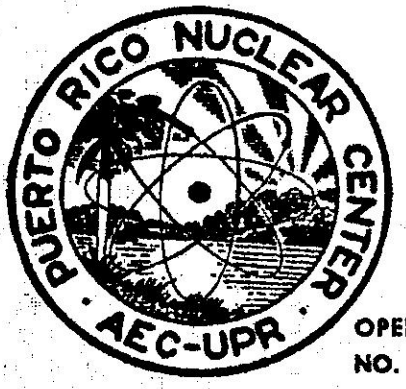
PRNC 38

PUERTO RICO NUCLEAR CENTER

RADIATION DAMAGE IN ORGANIC CRYSTALS

Progress Summary Report No. 2



OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT
NO. AT (40-1)-1833 FOR U. S. ATOMIC ENERGY COMMISSION

STUDY OF RADIATION DAMAGE IN ORGANIC CRYSTALS USING ELECTRICAL CONDUCTIVITY

Amador Cobas and H. Harry Szmant - Principal Investigators

Progress Report #2

Work performed at Puerto Rico Nuclear Center
Rio Piedras, P.R., under U.S. Atomic Energy
Commission Contract AT(40-1)-1833 (Project 14)

March 1964

TABLE OF CONTENTS

INTRODUCTION:

This project is concerned with the effects of radiation on organic crystals. It is felt that such studies on well defined crystalline structures can provide a firm foundation for a later study of more complex materials including those of direct biological interest.

In the initial phase of this work we have studied the effect of neutron irradiation on the electrical conductivity of anthracene crystals. The choice of electrical conductivity is based on evidence that this parameter is most sensitive to the presence of impurities or defects [1]. Our results show that it is possible to detect quantitatively radiation damage at levels far lower than those that can be observed by other chemical or physical techniques. We expect that at some upper level of radiation damage it should be possible to correlate the electrical properties directly with optical and other properties of the crystals, thus providing an enlarged spectrum for the evaluation of radiation damage.

The choice of anthracene as initial material for study is predicated upon the fact that this substance has been studied more than any other organic material.

The effect of neutron irradiation on anthracene has been studied previously by Kommandeur[2,3], but to the best of our knowledge, no other work on this subject has appeared since then. Since Kommandeur's work was done very early in the history of organic conductivity, we felt that it would be valuable to reopen and expand this work to include more

recent developments such as the introduction of charge-injecting electrodes [4], and the application of space-charge-limited current theory to organic crystals [5,6].

Below is a summary of the results obtained during the period July 1963-December 1963.

SECTION I. CRYSTALS

In order that our results could have a meaningful statistical interpretation it was necessary to produce our own crystals and for this reason we established a crystal growing station. In this station we used the relatively simple technique described by Kallmann and Pope[7]. This technique consists in preparing a saturated solution of anthracene in 1,2-dichloroethane at a temperature a few degress above room temperature and then cooling the solution slowly to room temperature. The surface of the solution is covered with a few milliliters of xylene to prevent rapid cooling at the surface. Xylene has a smaller density than dichloroethane and if poured carefully it will float on top of the solution. Sometime during the cooling process crystals will be formed and if the proper temperature gradient exists in the solution the crystals will neither sink to the bottom nor float to the surface. The crystals will grow slowly and should be fished out as soon as they attain an acceptable size. If the proper temperature gradient is not obtained the crystal

will sink before they grow to an acceptable size. At the bottom they continue to grow but no longer as monocrystals and therefore cannot be used in our experiment. If the crystals produced are unacceptable, the solution cannot be reheated and cooled again to make a second attempt to get good crystals because the xylene mixes slowly with the dichloroethane making a less dense solution in which it will be more difficult to get the crystals to float.

Our experience with the Kallmann-Pope technique to grow crystals is that more often than not we fail to produce good crystals. Each trial takes about half a day's work and many times our technician has spent weeks trying to grow crystals without any success. We have grown a total of 150 crystals ranging in thickness from 10 to 70 μ and from 0.3 to over 1 cm^2 in area. Many of these crystals break in the process of being mounted in the Kallmann-Pope cell or develop a leak while undergoing measurements.

We have tried to grow crystals using a modified Kallmann-Pope technique using 1,2-cis-dichloroethylene instead of 1,2-dichloroethane, and cooling without covering the solution with xylene. The dichloroethylene has a relatively high density and the anthracene crystals float. After the crystals are fished out they are cleaned

with xylene to eliminate smaller crystals which sometimes adhere to the surface of the larger crystals. Using this technique we have grown 25 crystals. The crystals are so large that sometimes they can be broken into two or three pieces, each one of which can be used for a separate measurement.

We have purchased from Harshaw Chemical Co. unselected anthracene crystals 10 mm x 10 mm x 5 mm which we have cleaved and polished to thickness of approximately 0.3 mm. We have also purchased from Harshaw Chemical Co. selected and polished anthracene crystals 10 mm x 10 mm x 0.3 mm and 10 mm x 10 mm x 1 mm. We have made measurements on some of these crystals which are included in this report.

SECTION II. RADIATION DAMAGE MEASUREMENTS

We have done electrical conductivity measurements on crystals ranging in size from 10 to 100 μ which were grown in our crystal growing station. We have also done electrical conductivity measurements on unselected Harshaw crystals which we cleaved and polished to a thickness of approximately 300 μ and on selected and polished Harshaw crystals of 300 μ thickness. These measurements were done with the Kallmann-Pope[8] cell using NaI-NaI, NaCl-NaCl, Na_2SO_4 - (NaI-I_2) electrodes and 3650A and 4360A light. The measurements were done before and after irradiating

the crystals with our one curie Pu-Be neutron source.

Fig. 1 shows measurements done on our crystal #54[(a)] using the NaI-I_2 electrode and light of 4360A before and after irradiation with neutrons. The curve showing log i vs log v after irradiation is incomplete because at that time our measuring instrument was a Cary 31 vibrating reed electrometer which was not capable of measuring the high currents obtained. In addition to the Cary Electrometer we now have a Keithley Electrometer Model 600A which allows us to read currents as high as one ampere. Fig. 2 shows measurements done on our crystal #143 before and after irradiation in which the values of i after irradiation were measured with the Keithley Electrometer. Figs. 3, 4, 5, show measurements done on our crystals #S-4, #A-2(H), and #SH-1 using the NaI-I_2 electrode and a 4360A light source. Crystals #54 and #143 were grown using the Kallmann-Pope technique. Crystal #S-4 was grown using our modified Kallmann-Pope technique. Crystal #A-2(H) was cleaved and polished from a Harshaw unselected crystal and crystal #SH-1 is a selected and polished Harshaw crystal of 0.3 mm thickness.

Fig. 6 shows measurements done on crystal #HC-1 using the Na_2SO_4-Na_2SO_4 electrode and light of 3650A before and after irradiation.

