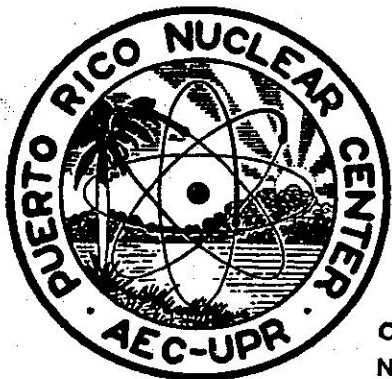# PUERTO RICO NUCLEAR CENTER

SOLID STATE PHYSICS PROGRAM

RADIATION DAMAGE IN ORGANIC CRYSTALS

Progress Summary Report No. 1

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

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Progress Report # 1

July 1963

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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.

The initial phase of this work consists in the study of 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). It should, therefore, become possible to detect quantitatively radiation damage at levels far lower than those that can be observed by other chemical or physical techniques. 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 and its preparation in single crystal form is relatively simple (2).

The effect of neutron irradiation on anthracene has been studied previously by Kommandeur (3,4), but to our best 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 (5), and the application of space-charge-limited current theory to organic crystals (6,7).

Below is a summary of the results obtained during the first six months of operation (January-June 1963) of this project.

SECTION I. RESULTS OF PRELIMINARY WORK AND DISCUSSION

Using the Kallmann-Pope technique (2), we have grown single crystals of anthracene using Eastman-Kodak anthracene X-480 and H-480. They range in thickness from 10 to 70μ and from 0.3 to over 1 cm^2 in area. These crystals were obtained from ethylene chloride and xylene as received from the supplier (Eastman) and also after redistillation in an all glass apparatus. No significant differences have been found between crystals grown using the solvents as received and after they were redistilled.

Kallmann-Pope cells (8), are now available commercially* and three of these cells have been purchased. We have found these cells very convenient to use because of the ease with which the electrolyte electrodes can be removed and reestablished without introducing any noticeable change in the system. Using these cells, an Osram HBO 100 watt lamp, several

*Cordair Co., 2 Clover Lane, R.D. 2, Dovern, New Jersey.

Corning filters and a Cary 31 vibrating reed electrometer, a few of the results reported in the literature have been confirmed. This part of our work has enabled us to test our equipment and to familiarize ourselves with the subtleties of the techniques.

Dark conductivity measurements, using 1M NaCl in both sections of the Kallmann-Pope cell, have shown that the electrodes are completely symmetrical, that is, the current flowing when one given side was at a positive potential (i+) was equal to the current flowing when that same side was at a negative potential (i-). These results are shown in Table I.

TABLE I.

SYMMETRY OF CONTACTS (Dark Current)

Applied Voltage (volts)	$i^+ \times 10^{13}$ amp	$i^- \times 10^{13}$ amp
2	8.0	8.0
10	32.0	32.0
50	160.0	160.0
100	300.0	300.0
130	400.0	400.0

We also found that the current-voltage relation (in the dark) was ohmic up to 100,000 volts/cm and that the resistivity of anthracene is of the order of 10^{14} ohm cm. The results are identical to those obtained by Pope and Kallmann (9). (See Fig. 1).

As was found by all other investigators (9,10), we observed that the photocurrent flowing when the illuminated face of the crystal was at a positive potential (i^+) was larger than when the illuminated side was negative (i^-). To observe these photocurrents we used 1M NaCl in both cell compartments and the light source of 3650 A. The results are plotted in Fig. 2 and the observed asymmetry is generally considered to be a consequence of the predominance of positive charge carriers, i.e. holes in anthracene. This is another confirmation of Pope and Kallmann's results (9).

Measurements with other electrode systems, such as 1M NaI saturated with iodine, were made and the ratio i^+/i^- was found to change drastically, as may be noted when comparing Tables II and III.

TABLE II.

HOLE INJECTION INTO ANTHRACENE

Applied Voltage (volts)	3650A Photocurrent (no iodine)		
	$i^+ \times 10^{10}$ amp	$i^- \times 10^{10}$ amp	i^+/i^-
2	100	2.9	3.4
10	2050	8.0	256
20	3200	11.0	291
50	3300	19.0	174
200	3500	60.0	75.0

i^+ and i^- refer to currents measured when the polarity of the side thru which the 3650A light entered was positive and negative respectively.

Intensity of 3650A light: 170 μ watt/cm^2

TABLE III

HOLE INJECTION INTO ANTHRACENE

:Applied :Voltage :(volts) :	: : : :	4360A Photocurrent (iodine electrode)			
:	: $i^+ \times 10^{10}$ amp	:	$i^- \times 10^{10}$ amp :	: i^+/i^- :	
: 2	: 0.33	:	0.07	: 4.71 :	
: 10	: 24.0	:	0.10	: 240 :	
: 20	: 105	:	0.18	: 583 :	
: 50	: 500	:	0.41	: 1220 :	
: 200	: 2700	:	2.0	: 1350 :	

i^+ and i^- refer to currents measured when the polarity of the face of the crystal in contact with the iodine was made positive and negative, respectively.

Intensity of 4360A light: $450\,\mu$ watt/cm^2

Kallmann and Pope (5) were the first investigators to observe the role played by iodine and to propose a mechanism by which iodine extracts an electron from anthracene, thus injecting a positive hole into the crystal. These results were discussed quantitatively by Kallmann and Pope (11) and also by Mark and Helfrich (6). The latter investigators believe that the free holes injected into the anthracene crystal can act as a virtual anode when the injecting contact is biased positive and the space-charge-limited hole currents follow. If this is so, then the currents observed by us using the iodine electrode are space-charge-limited. Fig. 3 shows the steady-state current-voltage characteristic of anthracene observed in our laboratory. It differs slightly from the one published by Mark and Helfrich (6) who used anthracene doped with traces of tetracene and a band of 3600-4000A.

On the other hand these same investigators report curves similar to ours in cases of pure hydrocarbons where the band employed to excite the electrode does not produce photocurrents in the crystals. The slight curvature observed by Mark and Helfrich and its absence in our work is attributed to the fact that our measurements were performed with 4360A light to which anthracene is practically transparent (10) and therefore free holes were being injected at the anode only, while Mark and Helfrich were generating free holes nonuniformly throughout the bulk of the crystal due to the light they used.

Fig. 3 shows that crystals grown from anthracene grades H-480 and X-480 gave similar results.

Before starting the study of radiation damage we checked the reproducibility of our experimental technique by removing the electrolyte electrodes after each measurement and replacing them just before the following measurement. The results shown in Fig. 4 demonstrate the reproducibility over a period of several days.

