation. Therefore curves were drawn, showing the value of the (static) output voltage at the terminals of the loading resistor of the 6810 tube, when (static, white)illuminations of different (relative) amounts, very accurately known, were falling on the cathode. In this way, the maximum output admissible was determined. Of course, when operating with transient lights, the admissible output would be greater, and therefore our procedure put us on the safe side.

The device which furnished different well definite light ratios was basically a screen with holes, to be opened or closed in various combinations, placed in front of a sheet of diffusing glass.

If for example only hole A is uncovered and light L_A is passing, we observe a current i_A. The like, current i_B corresponds to light L_B from hole B.

When both A and B apertures are uncovered, as far as the phototube is within its linear characteristic, current i_A+i_B must be observed and so on.

Between the phototube and the cell, there was normally an interferential filter, of about 150 Å bandwidth, and a honeycomb collimator, reducing the incident angle spread to less than 5°, to get good monochromatization. Two filters were used, a green,

centered at 5200 Å and a blue one, at 4700 Å . Fig. 4 shows the details of this set-up. Fig.3 shows a typical oscillogram.

All the measurements were made with the electroluminescent cell at room temperature. Only the results relative to the "green" Rayscent Panel will be discussed in this Note.

Measurements have been performed at three different values of Vmax, namely: 150,175,200 V. Independently, several values of the rate of voltage variation have been used, between 10 V/msec and 1000 V/msec.

Both voltage rises and descents have been used, and every measurement has been made once with the green filter and then repeated with the blue one. The quantities which have been measured using the rather large series of pictures taken have been: the height of the light pulse, the time for half-height, the "phase time", that is to say the difference between the instant of starting of the voltage and the maximum of the light pulse.

The results of all these measurements are reported in figg. 1,2,6,7.

It can be seen at first inspection that:

a) the height of the light pulse, for each value of Vmax, increases first with the rate of variation of the voltage, finally showing marked saturation;

b) that "green " and "blue" components behave in the same way, showing an almost constant ratio green/blue of roughly 5 times;

c) that this behaviour is common both to rises and descents of voltage, but, for each "color" the pulse height for rising voltage is always about 2 times greater than for voltage falling;

d) that (for both "colors") the ratios of the half-height time to the duration of the voltage step behave in a very peculiar way.

Such a behaviour, we think, may have interesting implications.

First, there ratios indicate that, at given dV/dt, the decay of luminescence due to voltage falling is much longer than for rising - whilst the pulse height is lower. This suggests a roughly equal integrated light output for both cases. Second, the dependence of these rations on dV/dt is very weak for rising voltage, and more sensible for falling voltage.

e) the "phase time" seems to be rather strictly correlated to the half-height times.

To these features, it must be added that:

h) important time dependent phenomena (which are besides already well known, Cfr. for example 2 c) have been observed. As viewed through our technique, their behaviour is the following; the light emitted in a certain transient, depends in an exceedingly strong way upon the time elapsed from the last transient undergone previously by the cell. If this time is very short, say, few thenth of a second, the light output is bigger of a factor of may be several hundred. This factor tends asymptotically to 1 when the time elapsed grows: at the room temperature, the value 1 is practically reached (in green cells-the only ones we are considering in this Note) after 7 minutes. We anticipate here that although no measurements vs temperature have been made by us so far they will be performed in next future. All the measurements reported in this Note have been done after "recovery" was sufficient, that is to say always 7 minutes separate two consecutive pictures. The phenomena are, no doubt, strictly connected with another feature;

i) cell polarization. No methodic measurements of this quantity have been made by us so far. It is important in this respect to

point out that, during the 7 minutes separating two pictures, the electroluminescent cell was kept with its electrodes short circuited.

Let us spent a few words, to remark that the experimental facts listed above, which come out from the application of our technique to these problems, are, we think, more free from spurious or accessory features than the data obtained with conventional excitation sources, such as periodic or exponential waves or voltage pips.

The present data should therefore be more suited to physical interpretation.

Finally, to complement the phenomenological survey, measurements of the dielectric constant and loss factor of the cell have been performed at various frequencies, as a function of the (sinusoidal) exciting voltage

The results are shown in fig.8. and 9.

It is remarkable the presence of a minimum around 20 Volts r.m.s. - and the strict similarity of behaviour of ε and tg δ vs. voltage.

3.- CONCLUDING REMARKS.

In the previous paragraph it has been pointed out the interest of using a technique of transients to investigate EL. Such a technique in fact affords to study easily and accurately the details of the structure of a single light pulse. It is clear that the "linear transients" used by us are the most suited ones.

It has finally been shown the interest of operating on unpolarized cells, recovered from previous excitations, and capable of only a very weak light output.

Last not least , it is obvious that the isolation of the different chromatic components is advisable in order to get results amenable to quantitative treatment.

All these requirements lead to a common point : to deal with extremely small intensities of light. Our present set-up cannot be considered as satisfactory from this point of view ,due to the considerable noise of photomultipliers. Therefore , the first experimental improvement we are considering is the adoption of an EMI 6915 "S" phototube ,especially tested for low noise and painted for usage at liquid N_2 temperature . These conjointed features are expected to improve the signal/noise ratio of a factor of about 500. In this way good quantitative analysis of the light peaks should prove feasible , and much more information should be obtainable about the mechanism involved in EL.

Another point which , as already pointed out ,deserves thorough investigation is the relation between light output and polarization - what of course also implies investigation of the polarization itself.

Our ideas about this point are forcely still in an early stage, but ,as to the experimental side, it appears necessary to dispose of demountable cells, that is cells whereby one electrode of the condenser can be removed at will. For this reason, we required Westinghouse Laboratories to supply us with phosphors powders of the same quality used in the commercial cells of our experiments. The powders are now available and we are therefore preparing luminescent sheets with these phosphors embedded in several dielectrics. Strictly related to the above point is that of the influence"of the "recovery" of the cell after excitation,upon the light output of which

the cell is capable when excited again. An apparatus has been built to study the recovery phenomena.