(a) The same measurements are shown in Fig. 6 of our Progress Summary Report No. 1.

SECTION III. DISCUSSION OF RADIATION DAMAGE RESULTS

The relevant experimental results are, firstly, that neutron irradiation produces a significant increase in the conductivity of thin crystals (10-50 μ) when measured by means of the NaI-I_2 electrode and a 4360A light source but not so when measured by means of the Na_2SO_4 electrodes and a 3650A light source, secondly, that the exalted conductivity decreases gradually to normal preirradiation levels, and thirdly, that neutron irradiation does not appear to induce exalted conductivity in thick crystals (0.3 mm) even when the measurements are carried out by means of the iodine electrode.

These results seem to indicate that the exalted conductivity depends on a surface phenomenon that involves an anthracene species "activated" by the neutron irradiation and an "activated" iodine species produced by the 4360A light source. The difference between "thin" and "thick" crystals can be explained in that little of the 4360A light reaches the face of the crystal exposed to the iodine solution in the case of the "thick" crystal. Since anthracene per se is rather transparent to 4360A light, it is probable that scattering rather than absorption of light is responsible for such difference.

In the preceding report it was suggested that the effect of fast neutrons may well be a dislocation of a proton from anthracene, and the formation of transient anthracene carbanions and anthracene-proton complexes. The following is a calculation of the increase in

the photocurrent that may be expected to be produced under our conditions of neutron irradiation and measurements by means of the iodine electrode.*

We estimate that after exposing a crystal to our neutron source for approximately 70 hours the crystal receives a dose of the order of 3×10^9 n/cm^2. Considering the cross section of hydrogen for neutrons of intermediate energy and considering the spatial distribution of the anthracene molecules in the anthracene crystal we estimate that approximately 10^4 dislocations per cm^2 were produced at the crystal surface after a 70 hour period of irradiation. Now, we shall consider the magnitude of the process that is assumed to take place between the "excited" iodine molecules and the "excited" anthracene species. In a 1 M solution of iodine there are 6.03×10^{23} molecules/liter or 6×10^{20} iodine molecules per cm^3. Rounding off the latter figure to 10^{21}, it permits to estimate that there are 10^{14} iodine molecules/cm^2 at the surface of the anthracene crystal in contact with the 1 M iodine solution. If the frequency of collisions between iodine and the anthracene crystals face is assumed to be 10^{12}/sec, then the number of collisions will be 10^{14}/cm^2 x 10^{12}/sec or 10^{26} collision/sec cm^2. A similar calculation following the procedure of Moelwyn-Hughes[9] gives the number of 10^{25} collisions/sec cm^2 and the latter figure will be employed in the calculations which follows. If we assume that the cross section of capture of iodine by an "excited" anthracene is 10^{-15} cm^2, then there is an area of $10^4 \times 10^{-15}$ or 10^{-11} cm^2 of "excited" anthracene at the surface, and the number of successful collisions between

*We gratefully acknowledge the aid of Professor Martin Pope (Physics Dept., New York University) in developing this numerical estimate.

iodine and "excited" anthracene is given by 10^{-11} cm^2 (capture area) x 10^{25} collissions/sec cm^2 or 10^{14} collisions/sec. Should each such collision produce an additional carrier then the resulting current would be 10^{14} x 1.6 x 10^{-19} coulombs/sec cm^2 = 1.6 x 10^{-5} amps/cm^2. In a crystal of 0.1 cm^2 surface this results in a current of 1.6 x 10^{-6} amps. This indeed is the magnitude of the "exalted" current which is indeed observed.

The effect of photoactivation on the iodine - "excited" anthracene interaction can be visualized in terms of an increase in the probability of interaction by the "excited" iodine. We must first calculate (see below) the distance from the crystal in the iodine solution which will permit an "excited" iodine to diffuse to the crystal surface during the transit time of the carrier in the bulk of the crystal. The use of the equation $D = \frac{\mu kT}{e} \simeq \frac{\mu}{40}$, and letting $\mu \simeq 10^{-3}$ cm^2/sec volt gives the diffusion constant $D = \frac{10^{-3}}{40}$ cm^2/sec. The value of the jump length $\ell = \sqrt{D\tau}$ where τ is the jump time. From this equation and from the value of the velocity of the iodine molecule one can calculate the value of the jump length and the jump time. The jump length is estimated to be 10^{-8} cm and the jump time 10^{-11} sec. We now estimate the transit time of a carrier in a 10 micron thick anthracene crystal when we apply a voltage of 30 volts to be $t = \frac{d^2}{\mu V} = \frac{10^{-2}}{1 \times 30}$ = 3 x 10^{-8} sec. Therefore in the interval of 10^{-8} sec an iodine molecule with a jump time of 10^{-11} sec produces 10^3 jumps. If we place a given iodine molecule at 10^{-6} cm from the surface. it will probably hit the surface at least once during an

interval of time equal to the transit time. This then, 10^{-6} cm, is the distance in the solution which is taken for the calculation of the number of "excited" iodine molecules which are produced by the absorption of light. With a molar extinction coefficient of 10^5 for 1 M iodine,

$$\epsilon \times c \times l = \ln \frac{I}{I_o} = 10^5 \times 1 \times 10^{-6} = 10^{-1}$$

and

$$I/I_o = e^{-0.1} = 0.9$$

Thus 10% of the light is absorbed, and with a light intensity of 10^{14} quanta/cm^2/sec there will be 10^{13} "excited" iodine molecules that can interact with the "excited" anthracene molecules at the surface of the crystal. We conclude, therefore, that there is ample reason why 4360A light increases the interaction between "excited" iodine and anthracene molecules and thus enhances the current.

It now remains to suggest the nature of the interaction between the "excited" species. As mentioned above, it is probable that neutrons produce anthracene carbanions and anthracene-proton complexes. The 4360A light is absorbed by iodine and most likely produces dissociation of the latter into iodine atoms. These iodine atoms can be thought to diffuse to the crystal surface (their diffusion rate will be even greater than that of the iodine molecules) and there we can visualize the occurrence of the process of electron transfer which produces iodide ions and anthracyl radicals,

$$I\cdot + A{:}^{(-)} \longrightarrow I{:}^{(-)} + A^{\cdot}$$

This process represents a hole injection mechanism which is more favorable than that which probably occurs in the dark,

$$I_2 + A:^{(-)} \longrightarrow I_2\cdot^{(-)} + A\cdot$$

or which occurs when the anthracene has not been exposed to neutrons,

$$I_2 + A:H \longrightarrow I_2\cdot^{(-)} + (A.H)^{(+)}$$
(process in the dark)

$$I\cdot + A:H \longrightarrow I:^{(-)} + (A.H)^{(+)}$$
(process under illumination)

In the anthracene crystals containing dislocated protons, thermal activation will eventually cause the return of the protons to the anthracyl carbanions: $(HA:H)^{(+)} + A:^{(-)} \longrightarrow A:H + A:H$ and this explains the gradual loss of the enhancement in the saturation current.