The effect of crystal thickness was also studied (Fig. 5) and the displacement in the curves of the different crystals follows the current-voltage response predicted by the theory of space-charge-limited currents as applied to organic crystals (6). The fact that crystals of different thicknesses give about the same saturation current seems to indicate that surface generation is the dominant mechanism of carrier formation.

SECTION II.   RADIATION DAMAGE MEASUREMENTS

In the initial stage of this investigation we are limiting the irradiation studies to the effects produced by neutrons from a 1 curie Pu-Be source delivering 1.5×10^6 n/sec. Using this neutron source, the anthracene crystals were irradiated with (a) fast neutrons only, and (b) with a mixture of fast and thermal neutrons. Returning to the results shown in Fig. 5 it can be seen that before irradiation different crystals produce the same slope of the straight line portion of the curve and that the value of the saturation current is also more or less the same. In accord with Mark and Helfrich's (6) theory, the value of this slope indicates a space-charge-limited current influenced by trapping. Furthermore, there is a relationship between the energy distribution of the traps and the slope of the curve, and between the concentration of the traps and the magnitude of the current.

Fig. 6 shows the behavior of the crystals after irradiation, and it is noted that the steep portion of the current remains unchanged but that the saturation level is very much increased. The increase was so large that the saturation current exceeded that capable of being measured by our instrument. This behavior was observed with crystals irradiated by placing them on top of the neutron source removed from the paraffin box which is normally used for radiation protection.

Crystals were also irradiated by placing them on top of the neutron source while it was inside the paraffin box.   Under these conditions the saturation current was also enhanced (Figs. 7A and 7B), but notably to a considerably smaller extent regardless of whether the

irradiation was carried out over a short or long period of time (compare Figs. 7A and 7B). Here too, the slope as well as the magnitude of the current in the steep portion of the curve were unaffected by irradiation.

Since the difference in the behavior of the crystals subjected to neutron radiation was thought to be due to a difference in the availability and action of fast and thermal neutrons under the two exprimental conditions, a shielding arrangement was devised by means of boral that exposed the crystals only to fast neutrons. This was done by enclosing both the neutron source and the crystals in a small boral box. Under these conditions the effect of the radiation was identical with that obtained when the crystals were exposed to the neutron source while the latter was outside the paraffin box (compare Figs. 7A, 7B and 8).

Fig. 9 shows that crystals irradiated with fast neutrons also give a saturation current. This result was obtained by employing a wire mesh in order to reduce the intensity of the light source and consequently bring the current level down to the range of our instrument.

Besides the apparently different effects of fast and thermal neutrons another noteworthy observation is the ability of the irradiated anthracene crystals to recover the normal electrical behavior with time. This behavior is shown in Figs. 6-9 where the conductivity of a given crystal is recorded at different intervals of time after exposure to neutrons.

SECTION III. DISCUSSION OF RADIATION DAMAGE RESULTS

Unlike the previous work (3,4) on the effect of neutrons upon the conductivity of anthracene crystals, our experiments employ low doses of radiation. This approach is chosen in order to be able to observe the gradual change in the radiation damage, and possibly differences in the radiation damage mechanisms, as the crystals are exposed to increasing doses of radiation. The results obtained so far indicate that doses of the order of 10^7 n produce measurable effects.

It is noteworthy that the only effect of neutron irradiation is to change the level of the saturation current of the anthracene crystals. The fact that the slope and the magnitude of the steep portion of the current-voltage curve are not affected by the radiation indicates the absence of a volume effect, i.e. there is no change in the number and the distribution of the traps. This behavior is not unexpected if one considers the low doses of radiation which were employed and the fact that a change in concentration of 10^8 traps/cm^3 escapes detection (12).

There remains the question of the change in the saturation current as a result in the radiation, and this is most probably a surface phenomenon.

If we assume that the main effect of the neutrons is to produce protons by elastic scattering with the many hydrogen atoms of the hydrocarbon, then we can visualize the ejected proton coming to rest as a protonated anthracene molecule (π-complex). At the same time the original collision should leave behind an anthracene anion. The resulting anion, by virtue of its low ionization potential, is expected to react more

readily with the iodine electrode than an ordinary anthracene molecule, and
in the process there are produced an iodide ion and the relatively stable
anthracyl radical. The latter upon combining with the dislodged proton
produces an electron-deficient anthracene species which is identical with
the hole that is obtained when nonirradiated anthracene crystals react with
iodine at the electrode contact. Thus, this mechanism suggests an explanation
for the increase in the currents that are observed with the crystals exposed
to fast neutrons, and it accounts for the absence of changes in the number
and energy distribution of traps, since, once the hole is formed, the
transport mechanism throughout the bulk of the crystal is unchanged.
Furthermore, the mechanism explains the recovery of the normal electrical
behavior induced either by thermal neutrons or by rest at room temperature
since either condition provides energy necessary to mobilize the dislodged
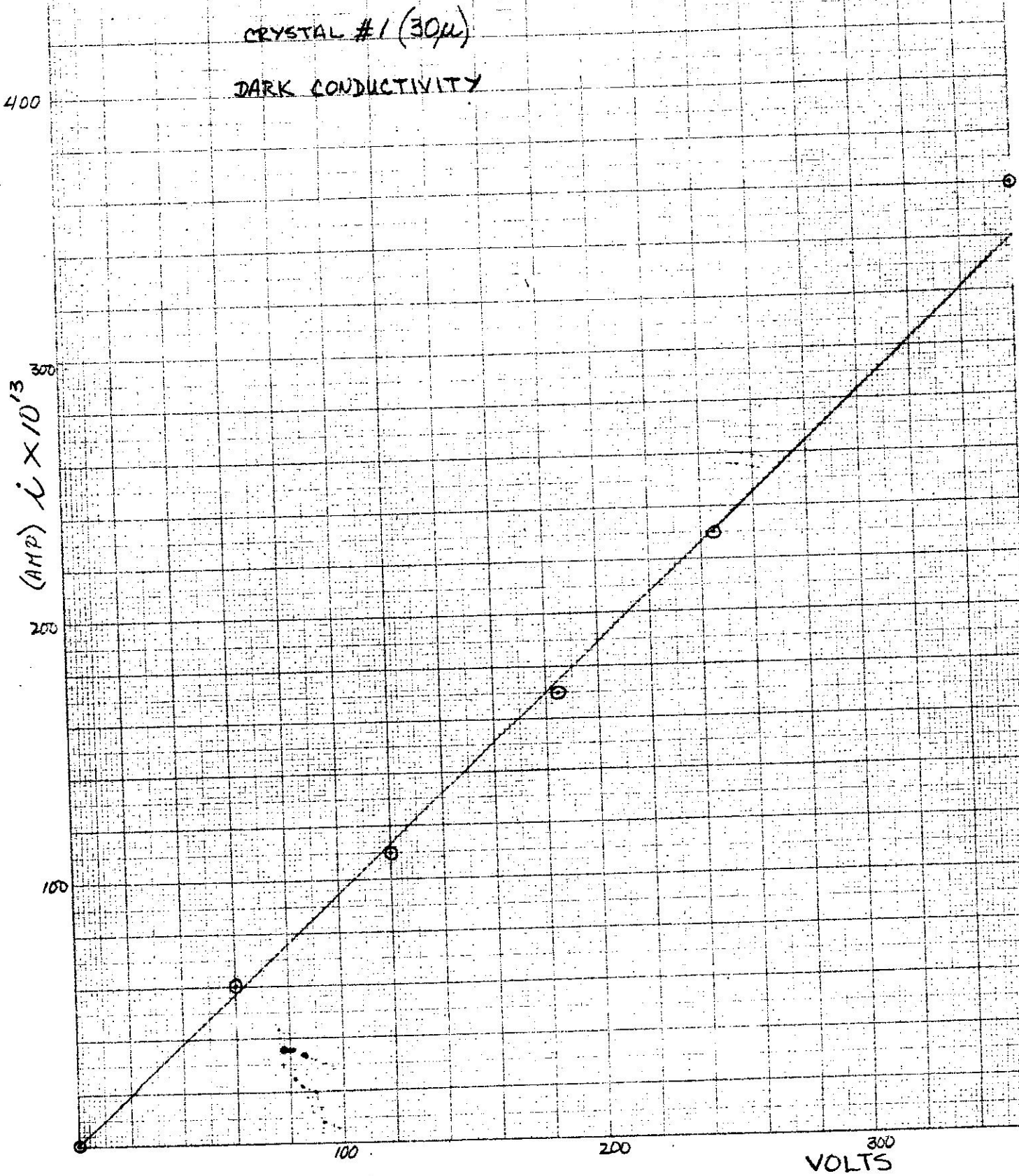proton for return to the anthracene anion.