The points listed in this paragraph will be developed in a next Technical Note.

ACKNOWLEDGMENTS.

It is a pleasure to gratefully aknowledge here dr. H.F.Ivey, of the Westinghouse Co. Research Laboratories, for generous supply of data and materials and professor B.Lavagnino of the Istituto Elettrotecnico Nazionale for the measurement of the dielectric parameters of the cells.

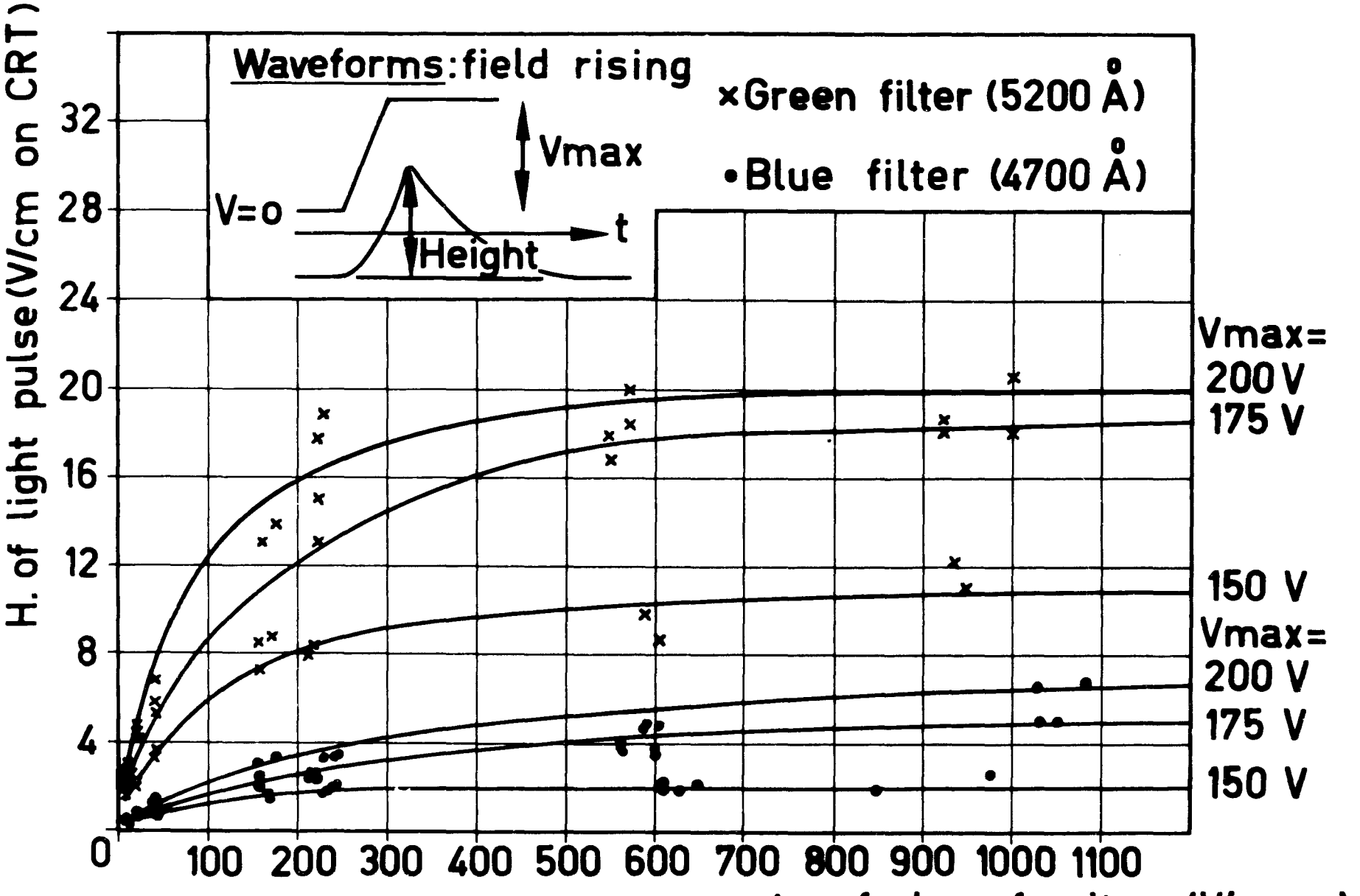

Waveforms: field rising
Vmax
V=o
t
Height
×Green filter (5200 Å)
•Blue filter (4700 Å)
H. of light pulse (V/cm on CRT)
32
28
24
20
16
12
8
4
0
100 200 300 400 500 600 700 800 900 1000 1100
rate of rise of voltage (V/msec)
Vmax=
200 V
175 V
150 V
Vmax=
200 V
175 V
150 V