An alternate explanation of the effect of the 4360A light source does not involve the formation of iodine atoms but revolves around the activation of a charge-transfer-complex at the crystal surface. The anthracene-iodine complex absorbs light in that range[10] and it can be assumed that a similar absorption will be given by the charge-transfer-complex produced from an anthracene carbanion and iodine. Both kinds of charge-transfer-complexes $\left(I_2 \cdots A:H\right)$ and $\left(I_2 \cdots A:^{(-)}\right)$ will be promoted by the absorption of light to the polar species $\left(I_2\cdot^{(-)} \cdots A.H)^{(+)}\right)$ and $\left(I_2\cdot^{(-)} \cdots A.\right)$, respectively, and the polar species then initiate a chain of electron transfer within the anthracene crystal.

SECTION IV. EQUIPMENT

In order to purify larger amounts of anthracene in connection with the growing of single crystals from the melt we have built a vacuum system to repurify the anthracene we obtain from commercial sources. Besides, we have purchased a Fisher Scientific zone refiner to further purify the anthracene after purification by sublimation in our vacuum system. We have also built an oven to grow anthracene crystals from the melt. Figs. 7 and 8 show our vacuum system, and zone refiner and oven, respectively, which have been assembled in the laboratory.

We have also built the optical and electronic equipment necessary to do steady voltage-light pulse transient photoconductivity measurements (Fig. 9) and other optical and electronic equipment necessary to do steady light-voltage pulse transient photoconductivity measurements. (Fig. 10).

The equipment for steady voltage-light pulse equipment has already been tested and is ready to be used for transient photoconductivity measurements. The steady light-voltage pulse equipment is being tested at present and should be ready for use in the near future. Figs. 11. 12 and 13 show pictures taken with an oscilloscope camera using our steady voltage-light pulse equipment.

BIBLIOGRAPHY

(1) Lampert, M.A., Rose, A., and Smith, R.W.: J. Phys. Chem. Solids 8, 464 (1959)

(2) Kommandeur, J.: Ph. D. Thesis, University of Amsterdam (1958)

(3) Kommandeur, J., and Schneider, W.A.: J. Chem. Phys. 28, 590 (1958

(4) Kallmann, H. and Pope, M.: J. Chem. Phys. 32, 300 (1960)

(5) Mark, P., and Helfrich, W.: J. Appl. Phys. 33, 205 (1962)

(6) Many, A. and Rakavy, A.: Phys. Rev. 126, 1980 (1962)

(7) Kallmann, H., and Pope, M.: Rev. Sci. Inst. 29, 993 (1958)

(8) Kallmann, H. and Pope, M.: Rev. Sci. Inst. 30, 44 (1959)

(9) Moelwyn-Hughes, E.A.: Phys. Chemistry, 2d. ed., Pergamon Press, New York, 45, (1961)

(10) Peters, J. and Person, W.B.: Am. Chem. Soc. 86, 10 (1964)