Another possible mechanism for the enhancement of the saturation
current by fast neutrons invokes a dislocation of the surface molecules.
This amounts to an increase in the effective surface area and thus can
account for the greater number of holes that can be formed at the contact.
The recovery mechanism in this case simply involves the relocation of the
dislodged anthracene molecules to their equilibrium lattice positions with
the activation energy provided by thermal neutrons or invironmental temper-
ature.

Finally, it can be suggested that anthracene anions, produced in accord with the first mentioned mechanism, favor the formation of an iodine complex more so than normal anthracene molecules. This should be so because in the charge-transfer complex the anthracene species plays the role of an electron donor, and thus the presence of anthracene anions at the surface must enhance the hole injection process by favoring the diffusion of the iodine to the surface.

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FIG. 1

CRYSTAL #1 (30µ)

DARK CONDUCTIVITY

FIG. 2

CRYSTAL #3 (34μ)

3650 Å PHOTOCURRENT

INTENSITY : 170 μWATT/cm²

FIG. 3

VOLTS

30μ thick

FIG 4

(Sample #10 (30μ))

VOLTAGE OF I₂ WAS
SATURATED BEFORE EACH
MEASUREMENT
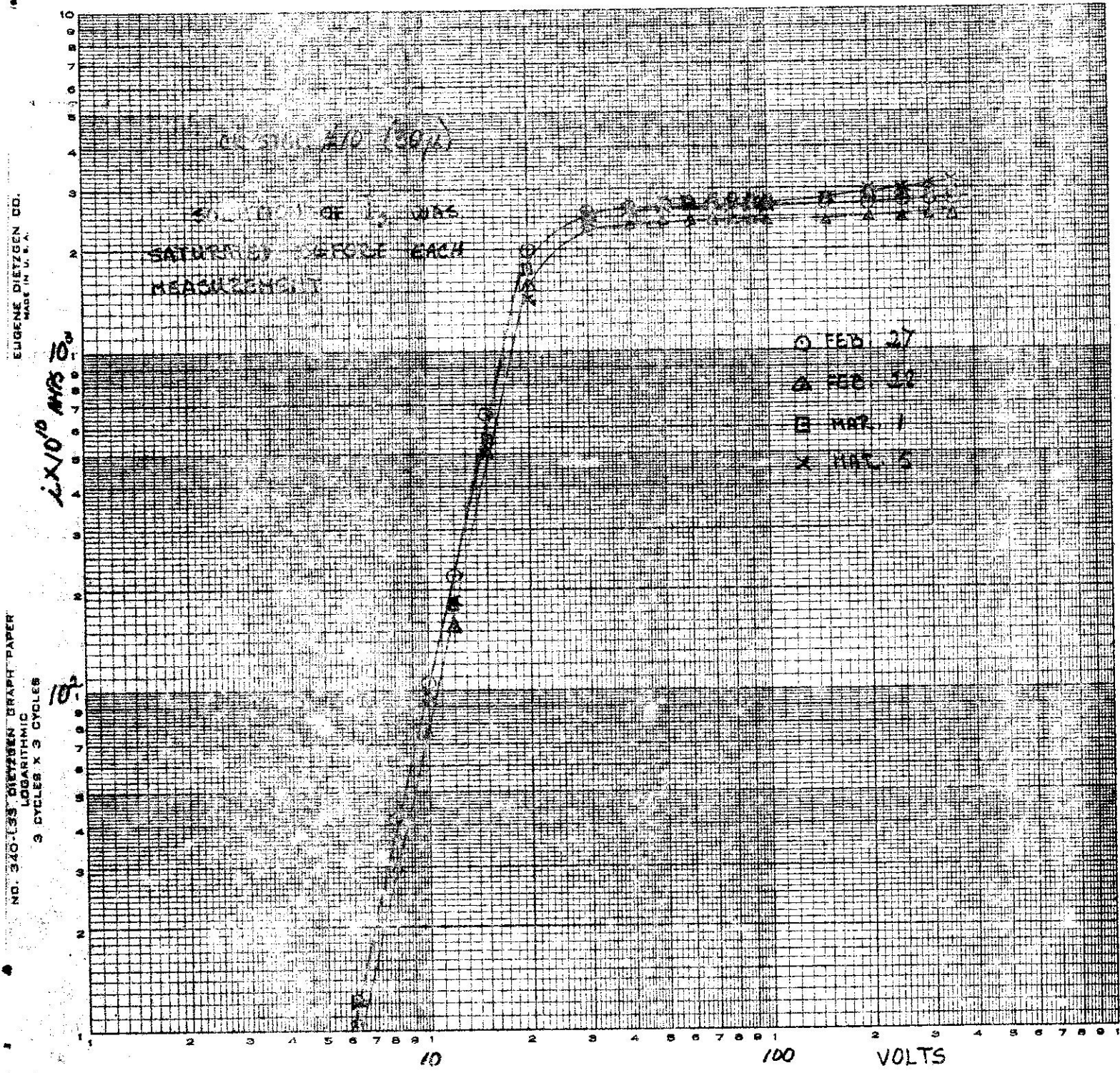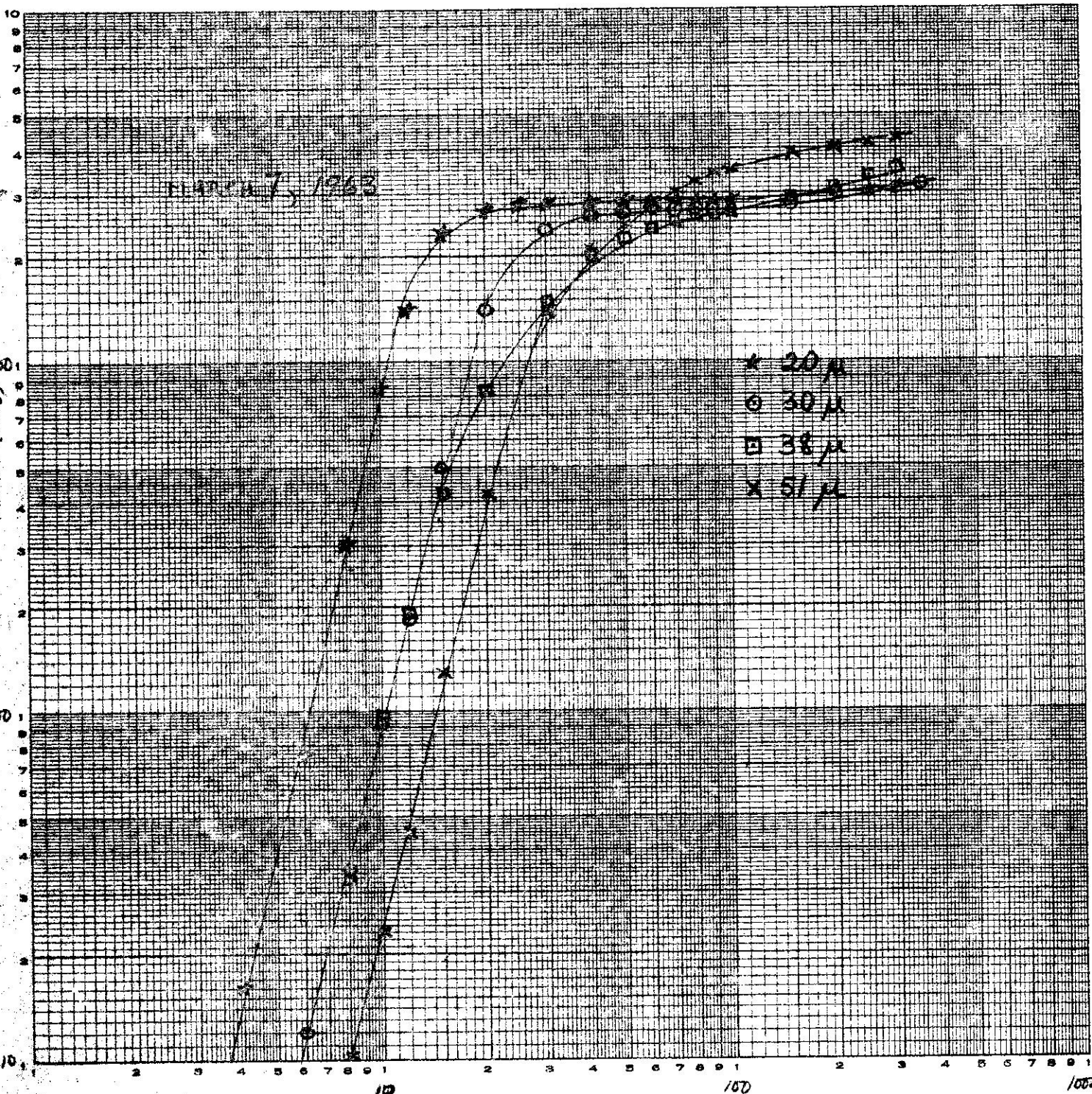
○ FEB. 27
△ FEB. 28
▢ MAR. 1
✕ MAR. 5

