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RADIATION AND THERMALLY HARDENED SWITCHING MATERIALS

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I. INTRODUCTION

Our aim has been to prepare and study materials in order to achieve more reproducible homogeneous single and polycrystalline materials capable of high speed switching between low and high conductive states. The low mobility of transition metal oxide insulators makes them excellent candidates. However, we had to avoid materials (such as VO_2) which undergo a first-order phase transition at a certain critical temperature with a concomitant structural transformation. A way around this problem was to find materials undergoing a large mobility and band structure transformation without a drastic change in the basic lattice symmetry. Such is the case of Ti_2O_3 , which was reported on at the first stage of this program. Our results on Ti_2O_3 showed the possibility of field switching materials which undergo a semiconductor-to-metallic transition only at liquid He temperature. Consequently, the next logical step appeared to be to choose a material which undergoes a semiconductor-to-metallic transition at a temperature much higher than Ti_2O_3 because it would have fewer free carriers to cool and freeze out free carriers.

Niobium dioxide, NbO_2 , was chosen as a next candidate for this investigation since it has a second order semiconductor-to-metallic phase transition at 1070°K . The electronic carriers have a low, anisotropic mobility at all temperatures. It was shown that the mobility in the low temperature phase ($< 1070^\circ\text{K}$) could be described in terms of small polarons. This indicates a localization of the single 4d electron of the Nb^{+4} ions via a pairing along the c-axis, stabilized by a lattice distortion. After we failed to switch bulk NbO_2 single crystal, we were able to develop radiation hard NbO/NbO_2 devices capable of shunting transient currents spikes of up to 80 Amp in times shorter than resolution of the apparatus (0.7 ns). We report here on the

preparation methods and physical properties of NbO_2 thin film on NbO substrate (Section II) and thinned stoichiometric NbO_2 , which has a similar characteristic to NbO/NbO_2 devices (Section III). Section IV describes non-stoichiometric effects on NbO_2 single crystal under DC field, as well as intense pulse fields in order to establish the mechanism of switching. We have also attempted to relate the mechanism to physical measurements on transport and structural properties, particularly nonstoichiometric effects on NbO_2 single crystal. Based on various experimental evidence, which includes scanning electron microscopy, we must improve the longevity and severe damage of our devices. Finally, Section V describes the polycrystalline form of devices ($\text{NbO}_{1.87}$) which demonstrated further experimental evidences to meet the specific requirement of radiation and thermally hardened switching material for devices. The summary shows a natural substitute for the more sophisticated single crystal technique and promises remarkable speed and power handling capabilities of new devices.

II. NbO_2 FILM ON NbO SUBSTRATE (A-TYPE DEVICES)

1) INTRODUCTION

A systematic analysis of the results obtained in the previous work periods of the ongoing contract led to the conclusion that the switching phenomena originally observed in needle shape crystals could not have been the bulk properties of NbO_2 , doped or not. Instead it occurred to us that very high fields are needed and therefore we should try thin films of NbO_2 on conducting substrates.

2) SAMPLE PREPARATION OF NbO/NbO_2

The NbO chips used in the course of the present investigation are prepared by Czochralski-Kyropoulos technique. The method used is the reaction of intimately mixed niobium (Nb) and niobium pentoxide (Nb_2O_5) powders in the tri-arc furnace, according to reaction (1)



The procedure followed was to press into pellets appropriately weighed powder mixtures of Nb metals (9.291 g) and Nb_2O_5 (8.861 g). Analysis of the starting materials by spectroscopic techniques showed the following impurities in the part per millions;

- For Nb metal $\text{Ta} < 100$, $\text{Fe} \sim 2$, $\text{Ca} < 1$
- For Nb_2O_5 $\text{Ta} < 50$, $\text{Si} < 1$, $\text{Ca} < 1$, $\text{Al} < 1$.

The pellets were then placed in the water cooled rotating graphite hearth of the furnace and electric arcs struck to them. This melted and reacted on the powder mixture in a circulating atmosphere of purified argon with a measured oxygen content less than 10 ppm. Under these conditions NbO appears to melt congruently (melting point of NbO : 2218°K), and the low resistance of the melt makes it very easy to maintain stable arcs which heat

the rotating melt uniformly. This technique¹ is effectively crucibleless since the bottom of the melt, in contact with the cooled graphite hearth, is solidified and forms its own crucible minimizing contamination. In order to grow crystals, a tungsten tip, attached to the heat pipe pulling rod was immersed into the melt and a fine neck produced by retracting and positioning it. Typically, the crystals were pulled at a rate of 2 inches per hour. However, when the seed crystal was used, it was possible to grow large crystals, typically $1 \times \frac{1}{4}$ inches. A typical crystal is shown in Fig. 1.

The stoichiometry of the niobium to oxygen ratios was determined by reoxidizing a known weight of the sample to Nb_2O_5 . The stoichiometry ratios used are quite close to $\text{NbO}_{1.00}$ accurate to within 0.5 atomic percent. The resistivity of the typical sample is 1.21×10^{-5} ohm-cm at 300°K . We have compared its resistivity to that given in previously published data for material of the same composition. Our results are in reasonable agreement with Chandrashekhah's measurements². The resistivity is very low and comparable to that of the element Nb from which the oxide is derived. Since NbO single crystal has a rock salt structure and cleaves very well, this NbO grown by Czochralski's technique can be cleaved into thin wafer $\frac{1}{3}$ to $1/10$ mm. thickness using razor blades. Small NbO chips, typically $1 \times 1 \times 0.5$ mm in dimension, were heated in the presence of a large amount of NbO_2 powder in vacuum and at various temperatures. When the chips were oxidized under partial oxygen pressure of NbO_2 , it proved easier to form NbO_2 on NbO surface if small amounts of Nb_2O_5 powder were added into NbO_2 powder. For example, 2 g. of NbO chips, 0.1 g. Nb_2O_5 ($\sim 1\%$ Nb_2O_5 of total NbO chips) and 8 g. of NbO_2 powder prepared freshly were sealed in a quartz ampoule and heated approximately for 24 hours at 850°C . Then an NbO_2 layer was formed all over the surface of NbO chips. The thickness of the NbO_2 film varies from 1 to 10 μ approximately. (See Figs. 3 and 4).

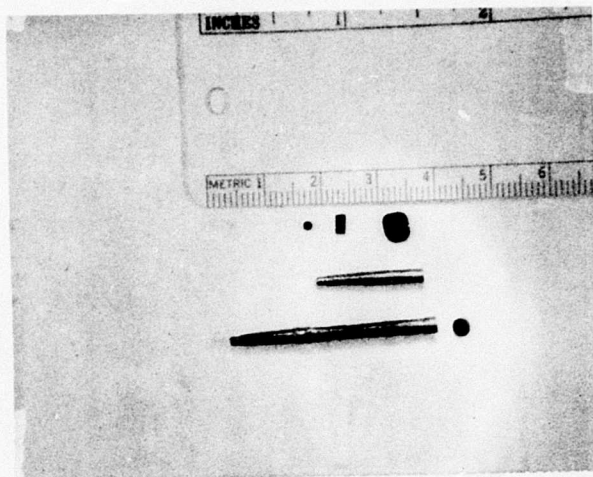


Fig. II - 1

Typical NbO single crystal and cleaved NbO chips

3) FILM STRUCTURE

In order to establish conclusively the nature of the NbO_2 coating which was formed on the NbO chips, we performed two tests. A first test was to run an X-ray diffraction pattern and the other was to examine a pure NbO crystal and a sample of NbO_2 films by ESCA.

The diffraction pattern of the prepared material was in good agreement with Magnelli's powder pattern of NbO_2 sample. Fig. 2 shows the diffraction pattern of the NbO_2 films on NbO chips. A faint foreign line is observed which is probably due to NbO. This in itself is quite convincing. In addition, the resistivity measurements indicate an NbO_2 thickness of $\sim 1 \mu\text{m}$, which is confirmed again by scanning electron microscopy (SEM).

ESCA measurements show a thin layer (15 to 20 Å) of NbO_2 present in the virgin cleaved NbO starting material. This indicates, consistently with other works, that the first higher Nb oxide is NbO_2 . Furthermore, the ESCA spectra of our NbO_2 film turned out to correspond exclusively to NbO_2 . After oxidation, the ESCA spectra showed the peaks shifting in energy, presumably due to changes in the surface to volume ratio of the polycrystalline oxide growth. Therefore both X-ray and ESCA show that the layer formed on NbO substrate is only NbO_2 , confirming that there is no intermediate state between NbO/ NbO_2 . Furthermore, there is no higher oxidation state, Nb_2O_5 .

We also confirmed this switching in an NbO_2 single crystal. An NbO_2 single crystal piece was lapped down to a thin layer, and annealed under vacuum or H_2 and Ar gas to produce a conducting surface as well as to reduce further the thickness of the specimen. The conducting edge of specimen was cut off from the sample. When the electric field was applied, we could get the same switching behavior, except a threshold voltage a little bit higher than with the NbO_2 thin film.

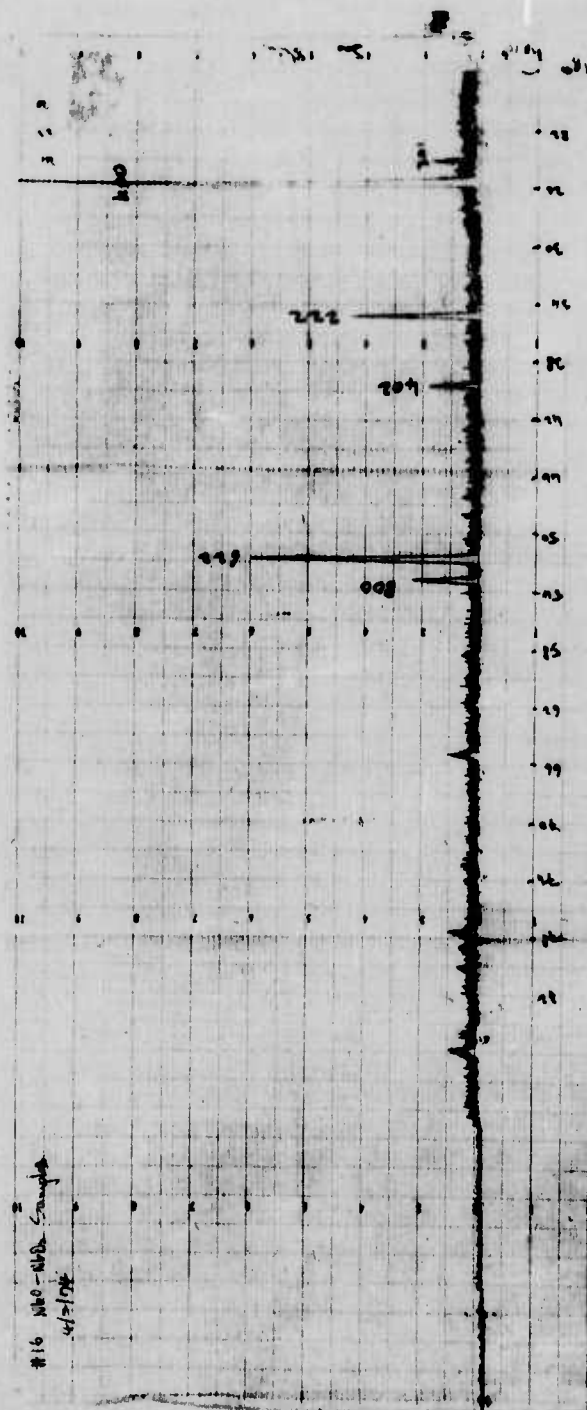


Fig. II - 2
X-ray diffraction patterns of NbO₂ film formed on NbO substrate

In order to study microscopic structure of the NbO_2 film and the relation between the DC resistance and film thickness, a few samples with different DC resistance were sent to Electronics Technology and Devices Laboratory, USAECOM, Fort Monmouth, N.J. for examination by Scanning Electron Microscope (SEM) techniques. Based on these SEM results, the following facts were recognized:

- 1) The thickness of a device with 50Ω of DC resistance turns out to be $0.1 \mu\text{m}$ thick, and NbO substrate was covered with a very fine grain of polycrystalline NbO_2 .
- 2) The thickness of $18 \text{ K}\Omega$ -device was found to be $1 \mu\text{m}$ thick, which was consistent with the estimated value by resistivity measurements. (See Fig. 3-A). The NbO_2 layer formed on the NbO single crystal was a larger grain size and was preferentially oriented perpendicular to surface of the substrate (See Fig. 3-B).
- 3) The NbO_2 layer of $130 \text{ K}\Omega$ device was $6.6 \mu\text{m}$ thick (Fig. 4-A) and well defined spots were interconnected and the grain size became reduced to ~ 0.1 to $0.2 \mu\text{m}$ (Fig. 4-B).

These results indicate that the DC resistance is proportional to its thickness of NbO_2 layer and a low resistance sample would be easily shorted with a few pulses due to a poorly formed structure.