FIGURE 1

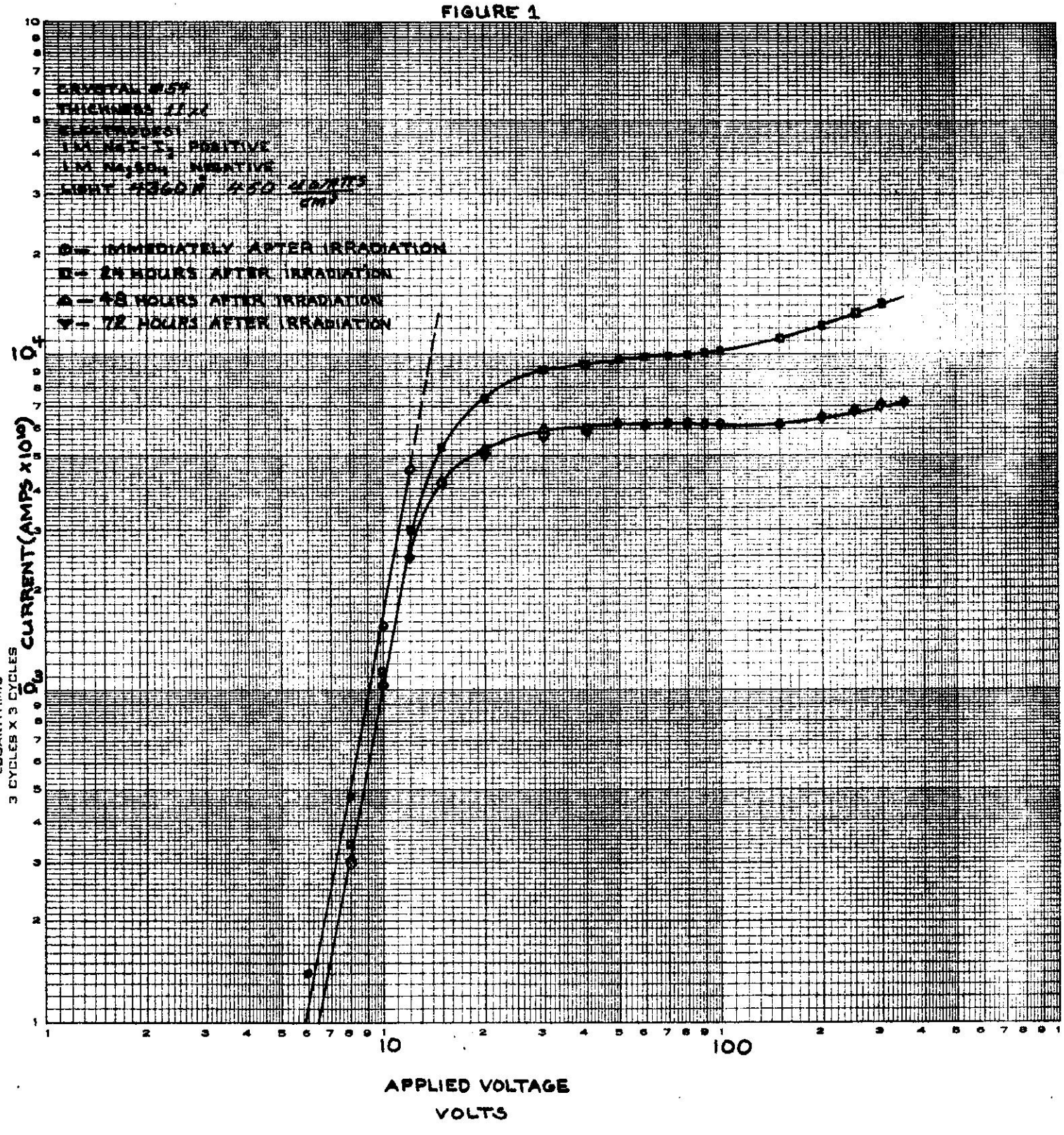


FIGURE 2

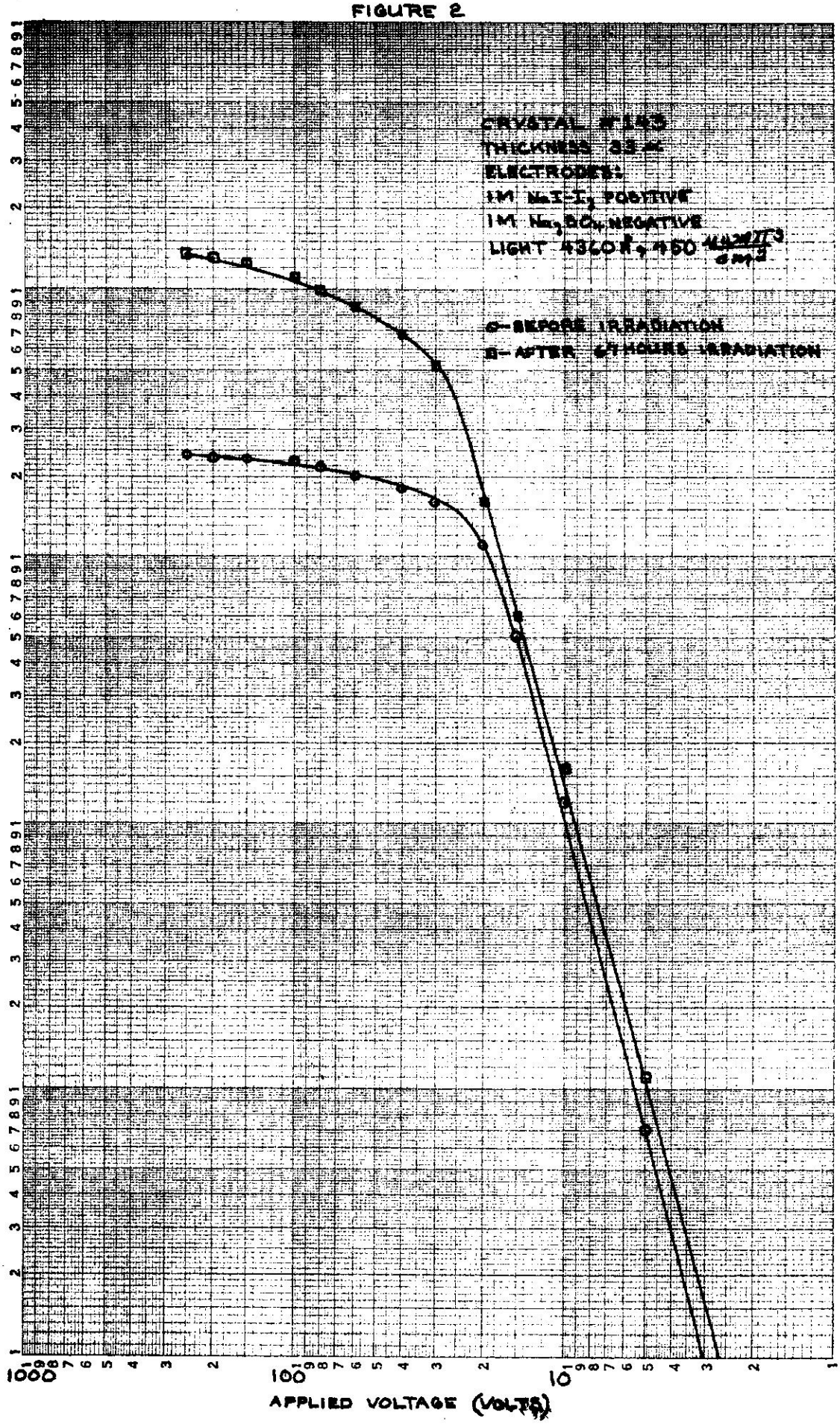


FIGURE 3

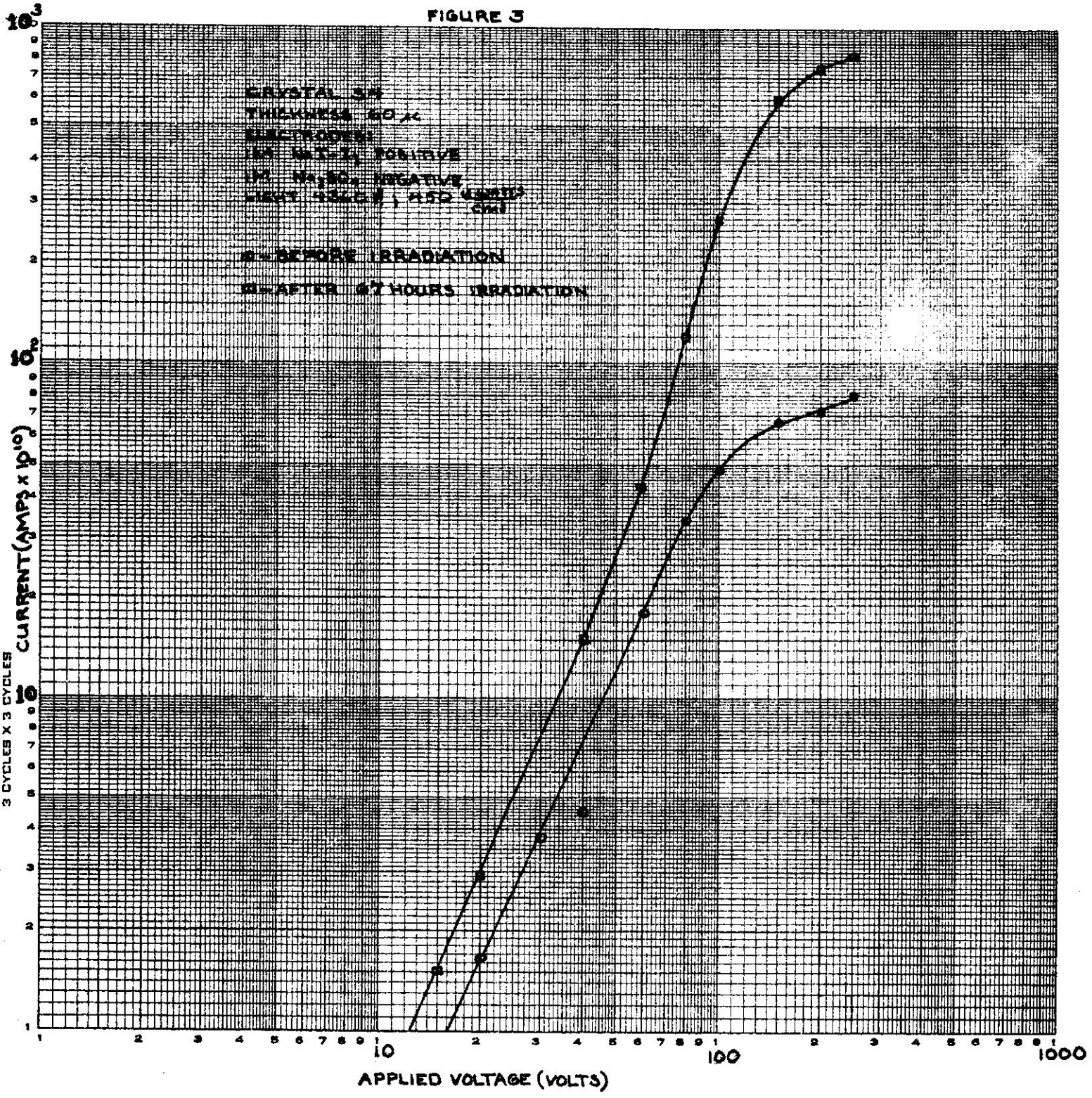

CRYSTAL 3/4