VOLTS

Fig 5

MARCH 4, 1963
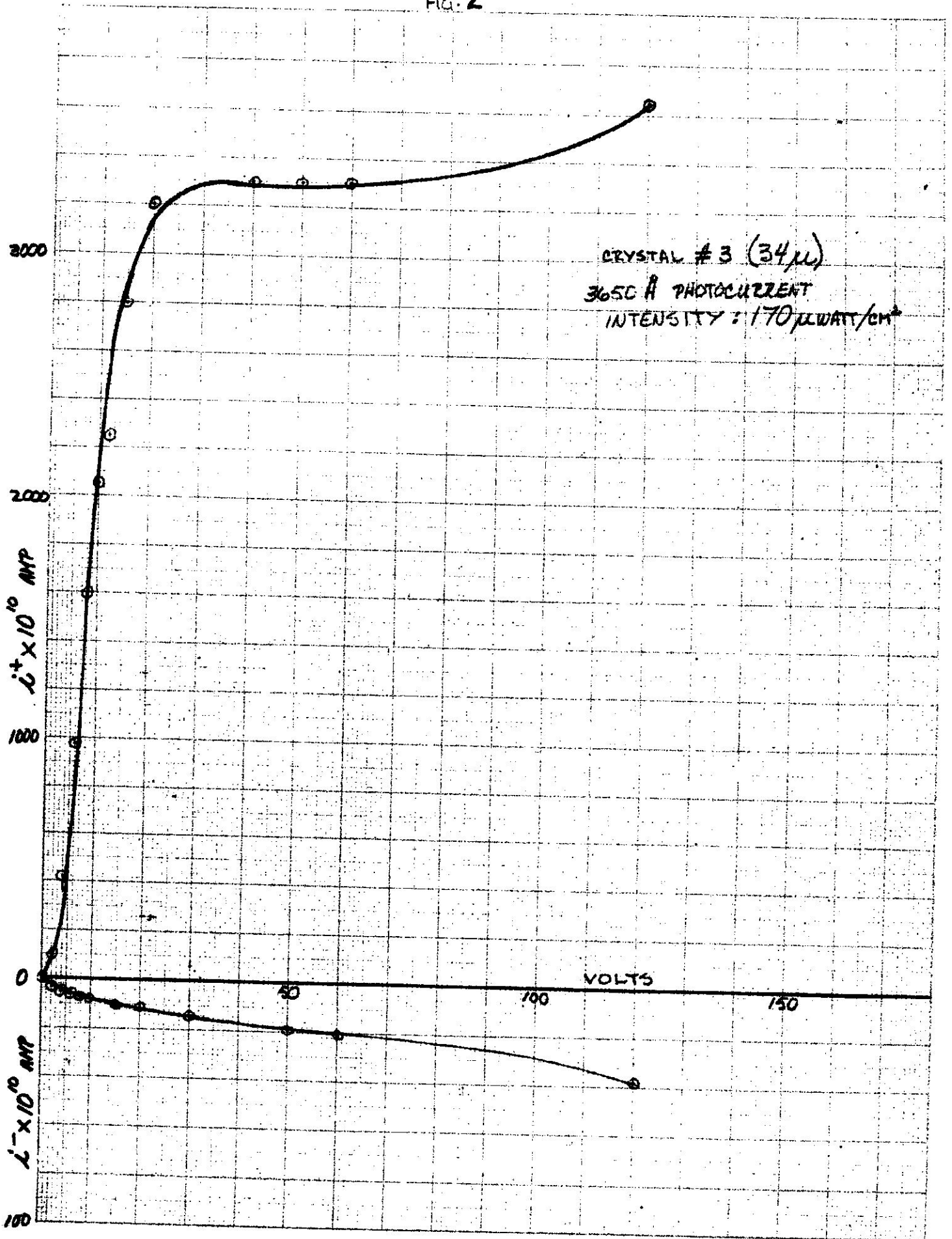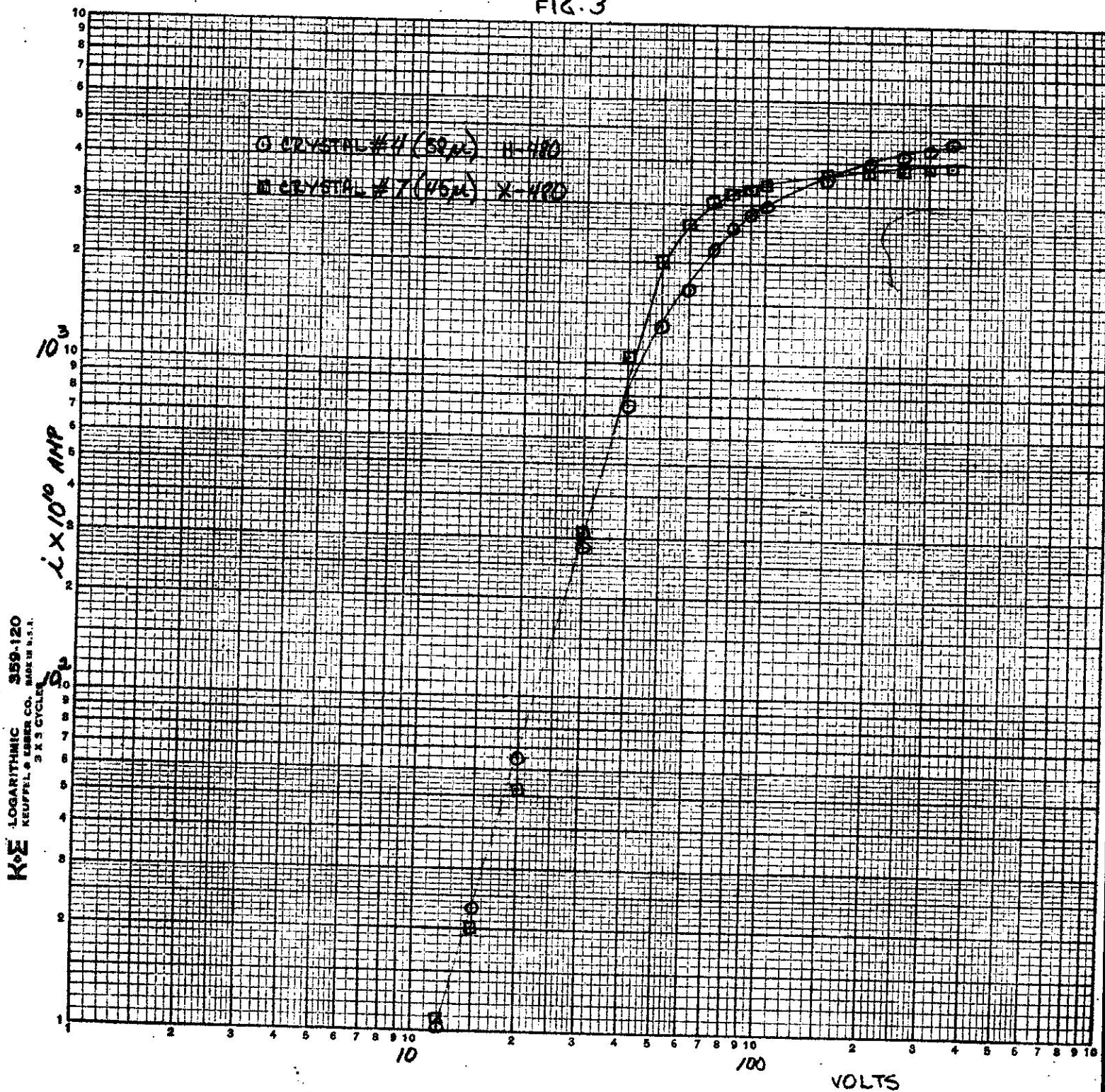
EUGENE DIETZGEN CO.
MADE IN U.S.A.

NO. 340-L33 DIETZGEN GRAPH PAPER
LOGARITHMIC
3 CYCLES X 3 CYCLES

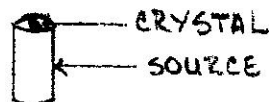$i \times 10^{10}$ (AMPS.)