fig. 1

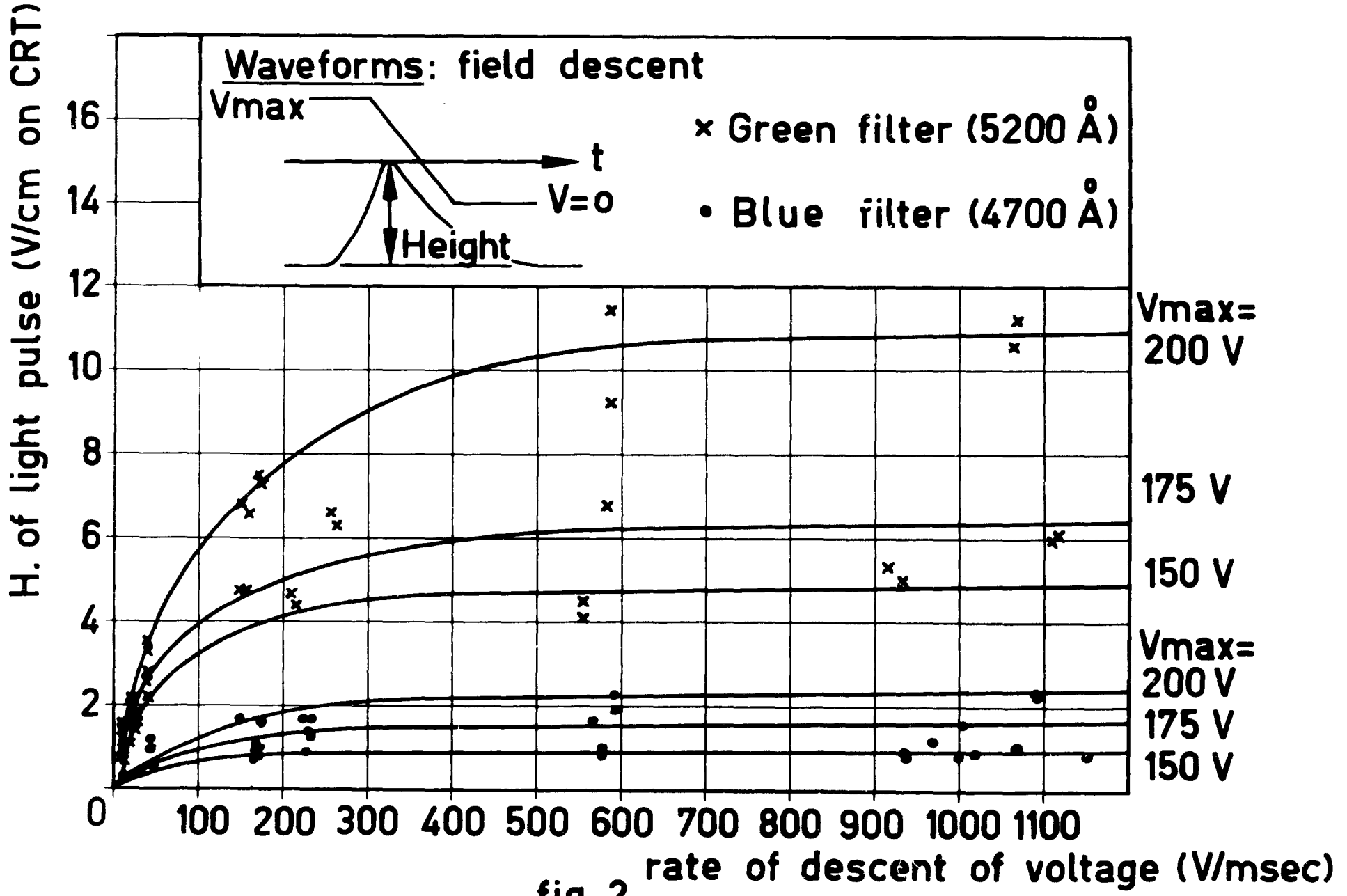

Waveforms: field descent
Vmax
t
V=o
Height
× Green filter (5200 Å)
• Blue filter (4700 Å)
H. of light pulse (V/cm on CRT)
0
2
4
6
8
10
12
14
16
100 200 300 400 500 600 700 800 900 1000 1100
rate of descent of voltage (V/msec)
Vmax= 200 V
175 V
150 V
Vmax= 200 V
175 V
150 V