THICKNESS 60 μ
ELECTRODES:
1ST $Na_2S_2O_4$ POSITIVE
2ND Na_2SO_4 NEGATIVE
LIGHT 436 mμ ; 450 microwatts/cm²
○ = BEFORE IRRADIATION
● = AFTER 67 HOURS IRRADIATION
CURRENT (AMPS x 10^{10})
LOGARITHMIC
3 CYCLES X 3 CYCLES
APPLIED VOLTAGE (VOLTS)
10
100
1000

FIGURE 4

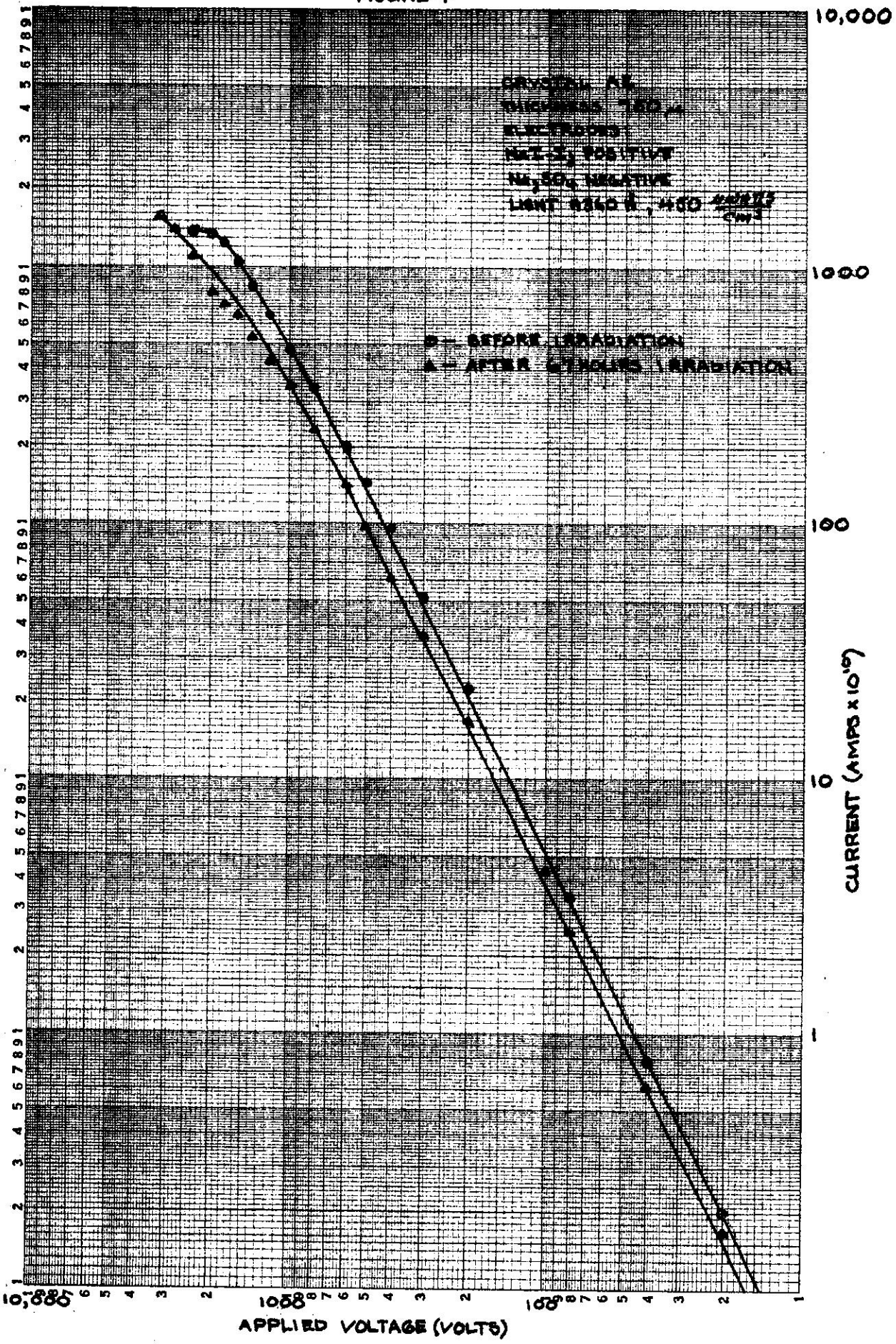
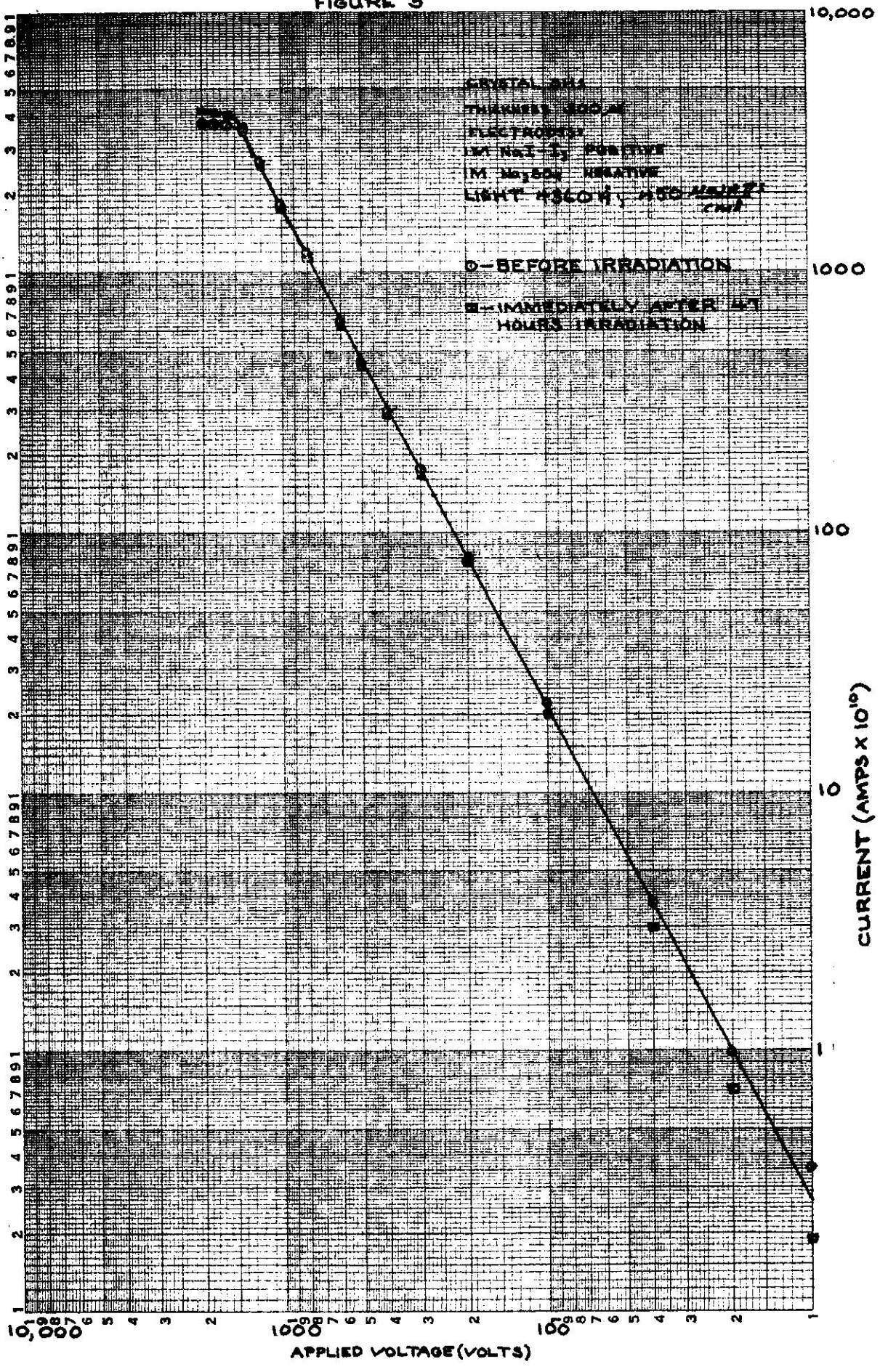