4) CHARACTERISTICS OF NbO/NbO_2 DEVICES

The chips obtained by the technique described above were placed for preliminary testing on a rhodiated copper plate, making contact on one side, and the assembly was completed by applying a pressure contact via a gold ball point (0.5 mm diameter) on the other side. Pulses of $0.1 \mu\text{sec.}$ duration

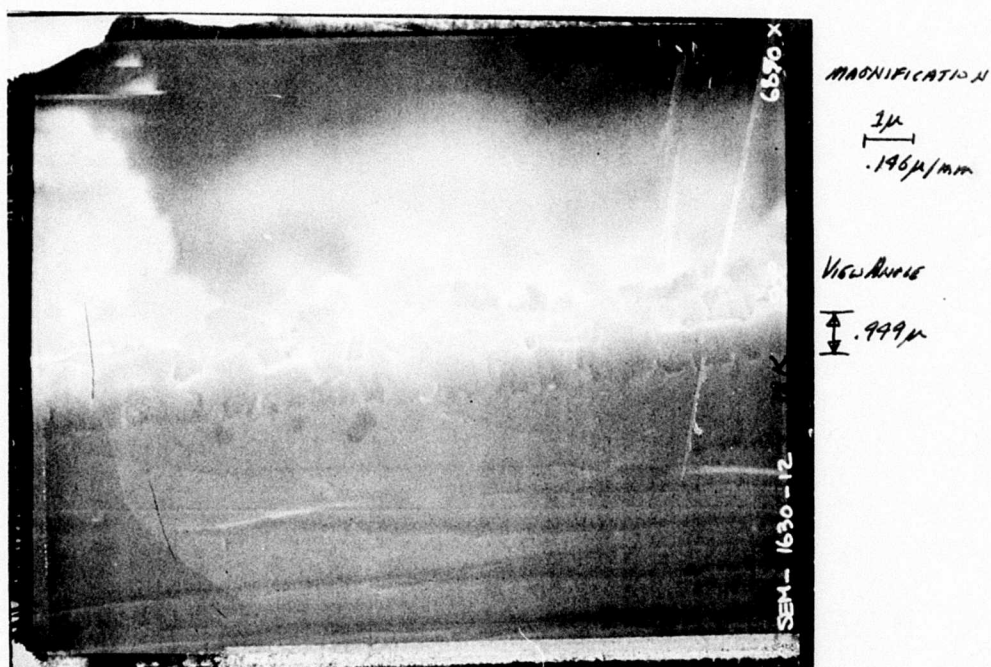
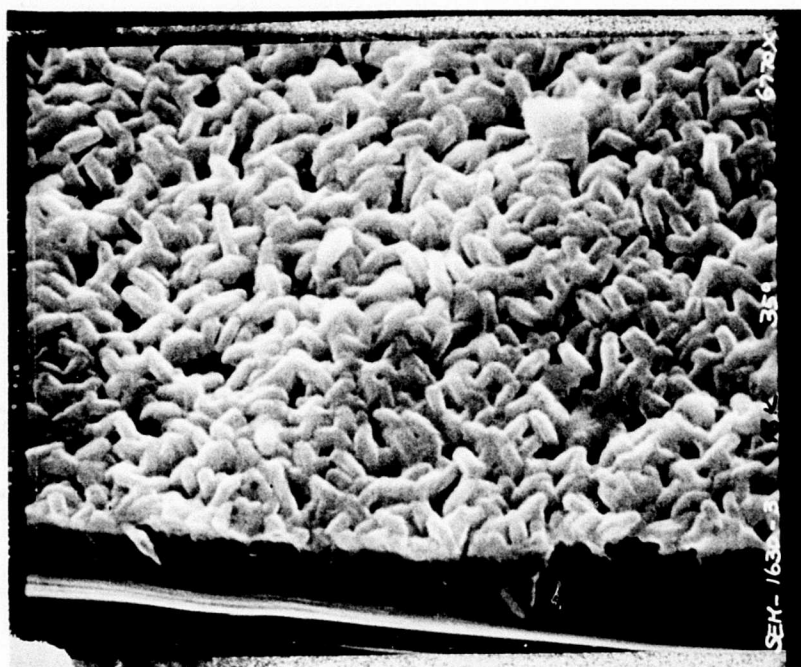


Fig. II - 3(A)

Scanning electron microscope (SEM) photograph showing
1 μ m thick NbO₂ layer grown on NbO substrate

#624
18K



MAGNIFICATION

24

VIEW ANGLE

Fig. II - 3(B)

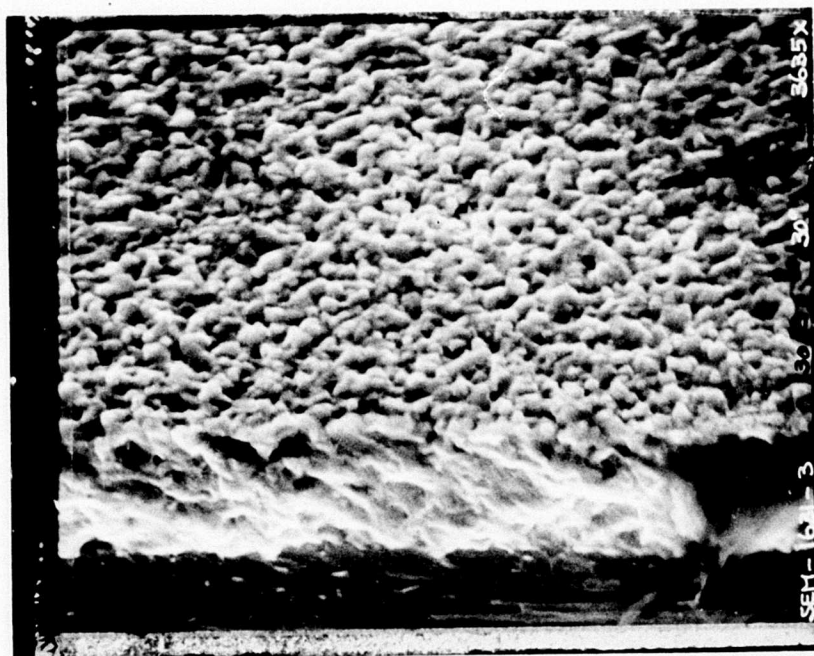
SEM photograph showing 35° angle view and columnar growth pattern of polycrystalline NbO_2



Fig. II - 4(A)

SEM photograph showing an edge-on view of a cleaved
device of which NbO_2 oxide layer is $6.6 \mu\text{m}$

711-1
130K,



MAGNIFICATION

2μ

VIEW ANGLE

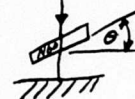


Fig II - 4(B)

SEM photograph showing that well defined spots were interconnected comparing Fig. II-3(B)

and 30 ns risetime were delivered by a Velonex model 350 pulse generator at a rate of 1 Hz.(Fig.5). The pulse's voltage was increased slowly while the sample response was followed on an oscilloscope in order to find the critical voltage at which it would switch. Typically, for a pure NbO_2 layer of thickness ranging from 1 to 10 μm , the off resistance measured with a D.C. multimeter varied from a few kilohms to several ten kilohms, but the threshold voltage did not change significantly and was of the order of 120 to 150 volts. The capacitance, measured at 10^6 Hz in the sample holder described above, was found to vary from 0.5 to 1.0 pF.

Furthermore, our effort has been directed towards packaging of the existing devices as well as systematization of production procedures. After discussion with Capt.Laplante of USAECOM, we have tried one microwave diode package presently available on the market. The motivation is obvious since microwave diode packages are designed to minimize capacitance and induction. It is also clear that the problems encountered in building microwave diodes are quite similar to the problems we ourselves are encountering. While we are not too enthused with the fact that these packages are point contact systems, we do feel however that it was an improvement on the pressure contact situation. The use of one of the packages turned out to be quite practical.

Finally, one of the stabler configurations was obtained using standard 1N23 (X-band) microwave diode packages (Fig. 6), manufactured by Microwave Associated International, Inc. Burlington, Mass. Because in this package the point contact is made by a spring loaded tungsten whisker the contact area is smaller and the off resistance of our devices varied, depending on the NbO_2 layer's thickness, between 20 and 500 $\text{K}\Omega$, as measured with a D.C. multimeter.

The threshold voltage was found to vary from 130 to 260 volts and the capacitance measured at 10^6 Hz was of the order of 0.5 pF.

In order to find out how well these devices would respond to fast risetime and high current (80 A) pulses, they were tested by Cpt. Laplante, USAECOM, Fort Monmouth, N.J., using a 50 Ω cable discharge pulser capable of output voltages up to 2000 V. The device response was photographed using a Tektronix 7904 oscilloscope with high speed writing capability and a maximum aperture camera system. This equipment allowed 0.7 ns risetime resolution of single shot pulses. Contrary to previous experience with other switching materials, such as amorphous semiconductors, no delay could be observed and within the limit of resolution (≤ 0.7 ns) the response of the device to the incident pulse appeared instantaneous. However, in amorphous switching, the device, once it did switch, traversed the negative resistance path on the I vs. V characteristic nearly instantaneously. In our devices, this post-switching negative resistance path is traversed in a measurable time with an 80% reduction in voltage in the first 10 ns. This was taken to indicate that the switching proceeds in two stages, the first one being electronic in nature and occurring in the first nanosecond while the second was a non-destructive thermal runaway resulting in filamentary high current density conduction. The second stage has long been known to occur, in materials such as NbO_2 which are capable of undergoing a semiconductor to metallic phase transition, if sufficient energy is dissipated in the form of Joule heating.

The maximum current tolerated by the devices was 80 A for pulse durations of 15 ns using the cable discharge pulser with the corresponding cable. A maximum current of 80 A for the maximum pulse duration of 160 ns, obtained using the longest cable, was also successfully tolerated by the device. In an attempt to investigate longer duration pulses, a Cober 605 P high power

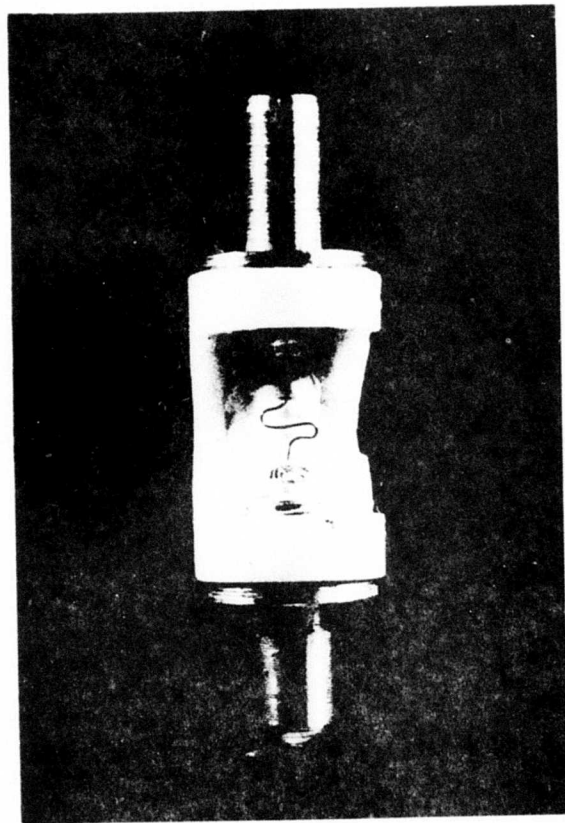


Fig. II - 6

Standard X-band 1N23 microwave diode package A-type
device is mounted with tungsten whisker contact

pulser was used to apply up to 3 ms single shot pulses at its maximum current of 11 A. The addition of an appropriate pulse transformer allowed the application of 1.0 μ s duration pulses at a maximum current of 22 A. These results are reported fully elsewhere.³

Some results of these specimen tested by Cpt. Laplante are summarized in Table 1. Based on these results, which include scanning electron microscopy done by Mr. Charles Cook of the Electronics Technology and Devices Laboratory, U.S. Army Electronics Command, Fort Monmouth, N.J.:

- a) The tungsten whisker making pressure contact in the diode packages was considerably eroded after a few pulses (2000 volt) indicating that high temperatures are reached by the tip. (See Fig. 6).
- b) During pulsing the NbO_2 layer oxidizes in the contact areas because of the high temperatures developed.

Potting the assembly electrodes/chip in the diode package with 5 minute epoxy from Devcon Corp. appeared to be the simplest solution. We found that the typical off resistance of a potted device was of the order of $\sim 150 \text{ K}\Omega$. During pulsing (1 Hz, 630 volts pulse amplitude and 0.1 μ sec. pulse width), the off resistance would increase to $20 \text{ M}\Omega$ and then would completely open after a few hours. Given the erosion of the tungsten contact shown by the SEM pictures after repeated pulsing, it was reasonable to assume that the epoxy prevented the spring action forcing a gap to form, and inducing open circuit failure.