fig. 2

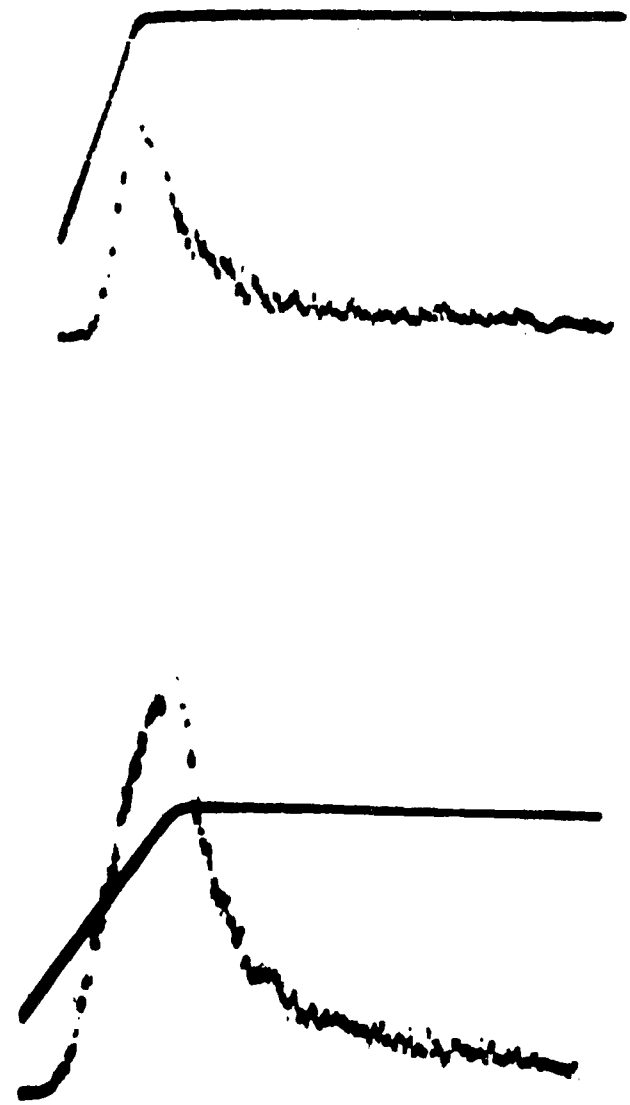


fig. 3

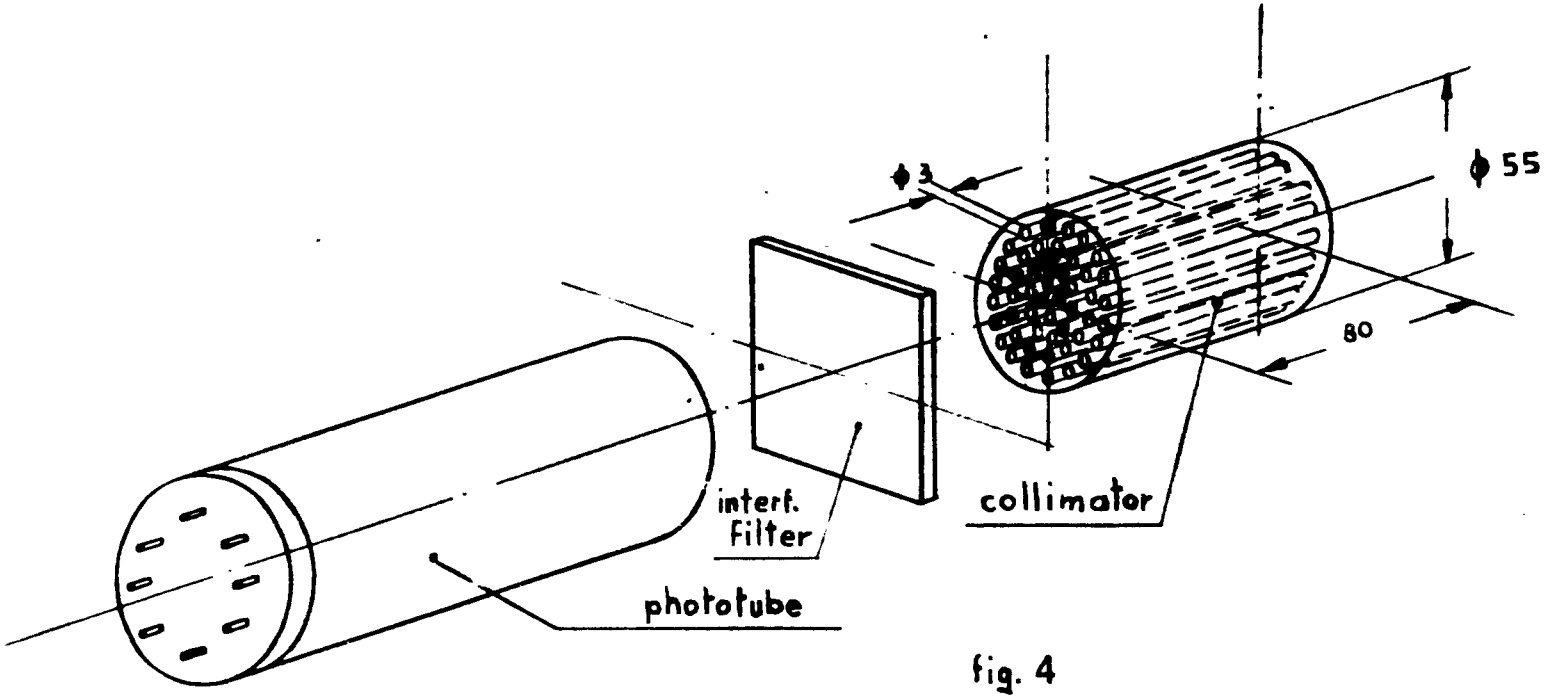