10,000
1000
100
10
1
CURRENT (AMPS x 10⁻⁹)
APPLIED VOLTAGE (VOLTS)
10,000
1000
100
LOGARITHMIC
3 CYCLES X 5 CYCLES

FIGURE 5



EUGENE DIETZGEN CO.
MADE IN U. S. A.

NO. 340-L35 DIETZGEN GRAPH PAPER
LOGARITHMIC
3 CYCLES X 5 CYCLES

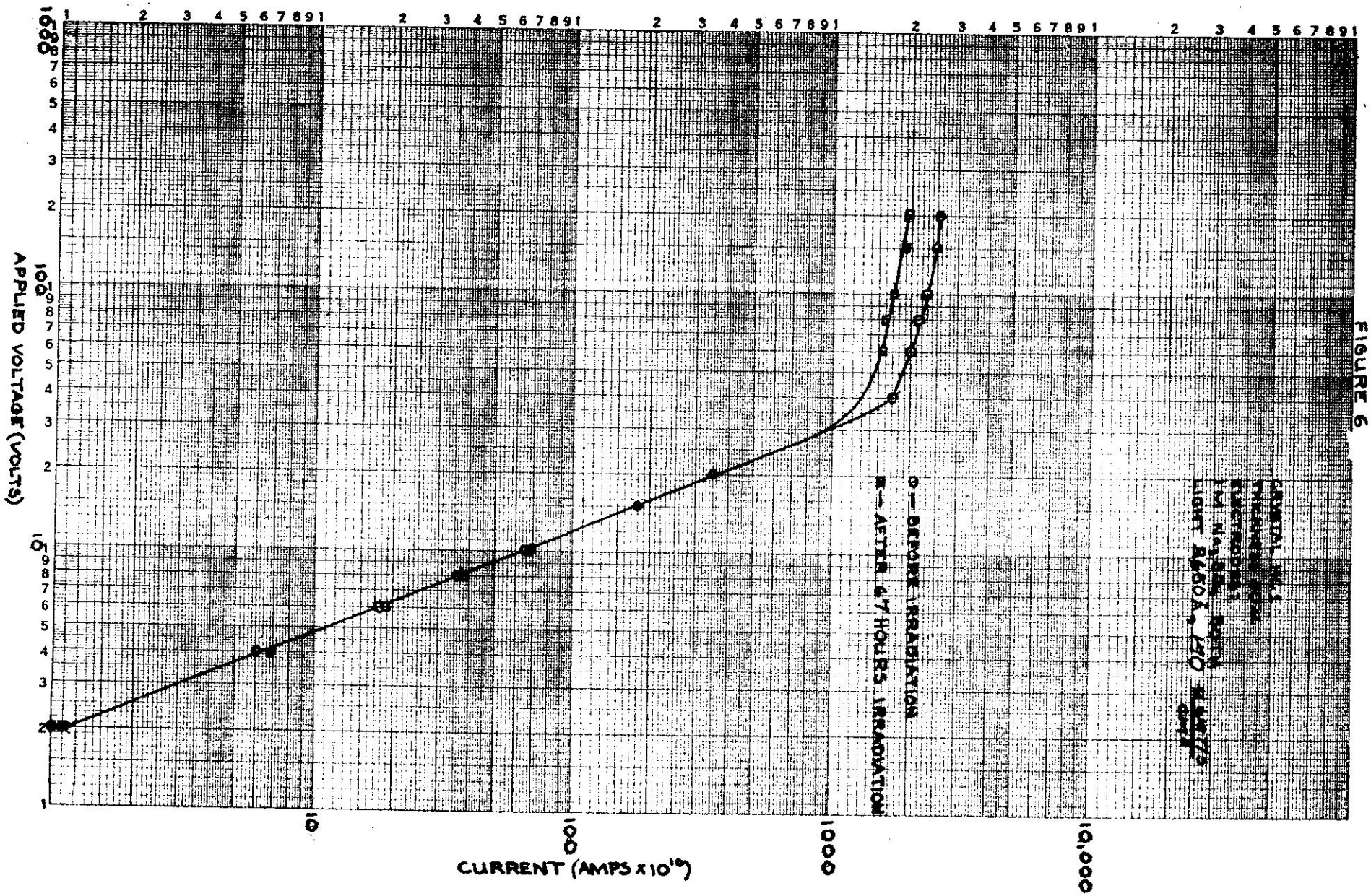


FIGURE 6

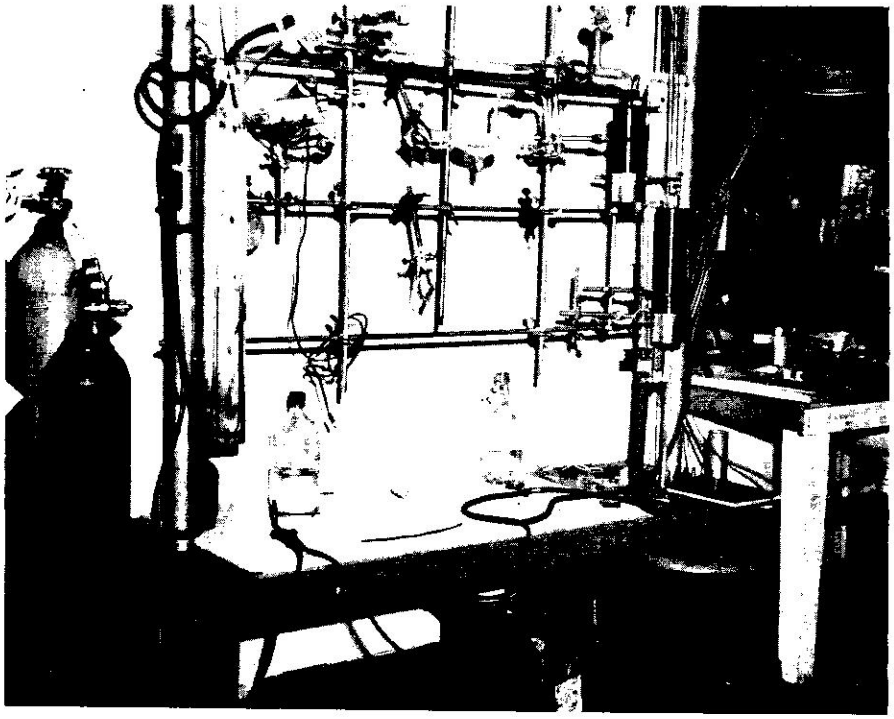


FIG. 7 VACUUM SYSTEM

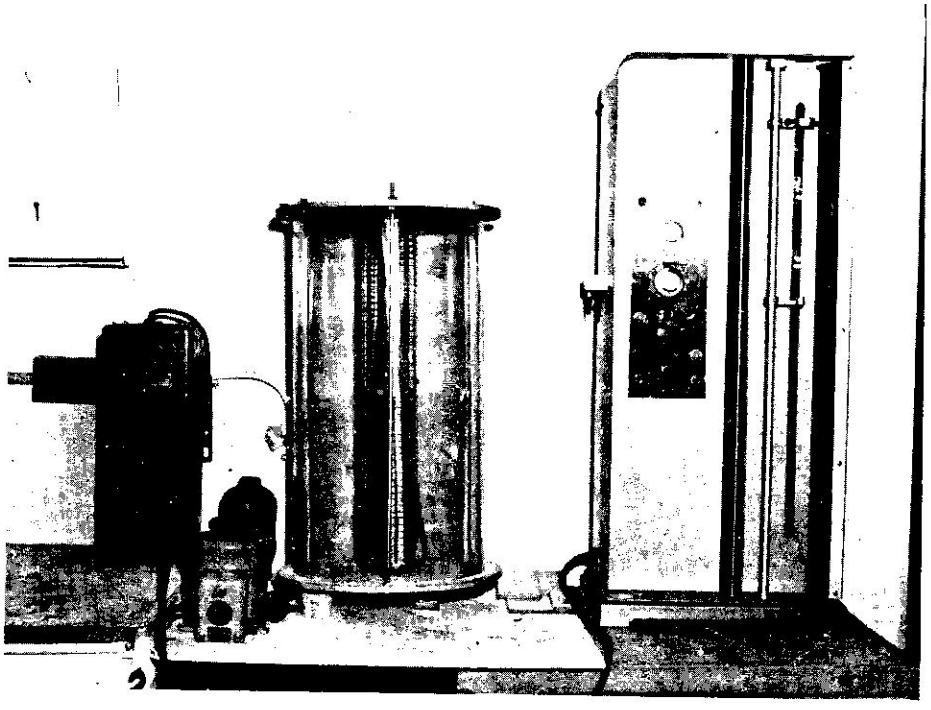