Indium has a low melting point but a high boiling temperature. We decided to place a bead of In at the end of the tungsten whisker. Heat would

TABLE II-1

Switching Characteristics of $\text{NbO}_2/\text{NbO}/\text{NbO}_2$ (A-type) Devices

Devices	I_p (mA)	V_p (volts)	V_{th} (volts)	V_{th} (volts)	$R_{30\text{mhz}}$ ($K\Omega$)	$C_{30\text{mhz}}$ (pf)
A-1	1.0	14	250	250	17.9	0.37
A-2	0.8	36	700	180	14.1	0.33
A-4	1.0	40	460	300	7.9	0.44
A-5	1.0	50	640	380	22.7	0.41
A-6	1.3	34	300	100	9.2	0.50
A-9	1.2	25	100	70	25.2	0.60
A-11	1.0	16	90	80	7.4	0.40
Average	0.90	31	360	194	14.9	0.44

Note

- 1) Specimen were mounted in 1N23 diode package and contact was made with tungsten whisker.
- 2) The threshold voltage was determined by minimum voltage needed to switch a device for a 1 ns pulse width.
- 3) I_p and V_p were measured in a curve tracer.



Fig. II - 6

The eroded NbO_2 layer after a few 2000 volts pulses
while contact was made with tungsten whisker

only melt the In and insure a better contact. Now the In induced short circuit failure in the case of NbO_2 film on NbO substrate. However in the case of thin NbO_2 single crystal layer described in the next section, the results were quite satisfactory.

5) B-TYPE DEVICES

Attempts have been made at trying to develop a low voltage device by producing a different type of configuration. Instead of NbO/NbO_2 , we have attempted to make $\text{TiO}/\text{Ti}_3\text{O}_5$ devices. The method used was exactly the same as for the standard NbO/NbO_2 spike suppressors, i.e., we have annealed chips of TiO single crystals in sealed ampules in the presence of an excess Ti_3O_5 powder. This process was successful and we did obtain a coating of Ti_3O_5 on the TiO chips. The devices did switch at relatively low voltage compared to the NbO/NbO_2 devices. These devices are based on a configuration between a conducting substrate and an oxide which can undergo a semiconductor to metallic transition (SCM). Example: NbO (metallic)/ NbO_2 (SCM at 807°C) or TiO (metallic)/ Ti_3O_5 (SCM at 135°C). We also have tried VO/VO_2 and it does work. However the off resistance is somewhat low and the device fragile because of the closeness to the actual transition temperature (SCM at 65°C).

6) NbO_2 FILM ON NIOBIUM METAL SHEET

In order to confirm experimentally the possibility of using Nb-metal for device fabrication, we have performed measurements using $\text{NbO}_2/\text{Nb}/\text{NbO}_2$ thin film devices. This turned out successfully and would certainly be a cheaper approach to device construction. Since niobium metal exposed to an oxidizing atmosphere would first form NbO, and then NbO_2 , we would necessarily get the same NbO/NbO_2 configuration on top of an Nb electrode which should be no problem. The only question was whether the general grain structure of the successive layer would turn out to be too fragile for repeated pulsing.

TABLE II-2
Switching Characteristics of B-type Devices

	NbO_2/NbO	$\text{Ti}_3\text{O}_5/\text{TiO}$	VO_2/VO	
T_{SCM} ($^{\circ}\text{C}$)	807	135	65	Sem. to metallic transition temp. of semiconducting oxide
V_{th} (volt)	130	50	2 ~ 5	0.1 μsec pulse width from Velonix

Commercially available Niobium foil, 0.25 mm. thick, 99.99% pure, produced by Ventron Chemical Co. was cut into 2x2 mm. pieces, and then oxidized with partial pressure of NbO_2 powder at 900°C . The characteristics of this device are similar to that of the NbO/NbO_2 configuration; the off resistance (DC) was typically of the order of 30 K Ω and the device switched at ~ 85 volt, with 0.1 μ pulse width. Longevity tests have shown that the devices are somewhat more fragile than those produced from NbO single crystal chips.

7) Ti-DOPING EFFECT ON NbO SINGLE CRYSTAL SUBSTRATE.

Ti-doping was introduced in the original NbO single crystals on which the NbO_2 layers are grown. In this way, as NbO_2 is formed by oxidation, it is automatically doped by the Ti present in the proper portion. Its purpose was to improve the switching characteristics through reducing the energy gap and therefore the threshold voltage. In fact, the purpose of this doping was triple:

- a) It is hoped that Ti-doping reduces the oxygen affinity because Ti cannot be oxidized to the 5+ state, and therefore improves the lifetime of our devices.
- b) Ti-doping prevents fast dendritic growth also due to the high oxygen affinity for NbO.
- c) Ti-doping reduces the band gap and therefore the potential barrier to switching.

EXPERIMENTAL RESULTS

We have performed an experimental investigation on Ti-doping effect on NbO single crystals. Ti-doped NbO single crystals, $\text{Nb}_{1-x}\text{Ti}_x\text{O}$, with $0 \leq x \leq 0.1$ have been grown successfully and we have compared their switching characteristics to undoped NbO/NbO_2 thin film devices.

The Ti-doped NbO single crystals were prepared by addition of Ti metal (99.99%) or TiO_2 (99.995%) to the appropriate amounts of Nb and Nb_2O_5 mixture, as described in section II.

Various Ti-doped NbO chips were sealed in a quartz ampoule with enough NbO_2 powder, and then oxidized at 900°C for about 20 hours. The specimens were mounted between a rhodiated copper plate and a gold ball point (0.5 mm diameter). The threshold voltage was determined by using 0.1 μsec pulse width. The results were quite satisfactory, except for a low off resistance. The observed switching voltage decreased almost exponentially with x for doping concentration of titanium. The layers looked at by scanning electron microscopy proved to be considerably more dense and uniform than previously. Fig. 7 shows the effect of Ti-doping for the threshold voltages. A 10% Ti-doped thin film device switched at lower than 20 volts compared with switching voltages to ~ 85 volt of the undoped thin film device.

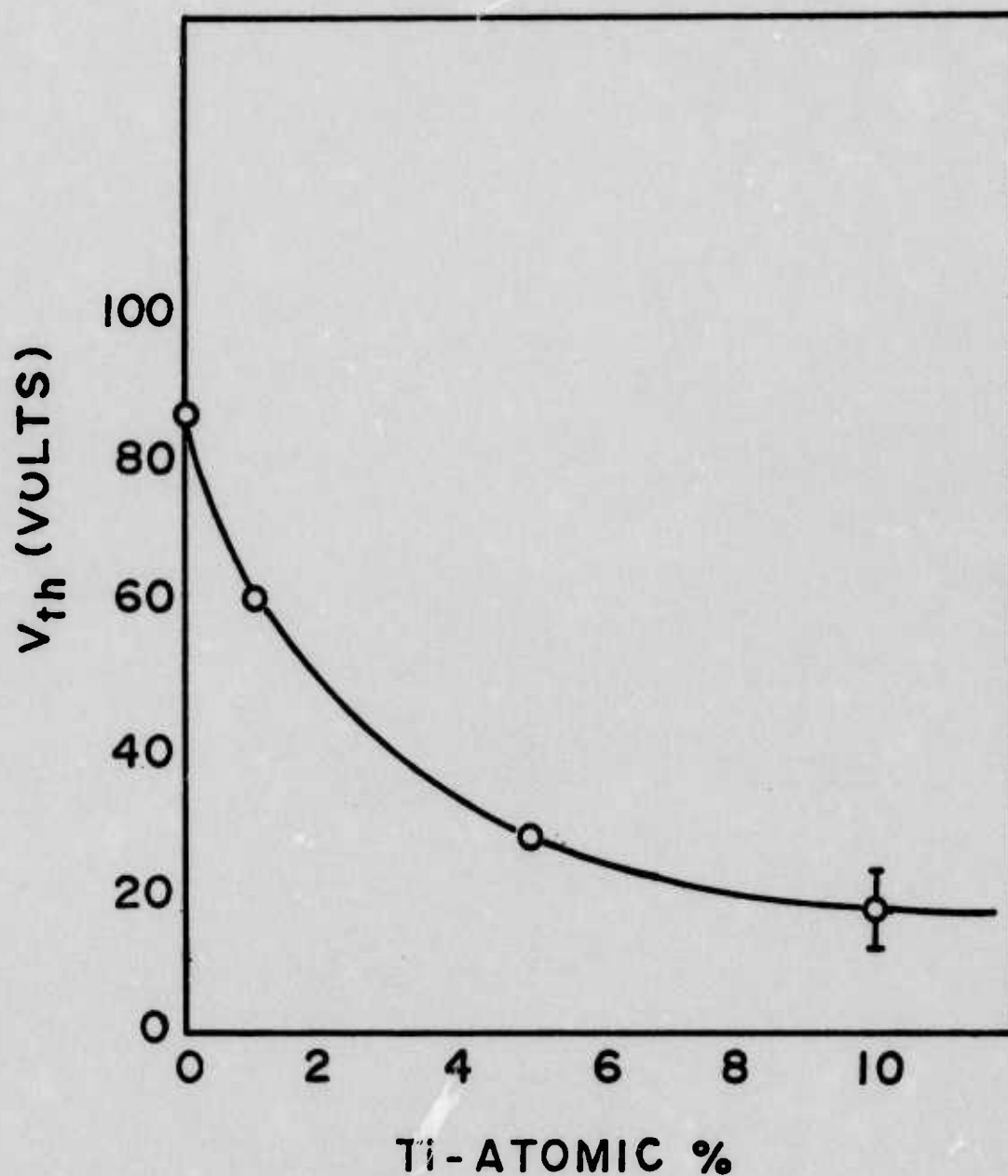


Fig. II-7

Threshold voltages vs. Ti-doping in $\text{NbO}_2/\text{NbO}/\text{NbO}_2$. Threshold voltages decreases exponentially with Ti-Atomic % in $\text{NbO}_2/\text{NbO}/\text{NbO}_2$ devices.

III. THINNED NbO_2 SINGLE CRYSTAL DEVICES (C-TYPE DEVICES)

1) BACKGROUND INFORMATION.

At the first stage of this program we succeeded in obtaining NbO_2 materials behaving as transient suppressors with high switching speeds, low trigger voltages and high current capability. However, when we prepared a better quality of NbO_2 single crystals, it gave negative results. Since then, our work has addressed itself mainly to the preparation of thin layers (1 to 10 μm) of NbO_2 on NbO single crystal chips described in detail in Section II. It would appear that in fact we did not switch in the original materials the bulk, but rather some layers of NbO_2 upon a conducting substrate of non-stoichiometric NbO_2 like $\text{NbO}_{1.87}$, which is described in the next sections. How this came about in the original preparation has not yet been elucidated but we are taking steps to test the switching of NbO_2 under intense fields by means of making thin single layers on a conducting substrate.

2) PREPARATION OF THIN LAYER OF NbO_2 CRYSTAL

While we were able to establish that the switching element is indeed the pure NbO_2 layer, the physical structure of that layer has become a point of interest because of the need to develop good electrode contact. More recently we have attempted to prepare NbO_2 single crystal chips thin enough to be switched. Since it is usually impossible to thin down a single crystal to the size of even 10μ we proceeded in the following manner: we lapped down an NbO_2 single crystal to the thickness of approximately 0.1 mm then further decreased the effective thickness by reducing the surface. As we have already reported, reduced NbO_2 had a lower conductivity than pure NbO_2 , hence the crystal surface once reduced became a very good electrode. It was possible to switch the single crystal chip. The threshold voltage turned out to be the well known ~ 300 volts with 0.1 μs pulse width. We

intended to further develop this approach because obviously this single crystal technique presents excellent electrode contact possibilities. We have since learned through experience that the NbO_2 layers produced by surface oxidation of NbO single crystals are fragile when submitted to long pulses (over 10 μsec pulse width). The advantage of NbO_2 single crystal devices are double, for one thing NbO_2 single crystals are considerably more resistant to oxidation because the existing surface is very small. For another, NbO_2 single crystals are flat and smooth which makes for very good electrode binding properties. We found that it was necessary to thin down a single crystal plate to a thickness of a few mils. When we made contact directly with Ag-paste and a screw in regular microwave diode package, the switching voltage was very high, of the order of 300 to 330 volts with a 0.1 μ pulse. These specimen were forwarded to USAECOM for testing. Some results provided by Cpt. Laplante are summarized in Table 3. The capacitance as measured by Cpt. Laplante turned out to be 2 pF which is only 3 to 4 times larger than our regular $\text{NbO}_2/\text{NbO}/\text{NbO}_2$ devices.

When contact was made, using tungsten whiskers with Indium and potted in epoxy, the results were similar but we found that devices were stable. It turned out that the I vs. V characteristic in these new types of devices is extremely reproducible and stable. These types of devices with proper contacts should be able to handle much larger currents and we have already checked that they can handle very long (100 microseconds) pulses.