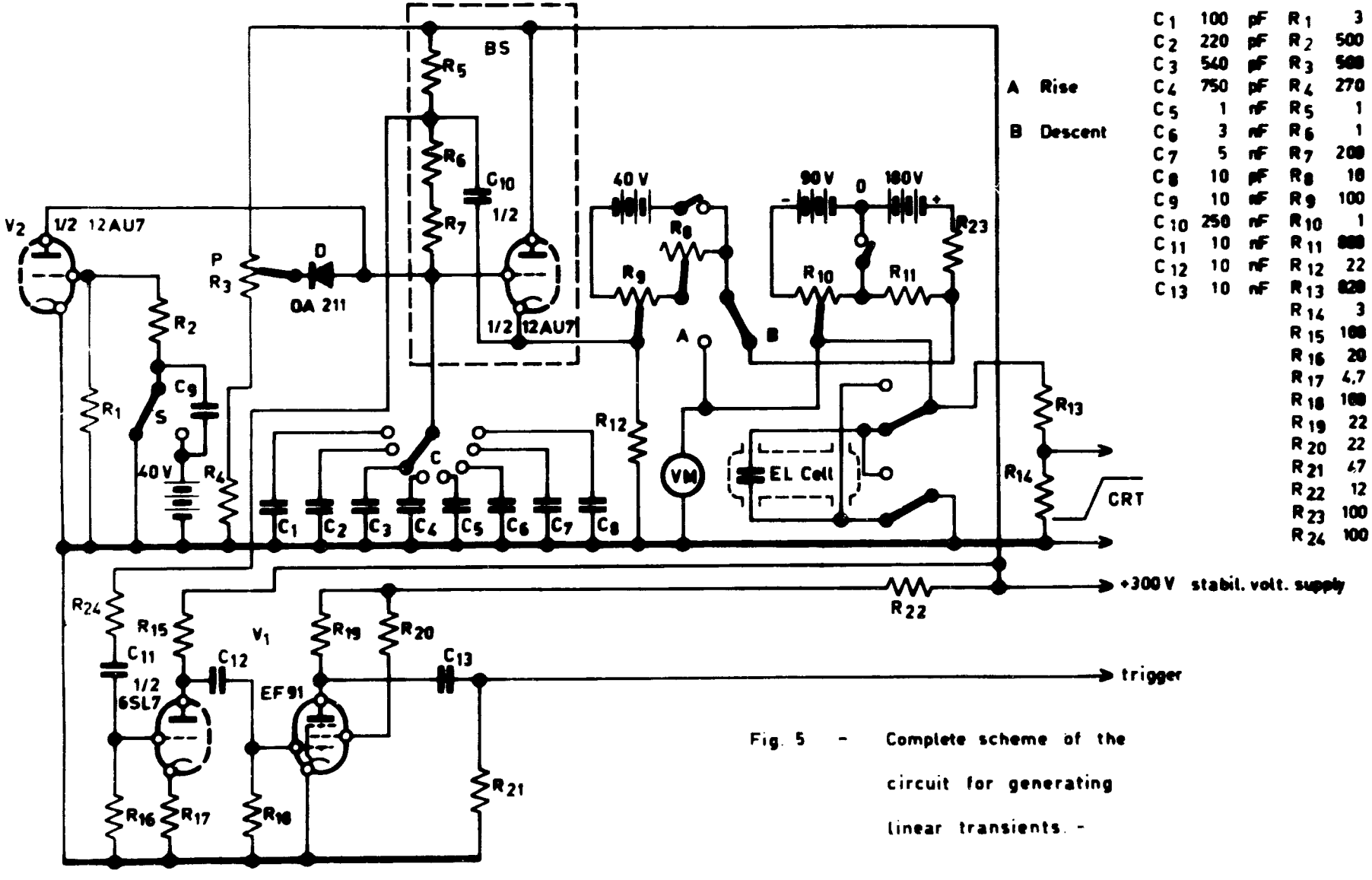
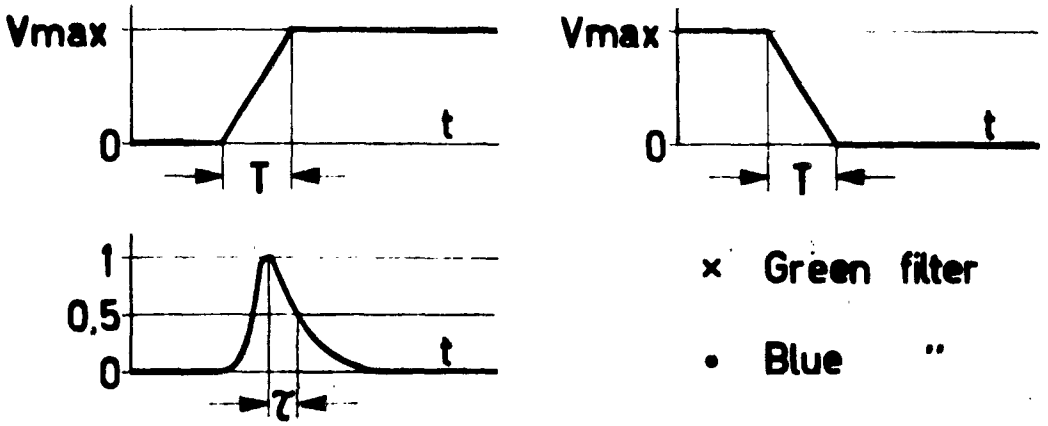