* 20 μ
⊖ 30 μ
⊟ 38 μ
✕ 51 μ

VOLTS

FIG. 6

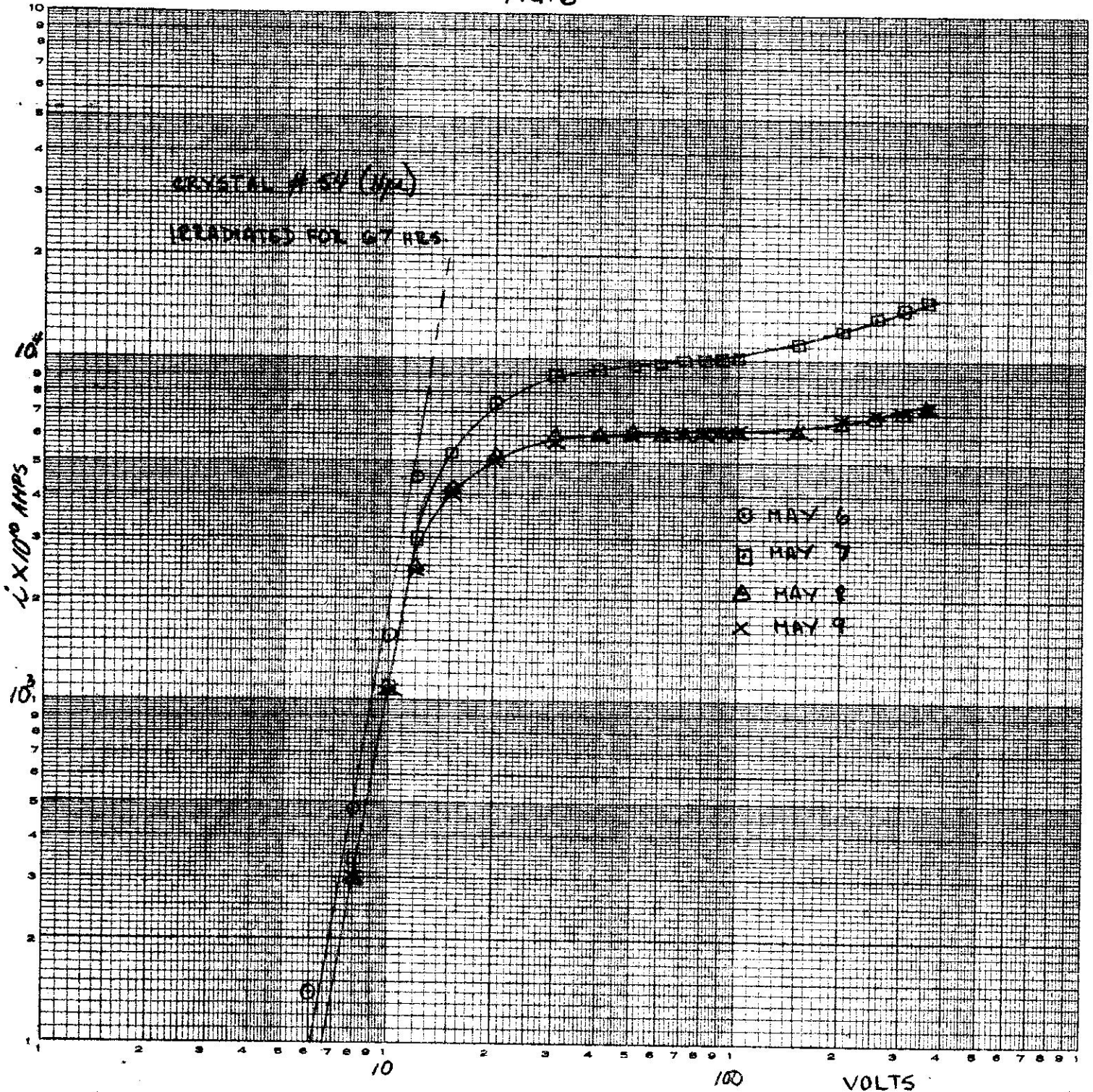crystal # 54 (11µ)
irradiated from May 3-2:00PM
to May 6-9:00 AM [FN] (nickel)
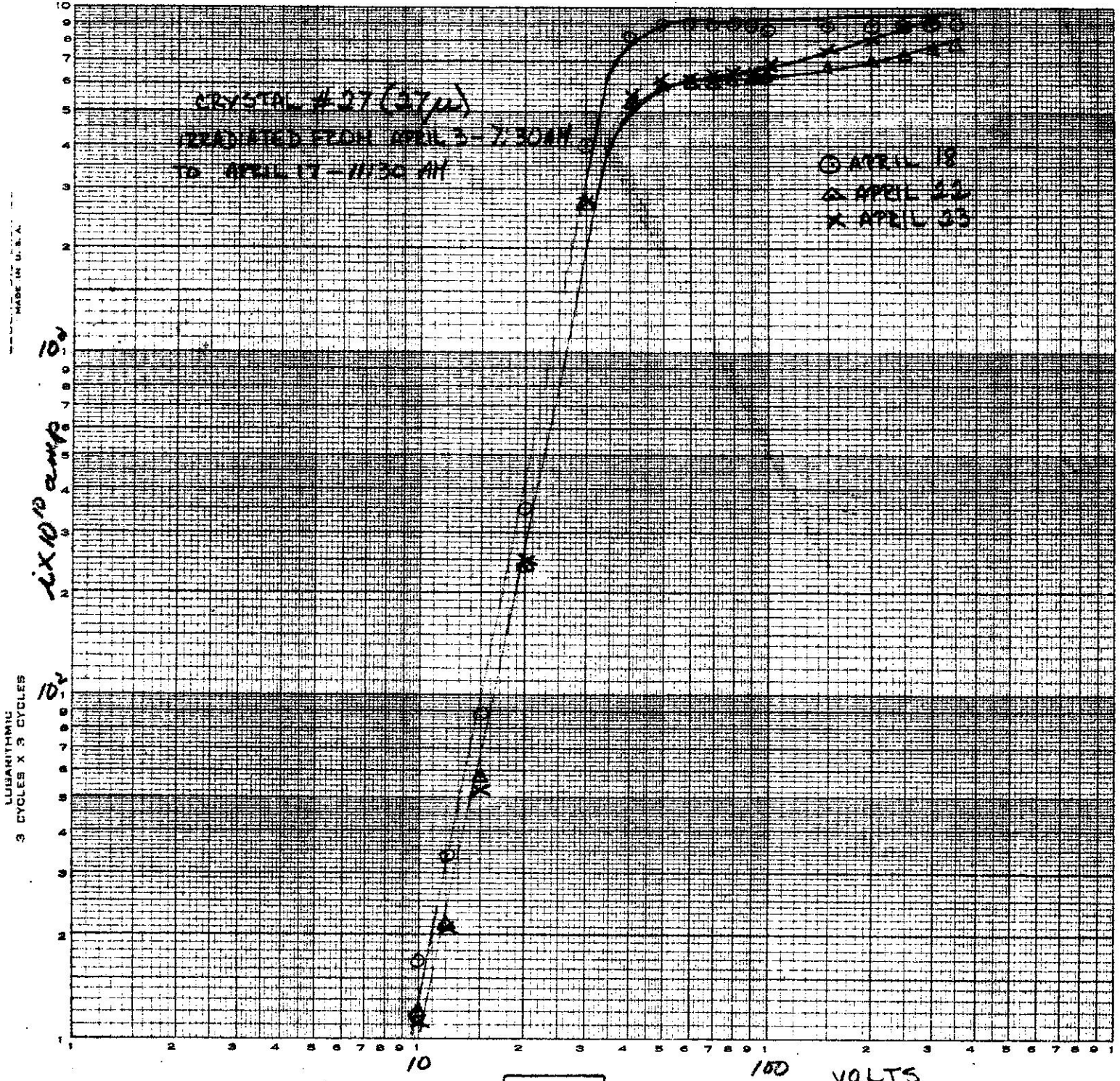
⊙ May 6 (AFTER IRRAD.)
□ May 7
△ May 8
✕ May 9