Table III-1

Switching Characteristics of Thinned NbO₂ single Crystal

	I_p (MA)	V_p (volts)	$V_{th}(1)$	$V_{th}(2)$	R_{30mhz}	C_{30mhz}
C-11	4.4	7.0	130	110	4.9	1.75
C-12	6.0	18	400	450	5.2	3.10
C-13	2.2	18	320	330	6.7	2.27
C-15	3.6	13	220	230	7.8	0.77
C-16	4.2	76	400	420	10.5	1.74
C-17	12.0	7.0	350	350	4.0	1.26
Average	5.40	12.6	303	350	6.9	0.85
C-14	4.0	17	350	350	6.9	0.85

Note

- 1) The first series of specimen are epoxied, indium contacted to sharpened set screw.
- 2) The threshold voltage was determined by minimum voltage needed to switch a device for a 1 ns pulse width.
- 3) I_p and V_p were measured in a curve tracer.

IV. NON-STOICHIOMETRIC EFFECT ON NbO_2 SINGLE CRYSTAL

1) OBJECTIVES

Our purpose has been to study more systematically high quality single crystals of NbO_2 under DC field as well as intense pulse fields in order to establish the mechanism of switching. We have in particular attempted to relate the mechanism to physical measurements on transport and structural properties, particularly the non-stoichiometric effect on NbO_2 single crystal.

2) INTRODUCTION

Niobium dioxide, NbO_2 , has a second order semiconductor-to-metallic (SCM) transition at 1070°K . Belanger et al. studied the transport properties of stoichiometric single crystal NbO_2 , and demonstrated that the mobility in the low temperature phase ($T < 1070^\circ\text{K}$) could be described in terms of small polaron

Considerable amount of work on controlled stoichiometric NbO_2 has been done in our laboratory. A large portion of this work concerned a study of single crystal NbO_x with $1.90 \leq x \leq 2.10$ and polycrystalline $\text{NbO}_{1.87}$. The latter material is studied in detail in the next section.

Jannick and Whitmore studied the transport properties in relation to the materials stoichiometry. They reported a very narrow range of non-stoichiometry ($2.003 \geq 1.997$) for NbO_x hardly affecting the transport mechanism. In the process of growing stoichiometric NbO_2 single crystals for various studies, we were led to question whether Jannick and Whitmore's claim of a very narrow compositional range of existence implied that a stoichiometric crystal could be pulled from a non-stoichiometric melt. This turned out not to be the case, and our Laue and thermogravimetric studies indicated that we could grow perfectly well defined large single crystals of composition $1.90 \leq x \leq 2.10$ in contrast with Jannick and Whitmore's result of $1.997 \leq x \leq 2.003$ obtained on powders.

3) STOICHIOMETRIC NbO_2 and $\text{Nb}_{1-x}\text{Ti}_x\text{O}_2$

For the purpose of gaining insight into the effects of the nonstoichiometry and of the Ti-doping on electrical properties, the relationship between stoichiometry and conductivity was studied in detail.

Large single crystals of NbO_2 , NbO_{2+x} with $x \approx \pm 0.1$ and $\text{Nb}_{1-x}\text{Ti}_x\text{O}_2$, $0 \leq x \leq 0.6$ have been grown by the Czochralski-Kyropoulos technique in a tri-arc furnace. Details of the equipment and methods of operation are described earlier in Sect.II. Analysis of the starting materials by spectroscopic techniques showed the following impurities in part per millions.

- For Nb metal	Ta < 100, Fe ~ 2, Ca < 1
- For Nb_2O_5	Ta < 50, Si < 1, Ca < 1, Al < 1
- For TiO_2	Si ~ 5, Na ~ 3, Mn ~ 1, Ca < 1
- For Ti metal	Si ~ 8, Fe ~ 3, Na ~ 1, Mn < 1

Laue photographs showed that crystals pulled without the benefit of a seed all had more or less the same orientation, with the growth direction inclined by about 16° to the c-axis. However when oriented seeds were used, it was possible to grow large crystals, typically 1. x 3/8 inch, with an orientation differing from that of the seed by no more than 5° . It proved easier to grow crystals with c-axis orientation than crystals with a-axis orientation, and the latter often developing twinning. However with proper seeding and necking, both c-axis and a-axis growth are possible. A typical crystal is shown in Fig. IV-1.

Spectroscopic analysis showed that the crystals grown by this method contained no new impurity and that the impurity level was no greater than in the starting materials. In addition, thermogravimetric analysis carried out on pieces taken from various places in the lengths of the boule indicated

excellent homogeneity and a control of the stoichiometry $x = \text{O}/\text{Nb}$ better than 0.1%. In a recent article, T. Sakata⁴ claims that crystals grown in arc-melting furnaces are highly stressed and therefore fragile and unsuitable for physical measurements. A standard micrographic investigation of our samples did not reveal any telltale microcracking, inclusions, or polycrystalline areas, and the Laue photographs exhibited very sharp, well defined spots indicative of a low density of random microscopic defects. Furthermore, for the purpose of Raman studies partially reported elsewhere⁵ uniaxial stresses of the order of 10^{10} dynes/cm² were applied to our crystals without damage. Consequently, we consider Sakata's position as to the quality of arc grown NbO_2 single crystals unjustified.

The transport properties of stoichiometric single crystal NbO_2 have been reported elsewhere⁶. It was demonstrated that the mobility in the low temperature phase ($T < 1070^\circ\text{K}$) could be described in terms of small polarons. This indicates a localization of the single 4d electron of the Nb^{4+} ions via a pairing along the c-axis, stabilized by a lattice distortion. Clearly ionic vacancies, such as non-stoichiometry would generate on the Nb or the O sublattices, will allow local lattice relaxations destabilizing the Nb-Nb pairs and increasing the conductivity. This is in effect very similar to what temperature does when it induces thermal vibrations in which the maximum amplitude of vibration is of the order of the lattice distortion stabilizing the Nb-Nb pairs, eventually breaking them. Table IV-1 shows our results for single crystals both rich and poor in oxygen. From the behavior of the resistivity it is quite clear that the compositional range of existence extends further than was previously reported⁷ and that the departure from stoichiometry does affect at least one transport property, namely the resistivity.

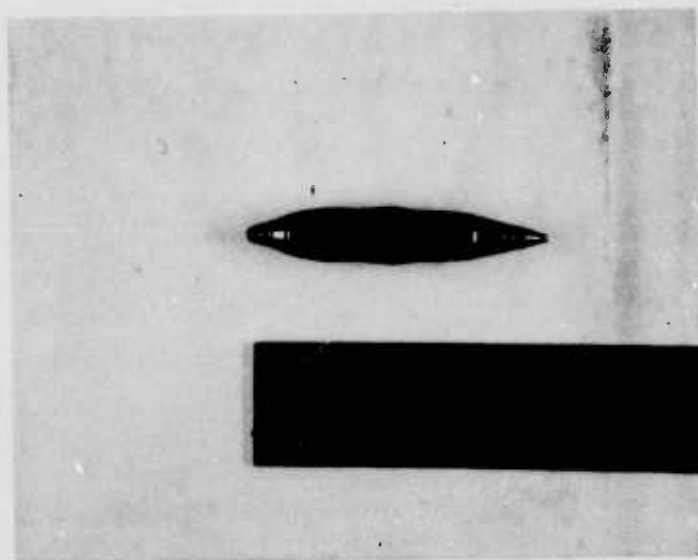


Fig. IV - 1
Typical NbO₂ single crystal

TABLE IV-1

Room Temperature Resistivity of $\text{NbO}_{2\pm x}$ in Relation to Stoichiometry

Compositions	Resistivity (10^4 ohm-cm)
$\text{NbO}_{1.90}$	0.0438
$\text{NbO}_{1.995}$	0.7962
$\text{NbO}_{2.00}$	1.336
$\text{NbO}_{2.005}$	0.378
$\text{NbO}_{2.10}$	0.1166

The effects of Ti^{4+} doping can in fact be analyzed along the same lines because Ti^{4+} has no d-electrons and breaks a Nb-Nb pair every time it is substituted for Nb^{4+} . Consequently for $0 \leq x \leq 0.17$ in the $Nb_{1-x}Ti_xO_2$ system the conductivity increases with x until for $x > 0.17$ the distortion disappears, all Nb-Nb pairs are destabilized and the material has a metallic conductivity. In this respect our results are very similar to the results reported by Sakata⁴. The main difference is that we measure a conductivity four times larger than the conductivity he reports for his polycrystalline samples. This difference is to be attributed to grain boundary resistance.

4) SWITCHING CHARACTERISTICS OF NbO_2 SINGLE CRYSTAL: MIXED CRYSTALLOGRAPHIC CONFIGURATION

The switching characteristics under several field conditions have been studied and it has been demonstrated that disorder rather than order could improve switching characteristics in the case of bulk NbO_2 single crystal.

In the first experiment we tested the qualitative influence of uniaxial stress in the direction of the applied pulses: in this configuration, we first verified that no switching was observed, whether for "c" or for "a" crystallographic orientations, when no stress was applied. This test was performed with single pulses 1 μ sec wide, covering the range 20-2500 V. On the other hand, when samples with either crystallographic orientation were subjected to uniaxial stress, switching was observed in the single pulse mode: i.e. above a certain threshold voltage a sudden decrease of the resistance of the sample could be observed. Without exception, at the threshold value, sparking at or near the surface of the samples took place. A check of the low voltage DC resistance of the samples before and after even a single pulse showed an irreversible change in the form of a decrease from an initial value of about 30 $K\Omega$ to a final value of about 3 $K\Omega$. The samples seemed to remain at this level indefinitely. A stereographic microscope

observations at low power showed that between the electrodes there was a distinct visible path in the sample where apparently the sparking took place. Mechanical removal of the path by the use of an airbrasive machine brought back the resistance to its original 30 K Ω value. Repeating the experiment under the same conditions showed reproducible behavior. Even in cases where samples were covered with silicon oil, remarkably enough, sparking occurred. The result of this experiment has to be taken only as preliminary since although the samples used were oriented about well-known crystallographic directions, their geometry was not the optimal for this kind of experiment. In order to be able to apply a known stress, the geometry was unsuited. So further experiments are planned in this direction by the use of a well-aligned pressure rig on which one can apply the desired pulses. It has to be noted that the switching took place when the stress was applied in the same direction as the electric field in both "a" or "c" directions.

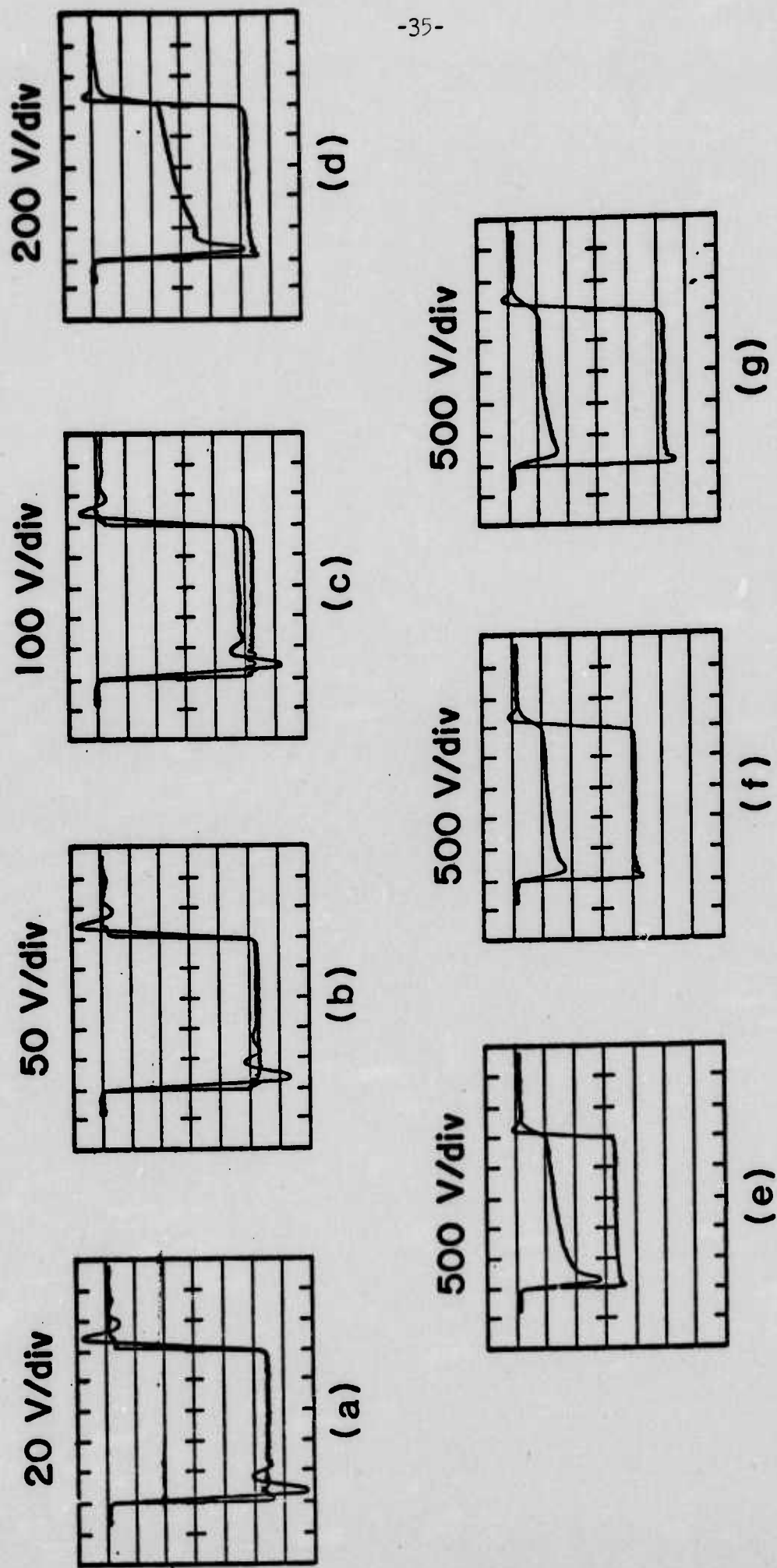
In the second set of experiments very thin samples were used. All had their "c" axis perpendicular to the surface. One side of the samples had a sputtered niobium film. In one of the experiments, electrodes were placed on the NbO₂ surface, along an "a" direction using Viking Alloy and Indium metal with the aid of ultrasonic scrubbing. Under these conditions, again, switching was observed. It has to be noted however that again the need of sparking was obviously present. The final drop of resistance was not by far as dramatic as the one observed in the samples described in our previous report. With this configuration, it can be seen that the actual pulsing takes place on a mixed crystallographic configuration as one can distinguish two different and well-defined paths: the first, a direct, surface line along an "a" direction; the other, through the sample, along the niobium film and again through the sample to the other electrode.