fig. 4



C_1	100	pF	R_1	3	MΩ
C_2	220	pF	R_2	500	KΩ
C_3	540	pF	R_3	500	KΩ
C_4	750	pF	R_4	270	KΩ
C_5	1	nF	R_5	1	MΩ
C_6	3	nF	R_6	1	MΩ
C_7	5	nF	R_7	200	KΩ
C_8	10	pF	R_8	10	KΩ
C_9	10	nF	R_9	100	Ω
C_{10}	250	nF	R_{10}	1	MΩ
C_{11}	10	nF	R_{11}	500	KΩ
C_{12}	10	nF	R_{12}	22	KΩ
C_{13}	10	nF	R_{13}	820	KΩ
			R_{14}	3	KΩ
			R_{15}	100	KΩ
			R_{16}	20	KΩ
			R_{17}	4,7	KΩ
			R_{18}	100	KΩ
			R_{19}	22	KΩ
			R_{20}	22	KΩ
			R_{21}	47	KΩ
			R_{22}	12	KΩ
			R_{23}	100	KΩ
			R_{24}	100	KΩ

Fig. 5 - Complete scheme of the circuit for generating linear transients. -


Vmax
0
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Vmax
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t
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1
0,5
0
t
τ
× Green filter
• Blue "

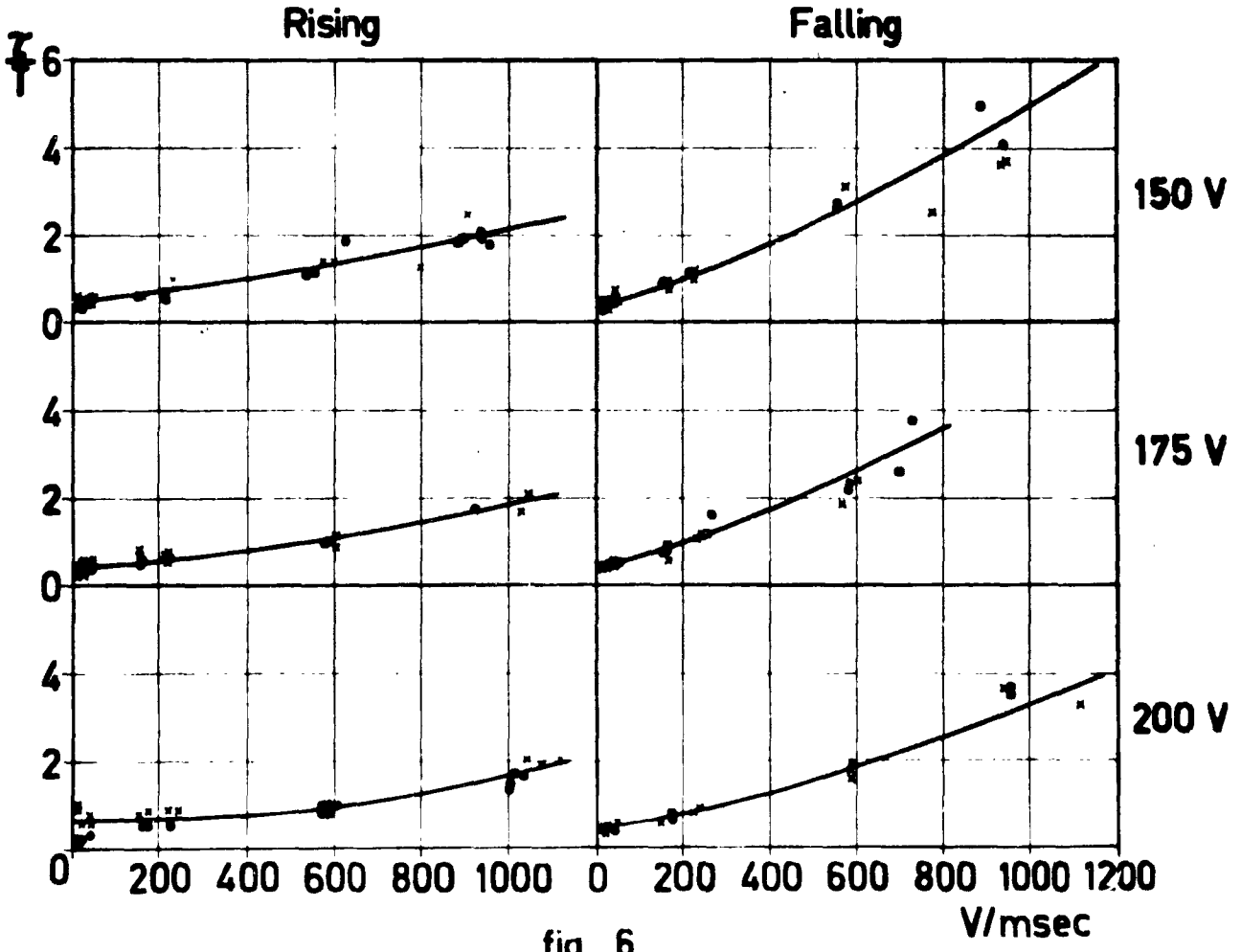
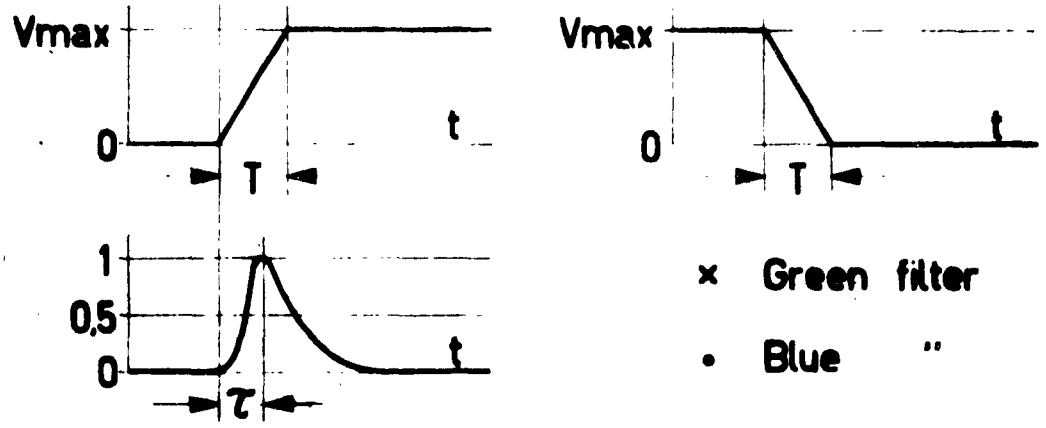
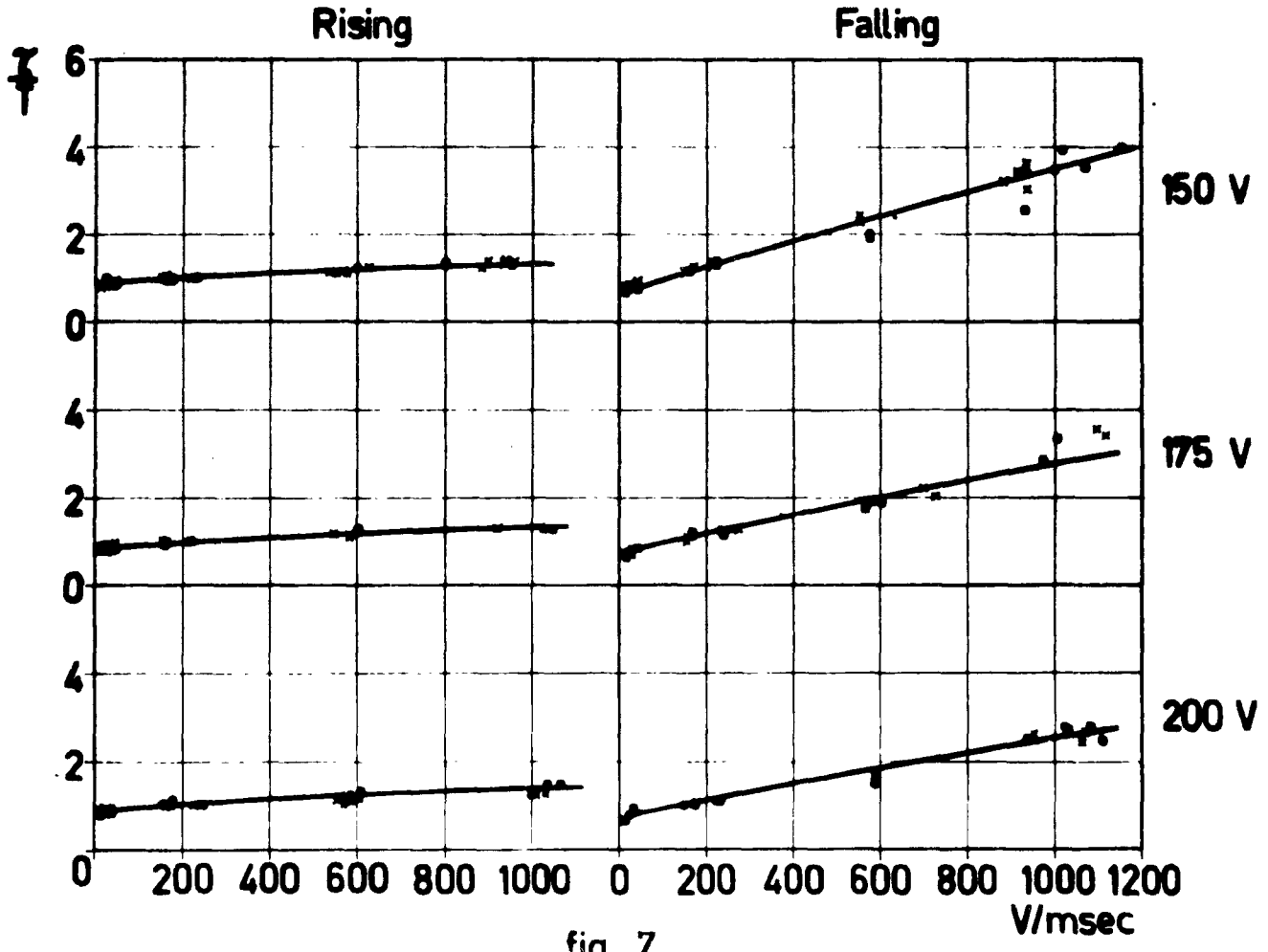