CRYSTAL # 54 (11µ)

IRRADIATED FOR 67 HRS.

⊙ MAY 6
□ MAY 7
△ MAY 8
✕ MAY 9

$i' \times 10^{10}$ AMPS

VOLTS

CRYSTAL

SOURCE

FIG. 7A

27μ thick

EXPOSED FROM APRIL 3-7:30 AM
TO APRIL 17-11:30 AM

○ *April 18*
□ *April 19*
△ *April 22*
✕ *April 23*

CRYSTAL #27 (27μ)
IRRADIATED FROM APRIL 3 - 7:30 AM
TO APRIL 17 - 11:30 AM

⊙ APRIL 18
△ APRIL 22
✕ APRIL 23

$i \times 10^{10}$ amp

VOLTS

PARAFFIN BOX →
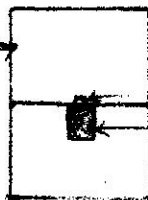
CRYSTAL
SOURCE

FIG. 7b

CRYSTAL # 29 (41μ)
IRRADIATED FOR 72 HRS.

⊙ APRIL 5 (BEFORE IRRADIATION)
▢ APRIL 9 (AFTER IRRADIATION)
△ APRIL 11

$i \times 10^{10}$ AMPS

10^3

10^2

10

10   100   VOLTS

MOUNTED CRYSTAL
SOURCE
PARAFFIN BOX

FIG 8

CRYSTAL #57 (3/μ)
IRRADIATED FOR 67 HRS.

⊙ MAY 9
□ MAY 10
△ MAY 13
✕ MAY 15

3 CYCLES X 3 CYCLES

$i \times 10^{10}$ AMPS

VOLTS

⊙ May 9
□ May 10
△ May 13
✕ May 15
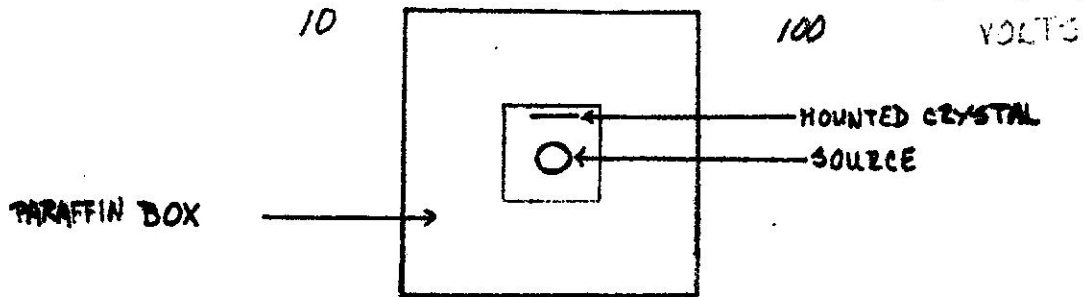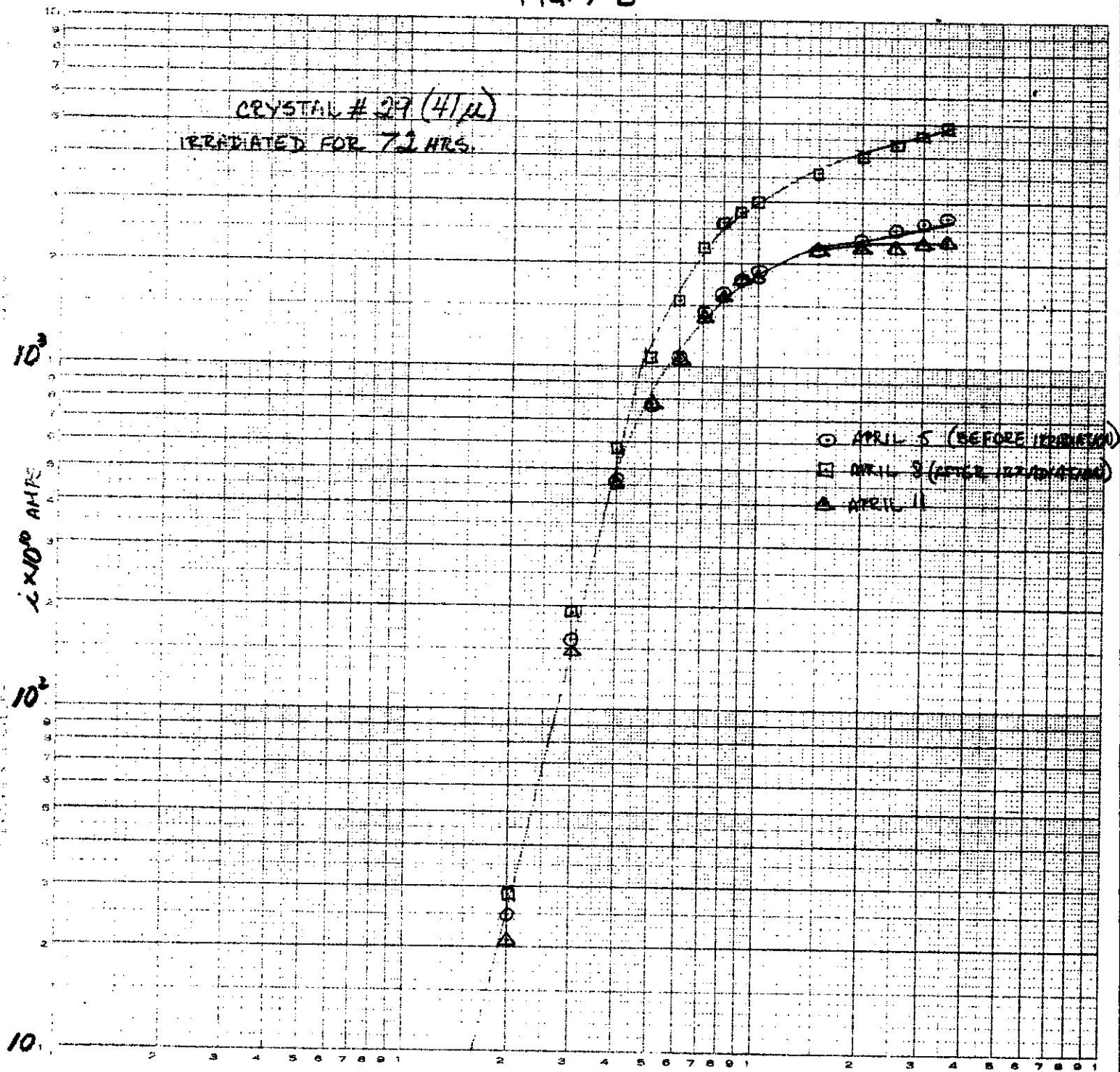
expired #57 (3/μ)
irradiated from May 6 - 2:00PM
to May 9 - 9:00AM (ukhid) [F.N.]