This configuration has the obvious drawback that excitation and switching directions are mixed by the geometry and therefore makes an evaluation of the process very complicated. The oscilloscope tracings are shown in Fig. IV-2 and Table IV-2. Using the same basic samples another experiment was performed: a channel was cut with an airbrasive machine removing a narrow portion of the Niobium sputtered film and leaving the NbO_2 surface exposed. Contacts were soldered at both sides of the exposed NbO_2 to the Nb film. Since in the past we experienced difficulties with the quality of the contacts, in this case we have to assume that the contacts are of high quality since the bonding between the Nb and NbO_2 should be excellent and the soldering with indium to the Nb film presented no problem. Once more, switching was observed in the "a" direction, in a single pulse (or repetitive up to 10 pulses per second), even immersed in silicone oil, but always preceded by the described sparking. The similarity of the results obtained when compared with the "mixed" configuration is remarkable, as can be seen by comparing the oscilloscope pictures taken in both cases as shown in Fig. IV-3 and Fig. IV-2(d).

The third experiment of these series dealt with a well defined geometry. Using a single crystal, a small amplitude AC was applied across the "c" direction of the sample whereas a variable DC bias was established across the "a" direction of the same crystal. The AC response along "c" was then monitored as a function of the DC applied along "a".

In order to make these measurements more defined a circuit was established in a balanced configuration as shown in Fig. IV-4.

The results obtained are plotted in Fig. IV-5 (a) where it can be seen that the resistance (AC) along the "c" direction changes with the applied DC voltage along the "a" direction. As shown in Fig. II-5(b), the resistance (AC) R_c along "c" and the resistance (DC) R_a along "a", scale over most of



Horizontal scale: 200 nsec/div
Vertical scale as shown

Fig. IV-2

TABLE IV-2

NbO_2 Switching: mixed crystallographic configuration
Single Pulse, 1 μsec Duration

Fig.	V_t (v)	V_s (v)	ΔV (v)	I (A)	R (Ω)	$E_{\min}$ (erg)
1-a	110	110	-	-	30	4
1-b	270	260	10	0.01	26	26
1-c	510	460	50	0.05	9.2	230
1-d	1100	420	680	0.68	0.62	2800
1-e	1650	450	1200	1.2	0.375	4800
1-f	2000	400	1600	1.6	0.250	6400
1-g	2500	350	2150	2.15	0.162	7600

V_t : Total voltage from Velonex pulse generator

V_s : Voltage across sample at end of pulse

ΔV : $V_t - V_s$

I : Current through sample

R : Resistance of sample at end of pulse

$E_{\min}$: Energy dissipated at the sample, assuming voltage across the sample constant and equal to V_s .

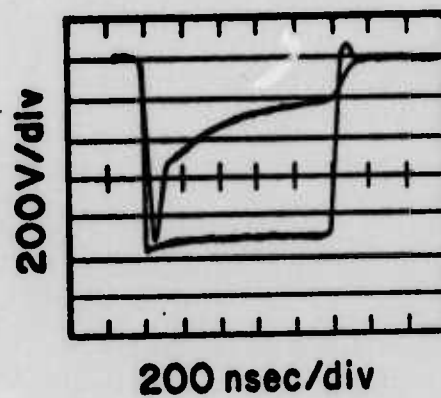


Fig. IV-3
Compare with Fig. IV-2(d)

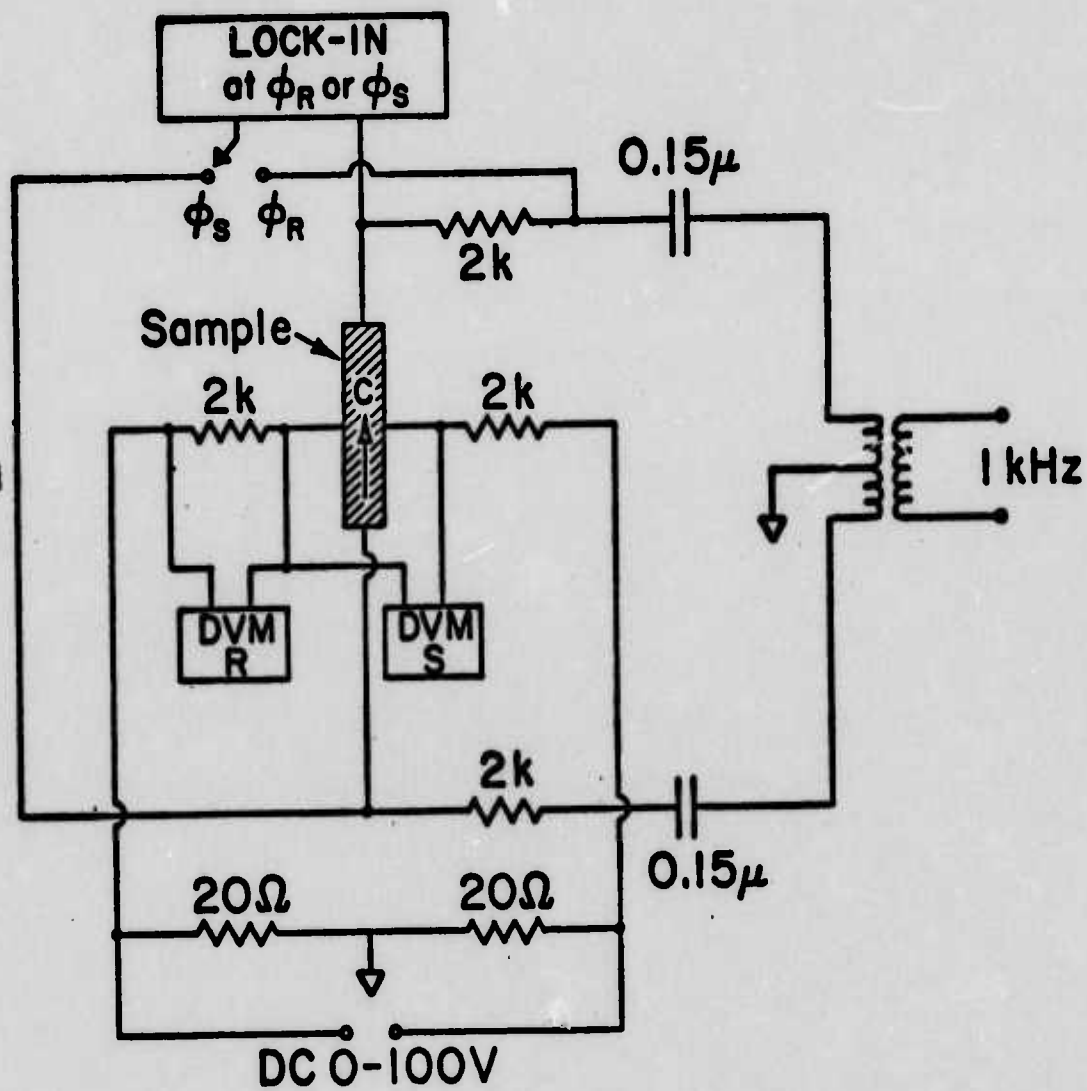
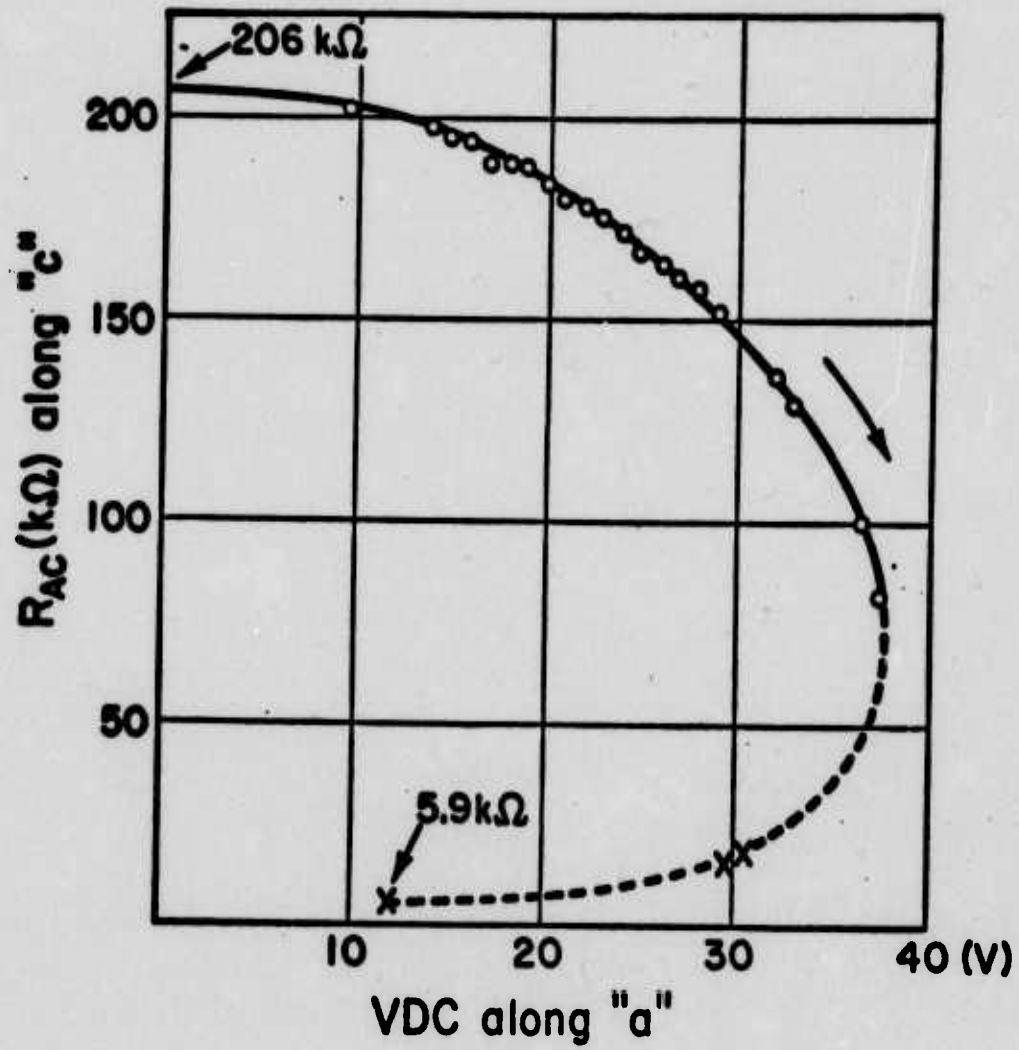
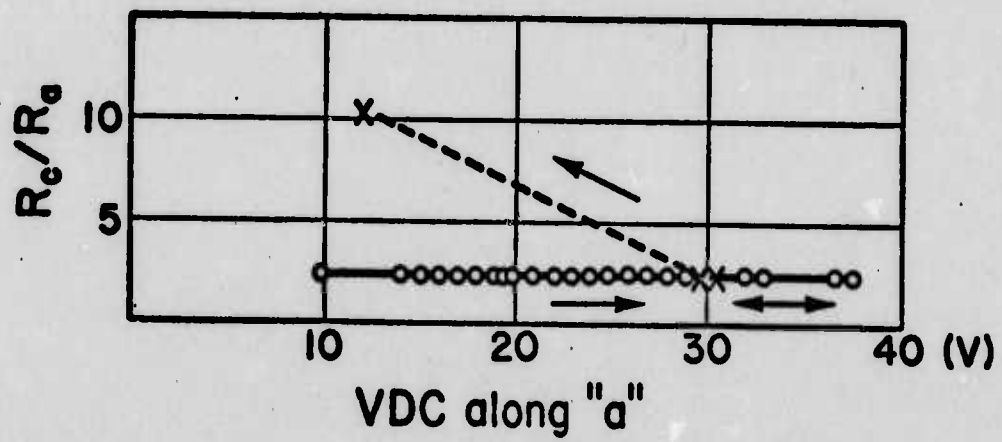


Fig. IV-4



(a)



(b)

Fig. IV-5

the range of bias applied, as would be expected from a thermal phenomena. Above 20 VDC along "a", the measured magnitudes required times of the order of several seconds to reach equilibrium.