Rising
Falling
τ
6
4
2
0
150 V
175 V
200 V
0 200 400 600 800 1000
0 200 400 600 800 1000 1200
V/msec

fig. 6


Vmax
0
t
T
Vmax
0
t
T
1
0,5
0
t
τ
× Green filter
• Blue "


Rising
Falling
τ
6
4
2
0
4
2
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4
2
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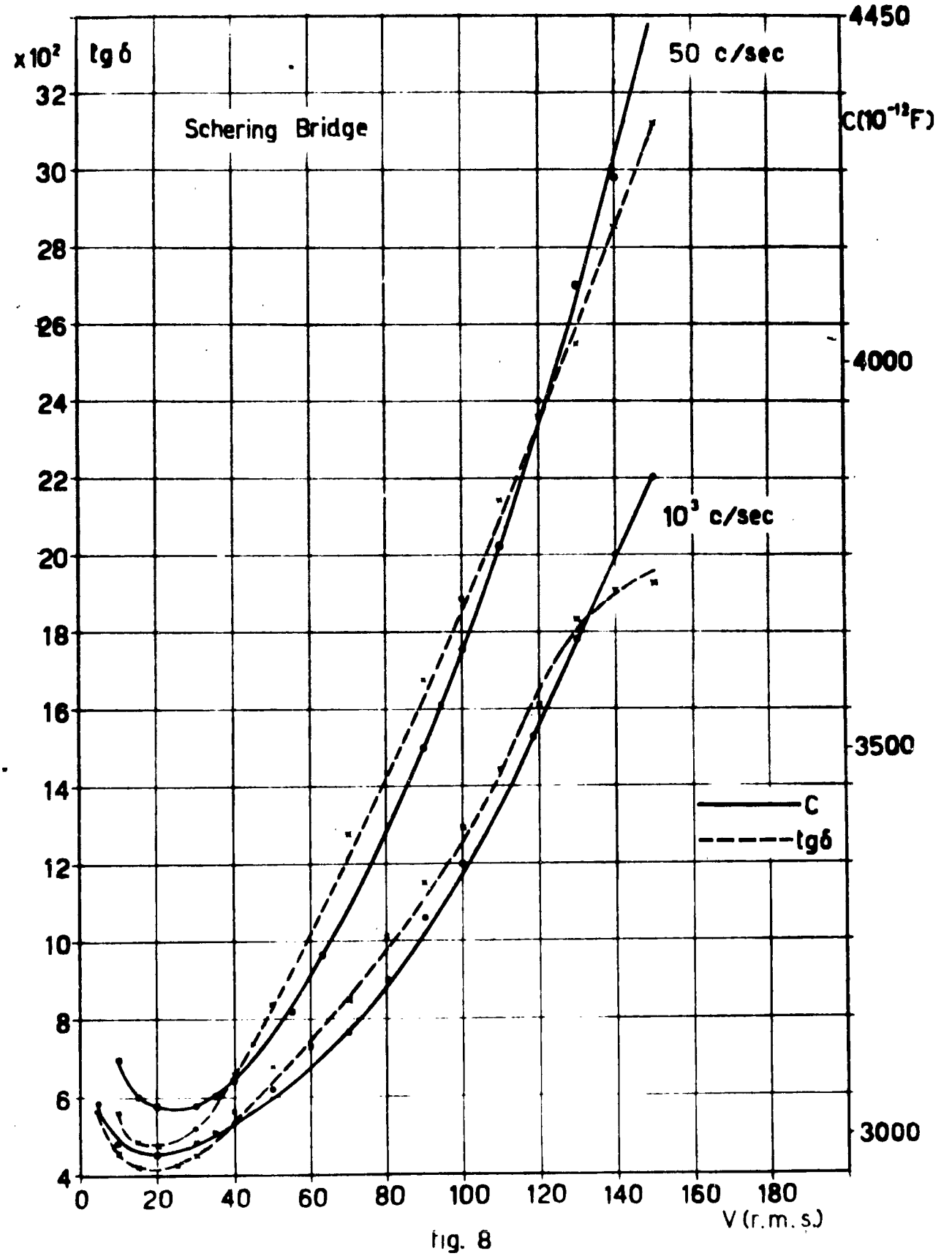
150 V
175 V
200 V
0 200 400 600 800 1000
0 200 400 600 800 1000 1200
V/msec