FIG. 8 ZONE REFINER AND OVEN

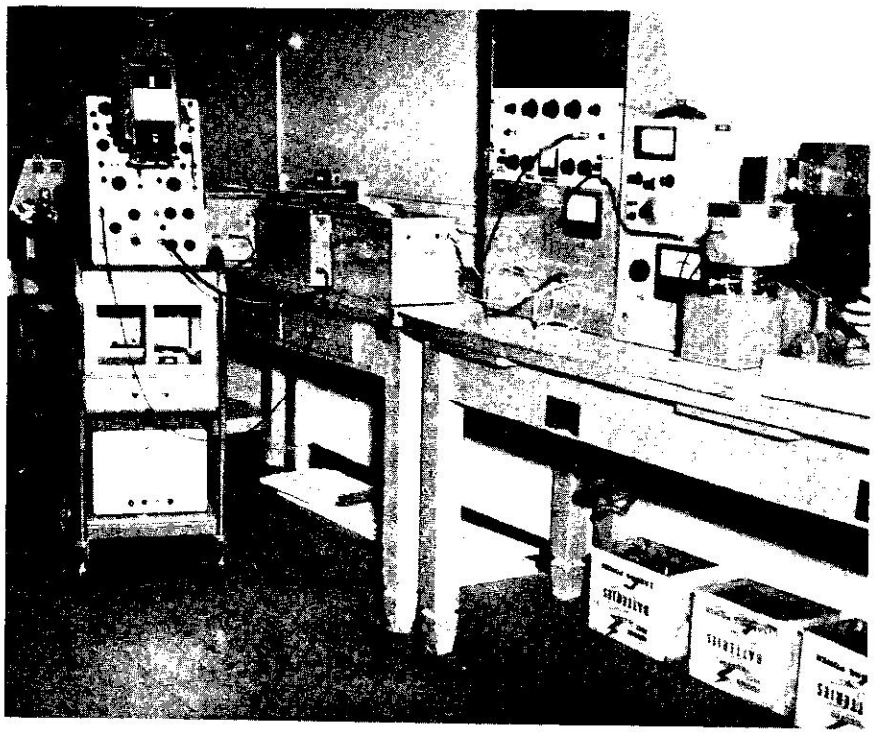


FIG. 9 EQUIPMENT TO DO STEADY VOLTAGE- LIGHT PULSE MEASUREMENTS

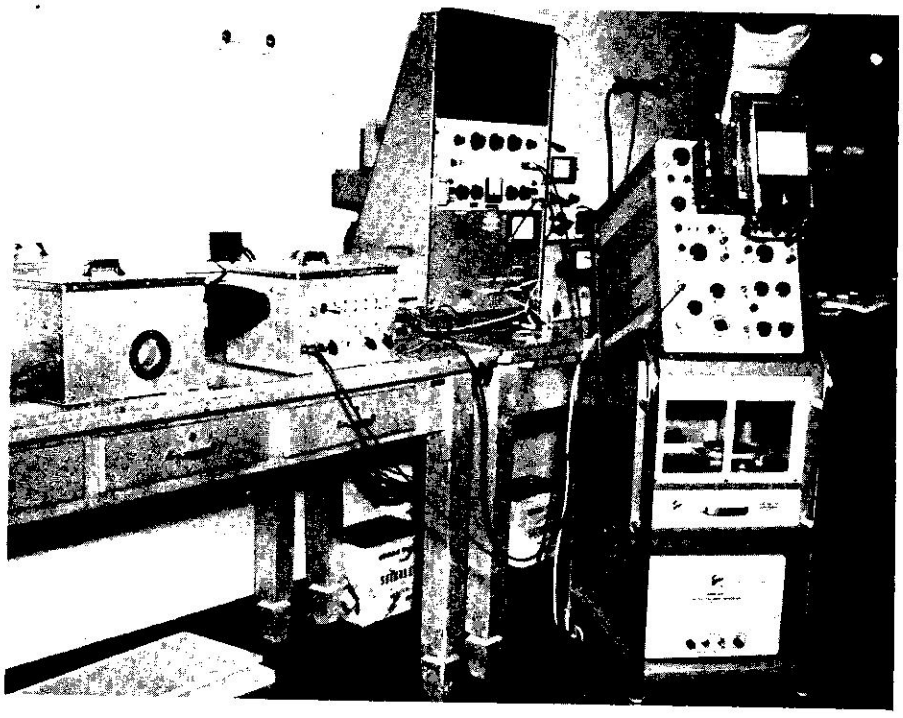


FIG. 10 EQUIPMENT TO DO STEADY LIGHT-VOLTAGE PULSE MEASUREMENTS

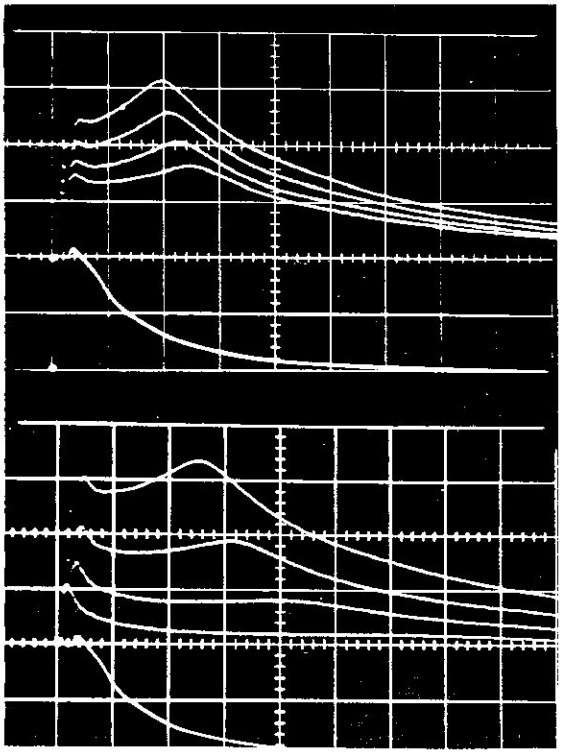


FIG. 11

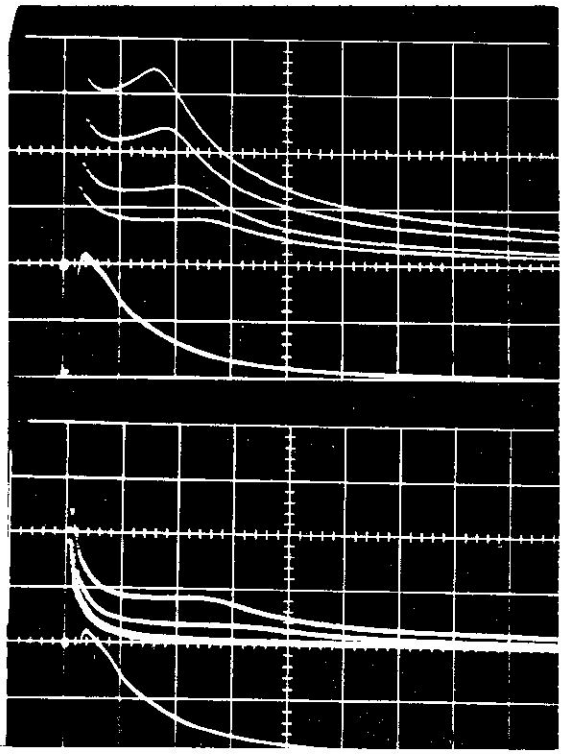


FIG. 12

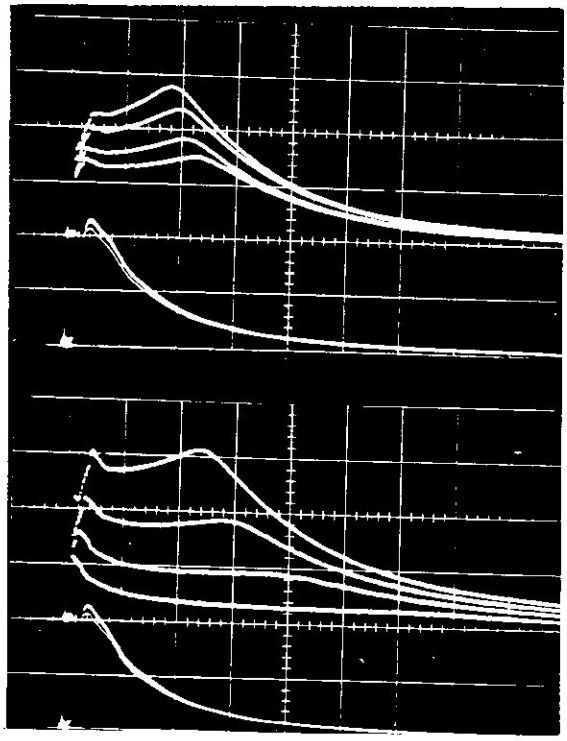


FIG. 13