A negative resistance region becomes readily apparent as shown in Fig. IV-6. The sudden change in the ratio of R_c/R_a shown in Fig. IV-5 at a nominal power supply voltage above ~ 70 V has yet to be explained. Further work in this configuration is in progress.

Fig. IV-7 shows the phase difference (ϕ_c) between I_c and V_c in the "c" direction. When the resistance R_c collapses, $\phi_c \rightarrow 0$.

Using samples described above in the second set of experiments (either configuration), a double pulse measurement was performed. In all cases a 10 pulses per second repetition rate was used, with each pulse 400 nsec wide, and variable delay between first and second pulse. The series of oscilloscope pictures in Fig. IV-8 show that complete recovery from the effects induced by the first pulse can be expected only after a time delay of more than 6 μ sec. These results were identical, as expected, with the ones obtained from a single shot configuration.

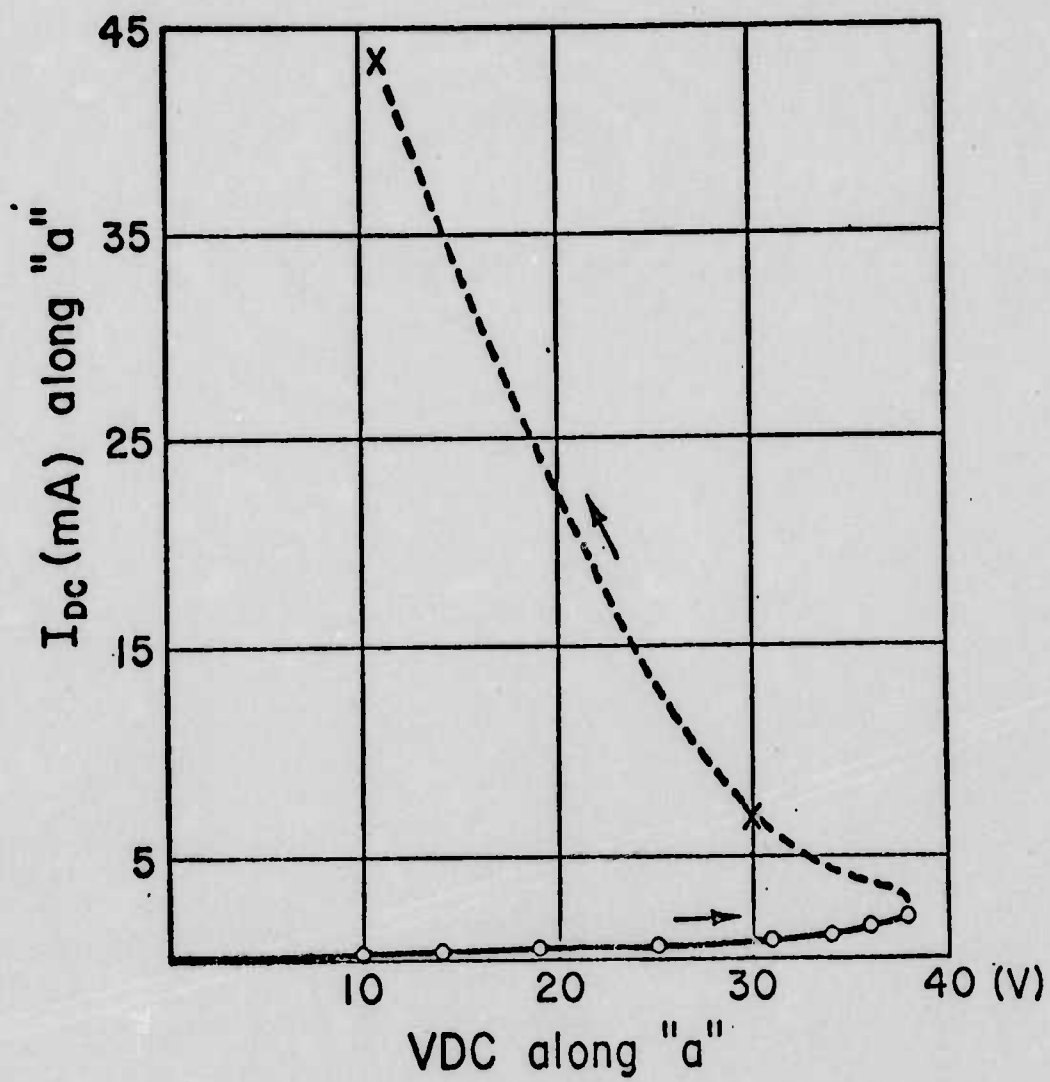


Fig. IV-6

$I_{DC}(11a)$ vs. $V_{DC}(11a)$

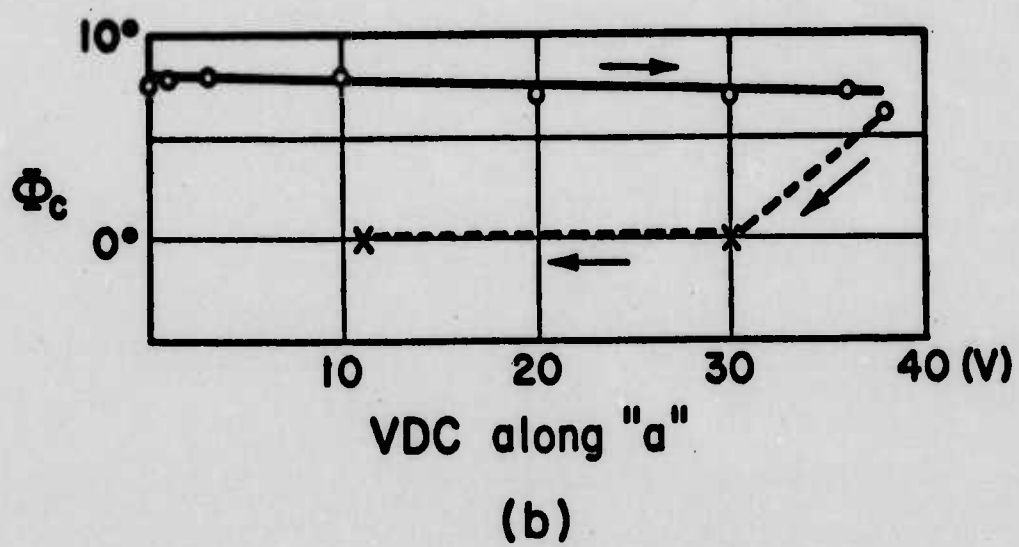
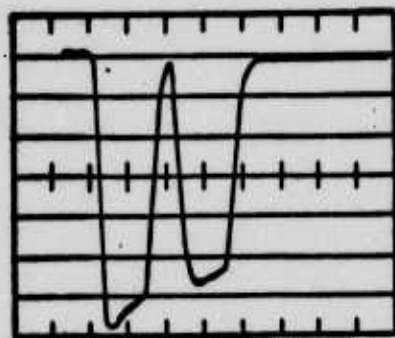
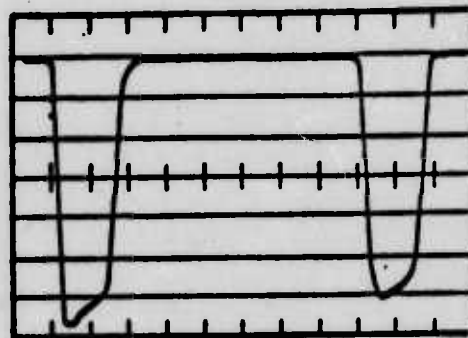


Fig. IV-7

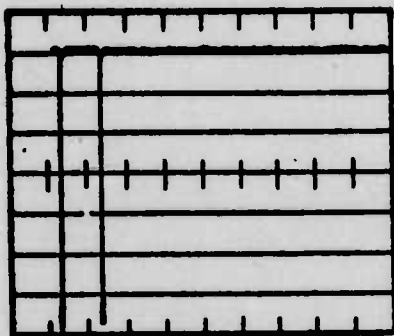
Phase difference ϕ_c between I_c and V_c in the "c" direction



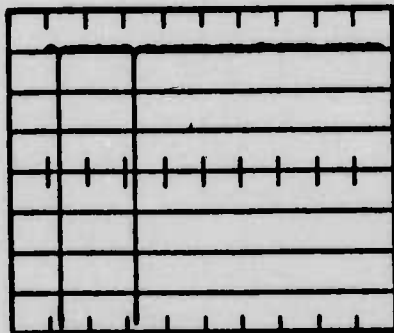
(a)



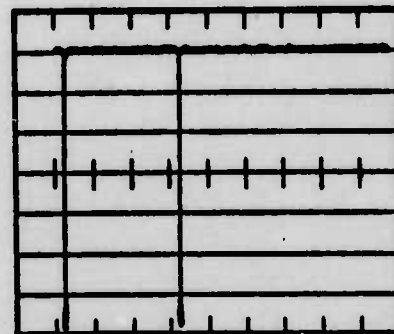
(b)



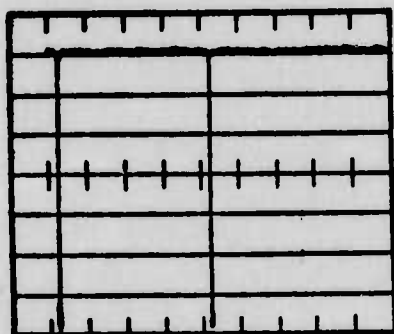
(c)



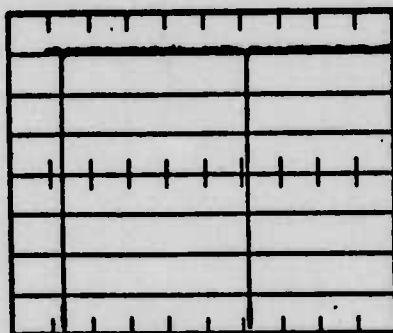
(d)



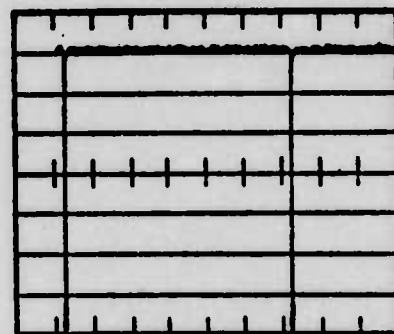
(e)



(f)



(g)



(h)

Vertical scale: 500 V/div

Horizontal scale: (a) and (b) 200 nsec/div

(c) to (h) 1 μsec/div

V - POLYCRYSTALLINE $\text{NbO}_{1.87}$ (D-TYPE DEVICE)

1) OBJECTIVE

To develop a polycrystalline form of devices capable of shunting transient current up to 80 A , in times shorter than 0.7 ns to meet specific requirements in the development of radiation and thermally hardened switching material for devices. Development goals were optimizing the nonstoichiometry of NbO_2 , since the switching voltage of nonstoichiometric NbO_2 is smaller than that of stoichiometric material.

2) INTRODUCTION

One of the difficulties in the mass production of such a NbO_2/NbO device is that the substrate has been obtained using a single crystal technology. While this material grows relatively easily, it is definitely an expensive step.

For this reason, it appeared reasonable to investigate the possibility of using nonstoichiometric niobium dioxide. In the process of studying nonstoichiometric NbO_2 we found that polycrystalline material of composition $\text{NbO}_{1.87}$ turns out to switch as the first type NbO_2/NbO does. The switching voltage is of the order of 170 to 200 volts and switching time when tested by Cpt. Laplante of USAECOM turned out to be the same as before, namely switching times faster than the resolution of the apparatus (about 0.7 ns). In addition, we found that the power handling capability is far better than those NbO_2/NbO devices.

3) PREPARATION OF POLYCRYSTALLINE $\text{NbO}_{1.87}$ SPECIMEN

Niobium metal and Niobium pentoxide powder produced by Johnson Matthey Chemicals Ltd. was weighed appropriately, pressed into pellets and then melted in a tri-arc furnace. $\text{NbO}_{1.87}$ crystal was pulled from the melt using NbO_2 single crystal seed. Details of the equipment and methods of operation are described earlier in Section II. The boules weighing several grams each were not single crystalline but denser than the melt. The oxygen gradient along the growth

direction was found to affect the switching threshold voltage. Specimens were cut from two different portions, top (#1) and middle (#2) part of the boule. Both specimens were tested at USAECOM by Cpt Laplanche.