fig. 7


x10²
tg δ
Schering Bridge
50 c/sec
10³ c/sec
C
tgδ
C(10⁻¹²F)
V (r.m.s.)
32
30
28
26
24
22
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18
16
14
12
10
8
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60
80
100
120
140
160
180
4450
4000
3500
3000

fig. 8

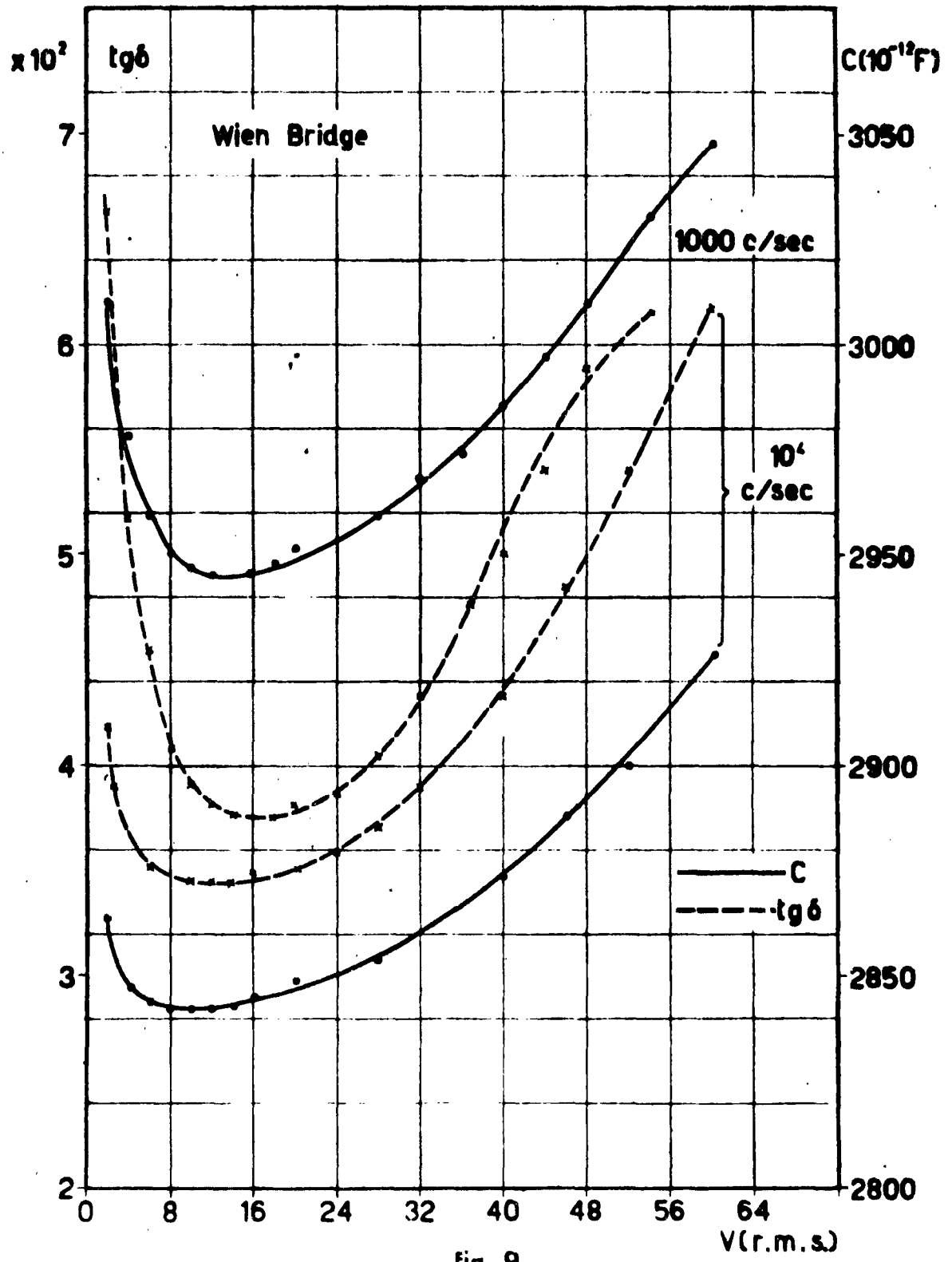
x 10²
tgδ
Wien Bridge
C(10⁻¹²F)
7
6
5
4
3
2
3050
3000
2950
2900
2850
2800
1000 c/sec
10⁴ c/sec
C
tgδ
0
8
16
24
32
40
48
56
64
V(r.m.s.)

fig. 9