BORAL SHEILDING
PARAFFIN BOX
CRYSTAL
SOURCE
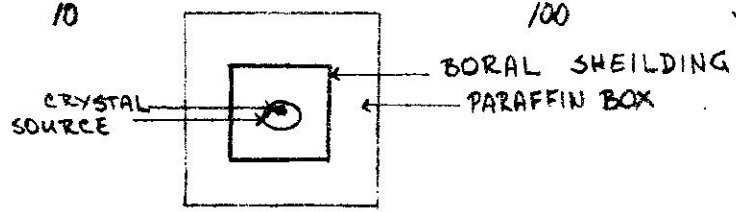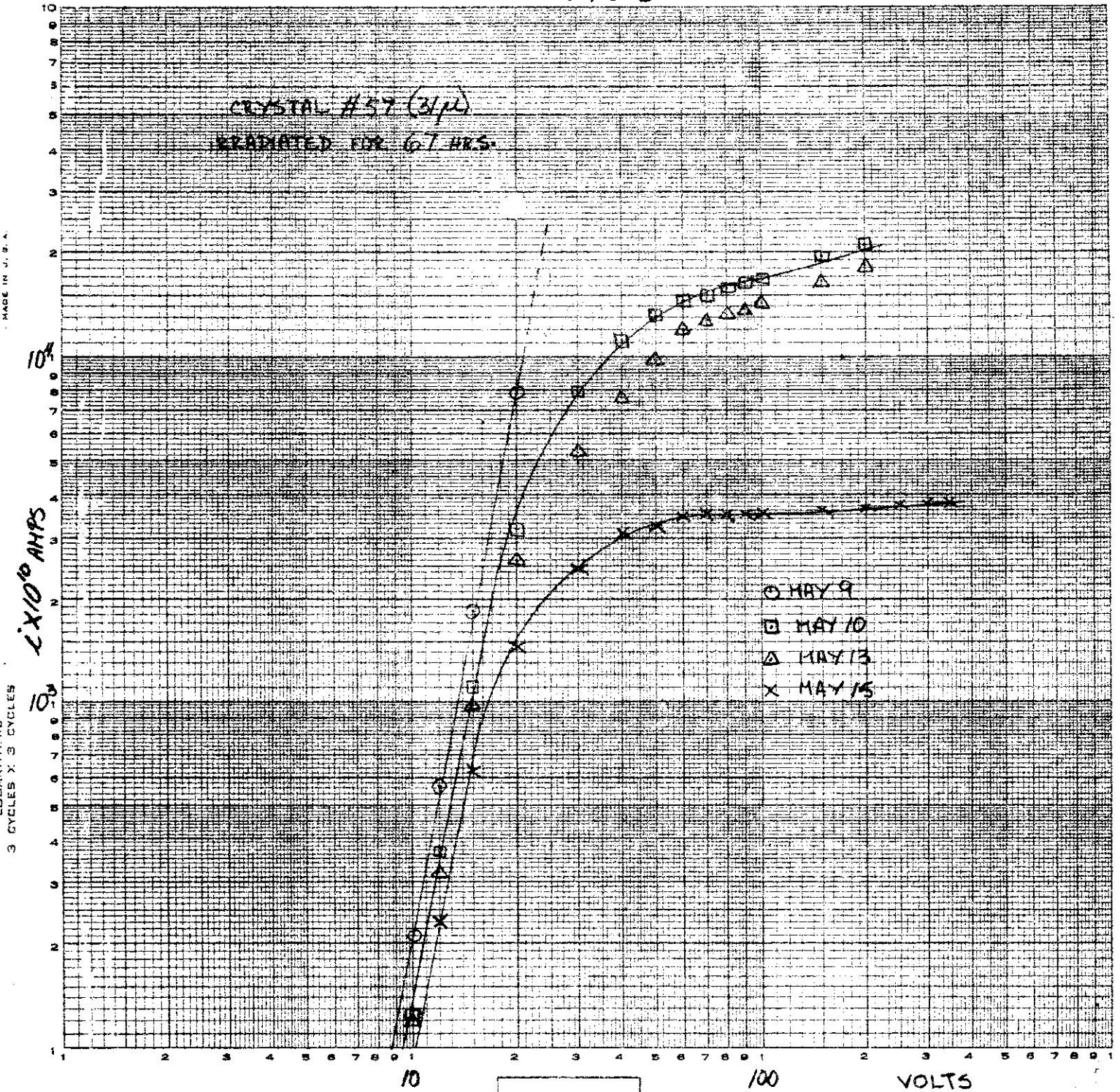
crystal #60 (34μ)
irradiated from May 10 - 2:00PM
to May 13 - 9:00AM [EM] (vrbrd)

⊙ May 13
☐ May 14
△ May 15

Fig 9

CRYSTAL # 60 (34μ)
IRRADIATED FOR 67 HRS.

⊙ MAY 13
☐ MAY 14
△ MAY 15

i x 10¹⁰ AMPS

VOLTS

CRYSTAL ON Al HOLDER
SOURCE
BORAL SHIELDING
PARAFFIN BOX

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

LOGARITHMIC
3 CYCLES X 3 CYCLES