4) RESULTS ON POLYCRYSTALLINE $\text{NbO}_{1.87}$

The specimen of polycrystalline $\text{NbO}_{1.87}$ were cut into approximately cube, 1.2 x 1.2 x 1.16 mm in dimension, and mounted in a 1N23 diode package. The contact was made with tungsten whisker.

i) Threshold voltage

One measurement was made with 6ns pulse width on top and middle cut specimen to determine the variation in threshold voltages with application of a single shot. The measurements of threshold voltage is comparable to those of previous investigations on NbO_2/NbO (Fig.V-1). It appears that the threshold voltage range was less spread compared to that of the NbO_2/NbO devices. In order to attenuate the signals, a 1000:1 probe was used. Therefore all the readings of vertical deflection recorded in the photographs correspond to volts/div. instead of mV/div. as recorded.

ii) Switching times

The switching from the high impedance to the low impedance state occur in times shorter than the resolution of the apparatus (≤ 0.7 ns). Thus switching time is quite similar to that of NbO_2/NbO and these $\text{NbO}_{1.87}$ devices exhibit essentially no delay for sufficiently high voltages (Fig. V-2)

iii) Power Handling capability

One measurement was made with 160 ns pulse width and 2000 V (80 A or Amperes limiting), and the other one was made with 1 ms pulse width and 1000 V (11 A limiting). All results are shown in Table V-1.

The polycrystalline $\text{NbO}_{1.87}$ (#1 specimen) with W-whisker contact could take more than 50 pulses when 160 ns, 2000 volts, (80 A) applied. This is remarkable compared to that of regular NbO_2/NbO devices. At most an NbO_2/NbO device could take only single pulses when contact was made with a tungsten whisker, and eventually melted and shorted to the NbO surface (See

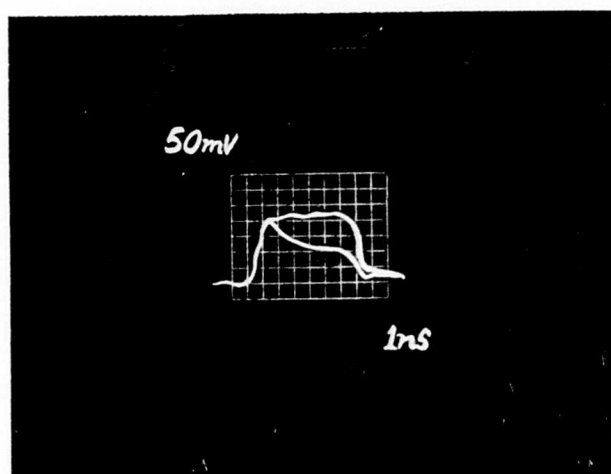


Fig. V - 1

Oscilloscope trace showing threshold voltage in a
 $\text{NbO}_{1.87}$ device under 6 ns pulse width

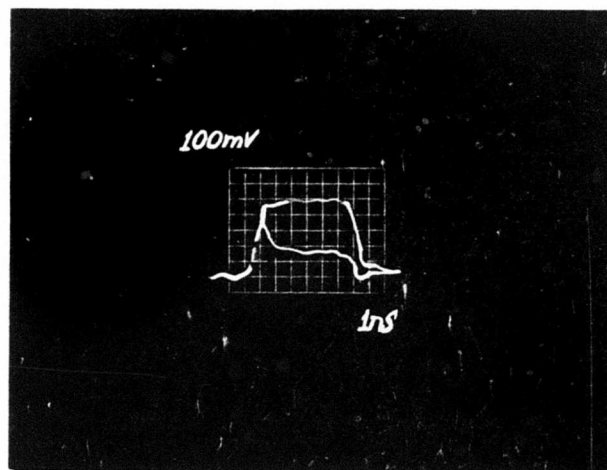


Fig. V - 2

Oscilloscope trace showing fast (≤ 0.7 ns) switching
in a $\text{NbO}_{1.87}$ device under 6 ns pulse measurement

TABLE V-1

Threshold Voltages of $\text{NbO}_{1.87}$ Devices

	Thickness	Contact	$V_{th}(1)^*$	$V_{th}(2)^{**}$
#1 (top)	0.046"	W-whisker	260 volts	35 volts
#2 (center)	0.056"	W-whisker	170 volts	-

* $V_{th}(1)$ was measured with 6 ns pulse width

** $V_{th}(2)$ was measured with 160 ns pulse width.

Fig.II-6). However, Cpt Laplante found that if contact was made with a Nb-ribbon (Fig.V-3), the NbO/NbO_2 device could take more than 50 pulses with 2000 volt-pulses without serious damage. For 1 ms pulse width, #1 sample with Nb-ribbon contact could take more than 95 pulses with 1000 volts (11 A limiting) again without serious damage. These measurements demonstrated that the power handling capability of the polycrystalline $\text{NbO}_{1.87}$ is far better than that of the previous NbO_2/NbO devices.

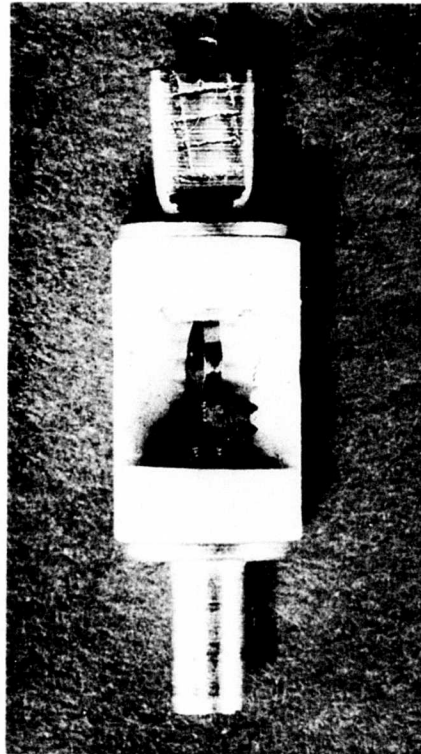


Fig. II - 5(B)

Tungsten whisker in 1N23 microwave diode package
was replaced by Nb-ribbon. The $\text{NbO}_{1.87}$ polycrystalline
device is mounted.

TABLE V-2

Comparison of switching characteristics between $\text{NbO}_2/\text{NbO}_2$ (A-type) Devices and $\text{NbO}_{1.87}$ (D-type) Devices

	NbO_2 film	$\text{NbO}_{1.87}$ ² (#1)	Remarks
V_{th} (1) ¹ (volt)	240 ~ 500	260	6 ns pulse W-whisker contact
V_{th} (2) (volt)	40 ~ 60	35	160 ns pulse W-whisker contact
Longevity test (# of pulses)	1 ~ 2	>50	160 ns, 2KV & 80 A pulses taken by devices W-whisker contact
Longevity test (# of pulses)	>50	-	160 ns, 2 KV and 80 A pulses taken by devices Nb-ribbon contact
Longevity test (# of pulses)		>95	1 ms, 1 KV, 11 A Nb-ribbon contact
Switching time (ns)	< 0.7	< 0.7	The resolution of the apparatus is ~ 700 ps.

1 - V_{th} determined by minimum voltage needed to switch device for a 6 ns pulse width. Threshold voltage varies depending on thickness of NbO_2 films (1 ~ 10 μm) as well as pulse width

2 - Sample thickness is 0.046"

VI. SWITCHING PROPERTIES

The field switching properties of NbO_2/NbO , stoichiometric and nonstoichiometric NbO_2 single crystal have been investigated. These include measurements of transient characteristics on NbO_2/NbO and DC measurements on $\text{NbO}_2 \pm x$, $x = 0.1$ as function of current and voltage.

The experimental measurements could be consistently interpreted in terms of the square-root field dependence of the Poole-Frenkel effect.⁸ It is hardly necessary to call attention to the fact that consistency does not imply correctness. As more results become available in the future experimentation, the conclusion reached below may be subject to alteration, but at this time, the Poole-Frenkel conduction via small polaron is adequate.

The I-V characteristic of a device, chosen to have a high threshold voltage is shown in Fig. VI-1. The curve was obtained at a different applied pulse voltage (100 ns pulse duration) and all occurring at the same time following pulse applications. For an applied voltage higher than the threshold voltage of 255 volts, the device exhibits the negative resistance behaviour to be expected from materials such as NbO_2 capable of undergoing a semiconductor to metallic transition and indicative of a filamentary process. Fig. VI-2 shows a plot of $\ln I$ vs. $V^{\frac{1}{2}}$ showing an electrode limited (Schottky barrier) to bulk limited conduction and then followed by a high conductive state. The values used in this graph are the same as those used before in Fig. VI-1. The graph clearly shows two successive straight lines at the lower values of V and I (see also Fig. VI-11). The points at which the straight lines character are interrupted may well have to do with the

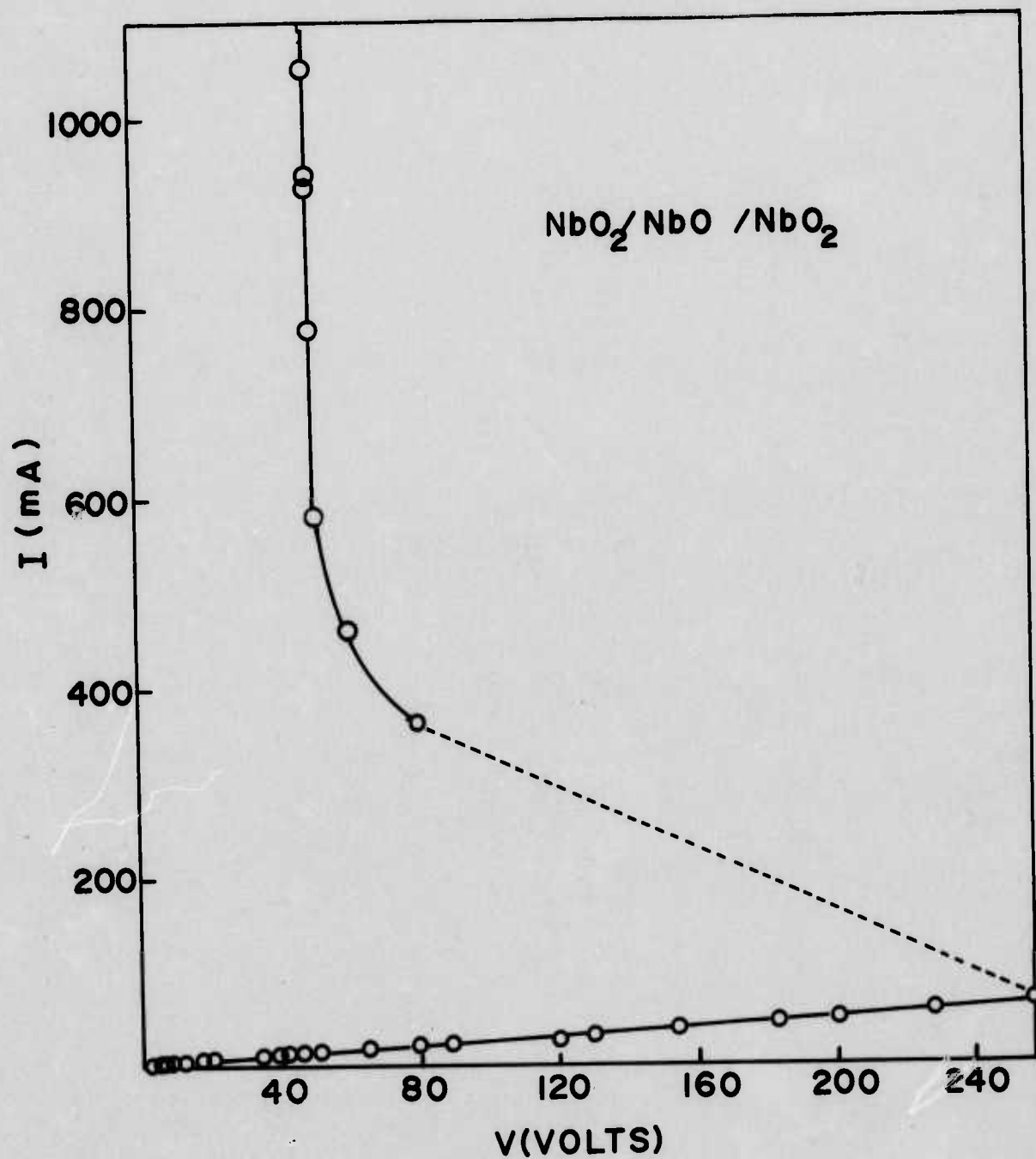


Fig. VI - 1

Current-voltage characteristic of NbO_2/NbO device
under pulse condition ($\tau = 100 \text{ ns}$)

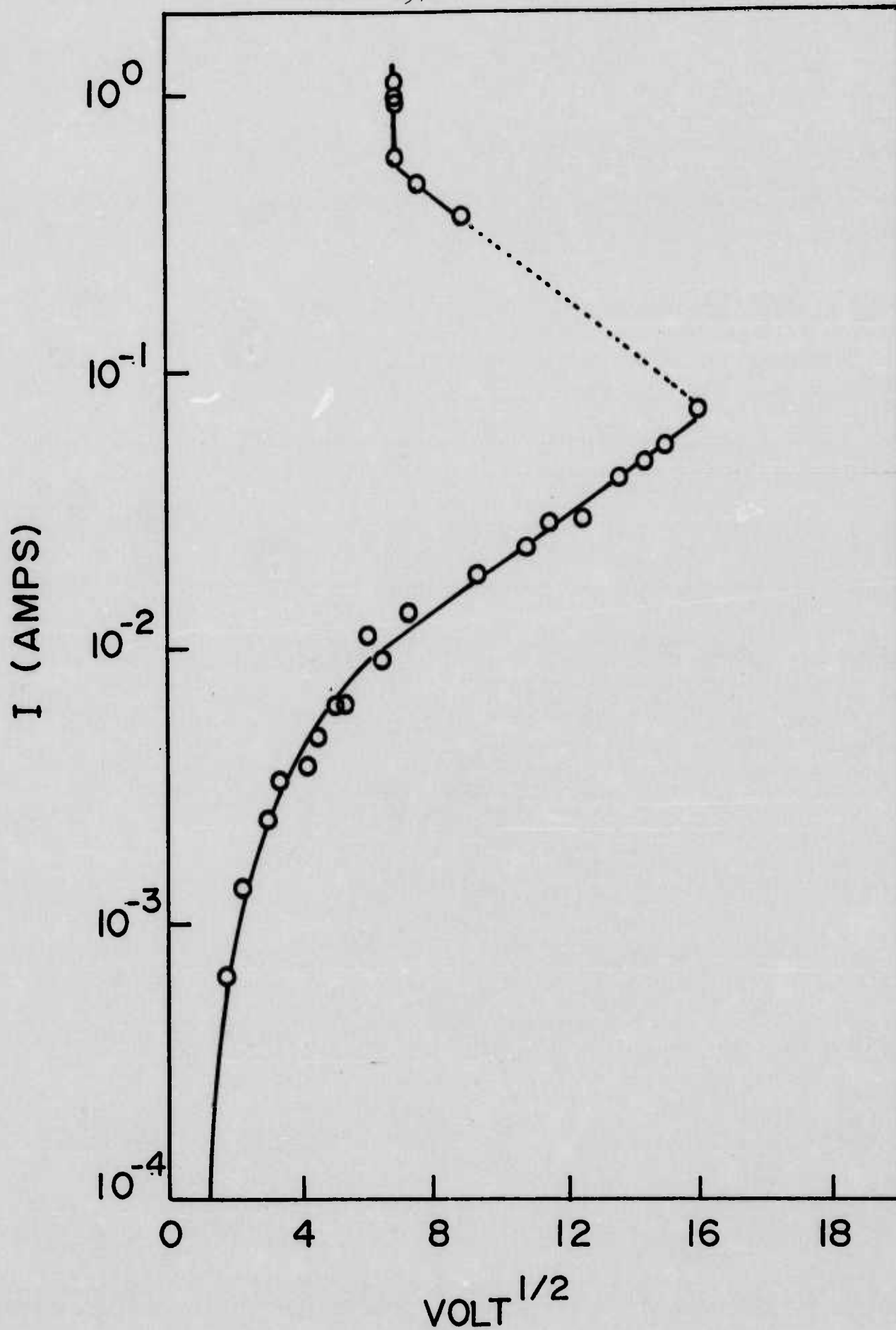


Fig. VI - 2

Linear dependence of $\log I$ vs $(volt)^{\frac{1}{2}}$ for NbO_2/NbO device

onset of a different mechanism for conduction. The linear dependence of $\ln V$ vs $V^{\frac{1}{2}}$ corresponds to the well known behavior of a Schottky barrier at the junction or Polle-Frenkel effect in the case of bulk material. These will be discussed later in detail, comparing them with d.c. measurements on NbO_2 single crystals.

In the past we experienced that there were always discrepancies in threshold voltages between our measurements and those of Capt. Laplante, USA ECOM. However, it was found that the minimum threshold voltage was dependent on the duration of the applied pulse. The variation of threshold voltages V_{th} with measuring time is shown in Fig. VI-4, as plot I vs. V for the same device with $\tau = 0.6 \mu$ to $10 \mu\text{sec}$. Attention is directed to the following features:

- 1) All the cases show common characteristics switching from a low conduction to a high conduction state, and a negative resistance region becomes readily apparent as shown in Fig. VI-4.
- 2) Fig. VI-5 shows the apparent parabolic increase in the threshold voltage from 25 volts when pulsed with $10 \mu\text{sec}$ pulse duration to over 360 volts when pulsed with 1 ns pulse width. A solid point in Fig. VI-5 was obtained from the average of ten devices measured by Capt. Laplante, USA ECOM (See table II-1). Empirically the following equation was obtained and is shown in solid line.

$$V_{th} = 372 e^{-\sqrt{t}/25}$$

It was noted that plots of $\log V_{th}$ vs $\sqrt{t}$ yielded a straight line. This is shown in Fig. VI-6.

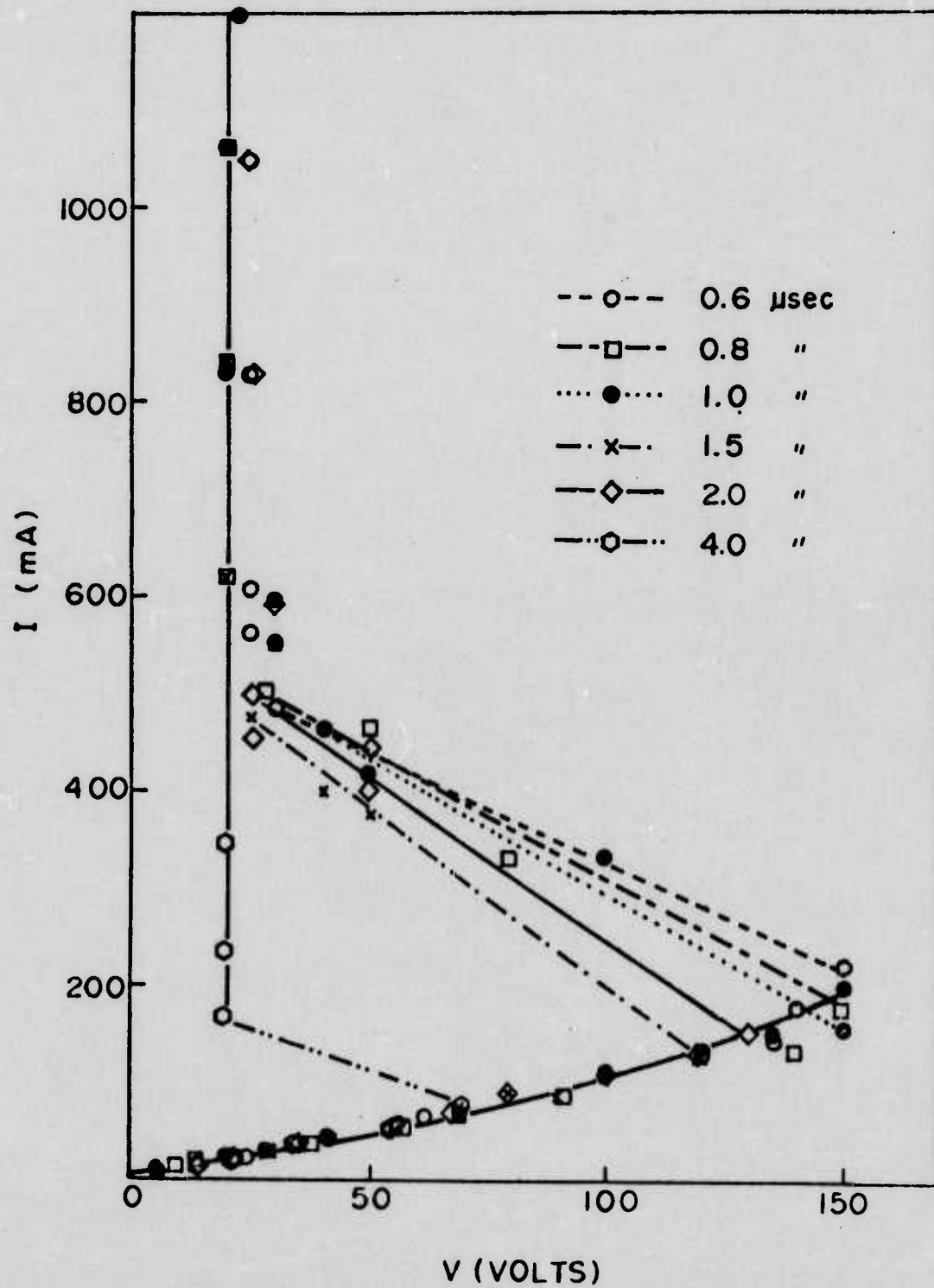


Fig. VI - 3

The variation of threshold voltage versus pulse duration (from 0.6 μsec to 4.0 μsec)

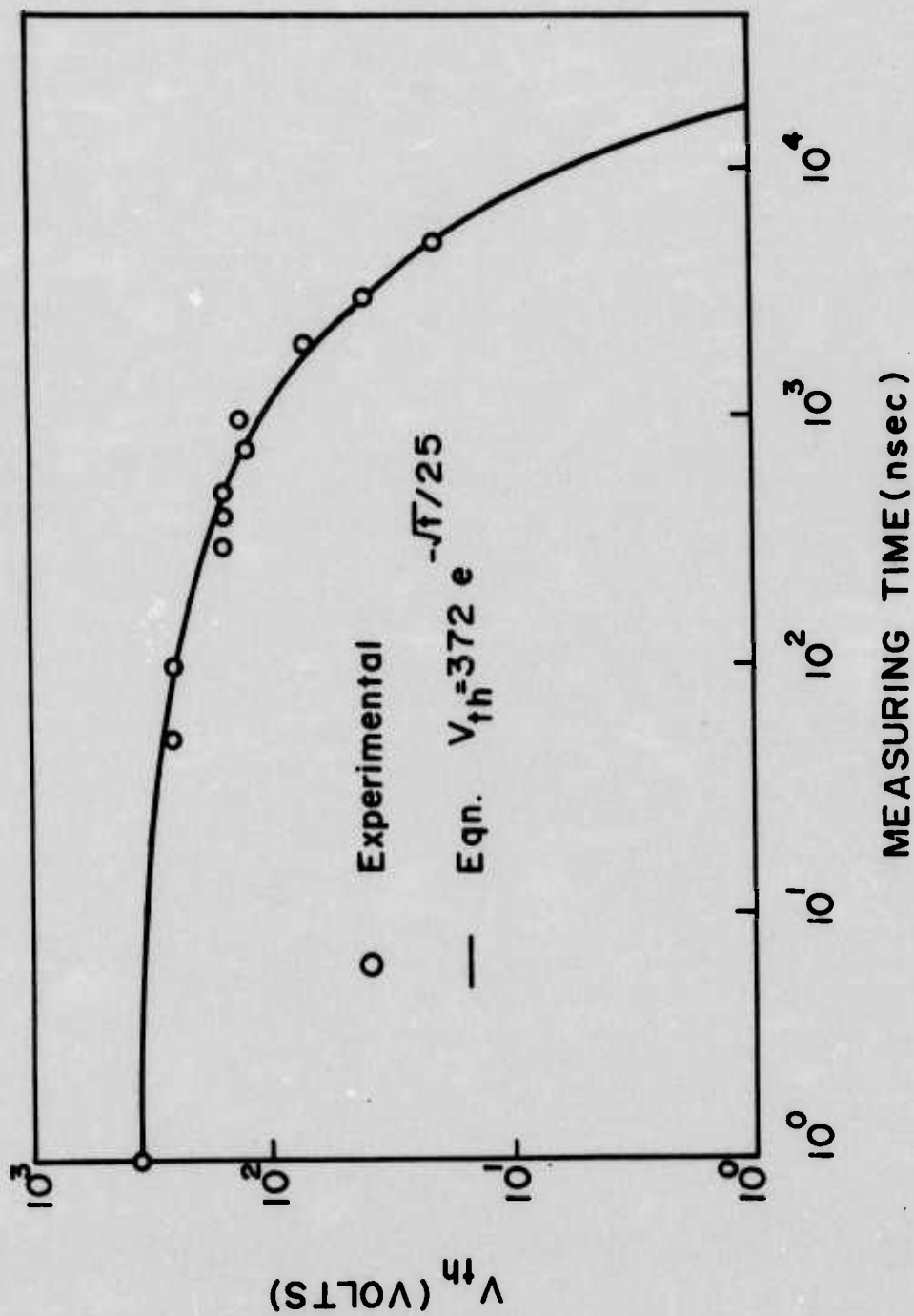


Fig. VI - 4

Threshold voltage (V_{th}) vs. measuring time (nsec)

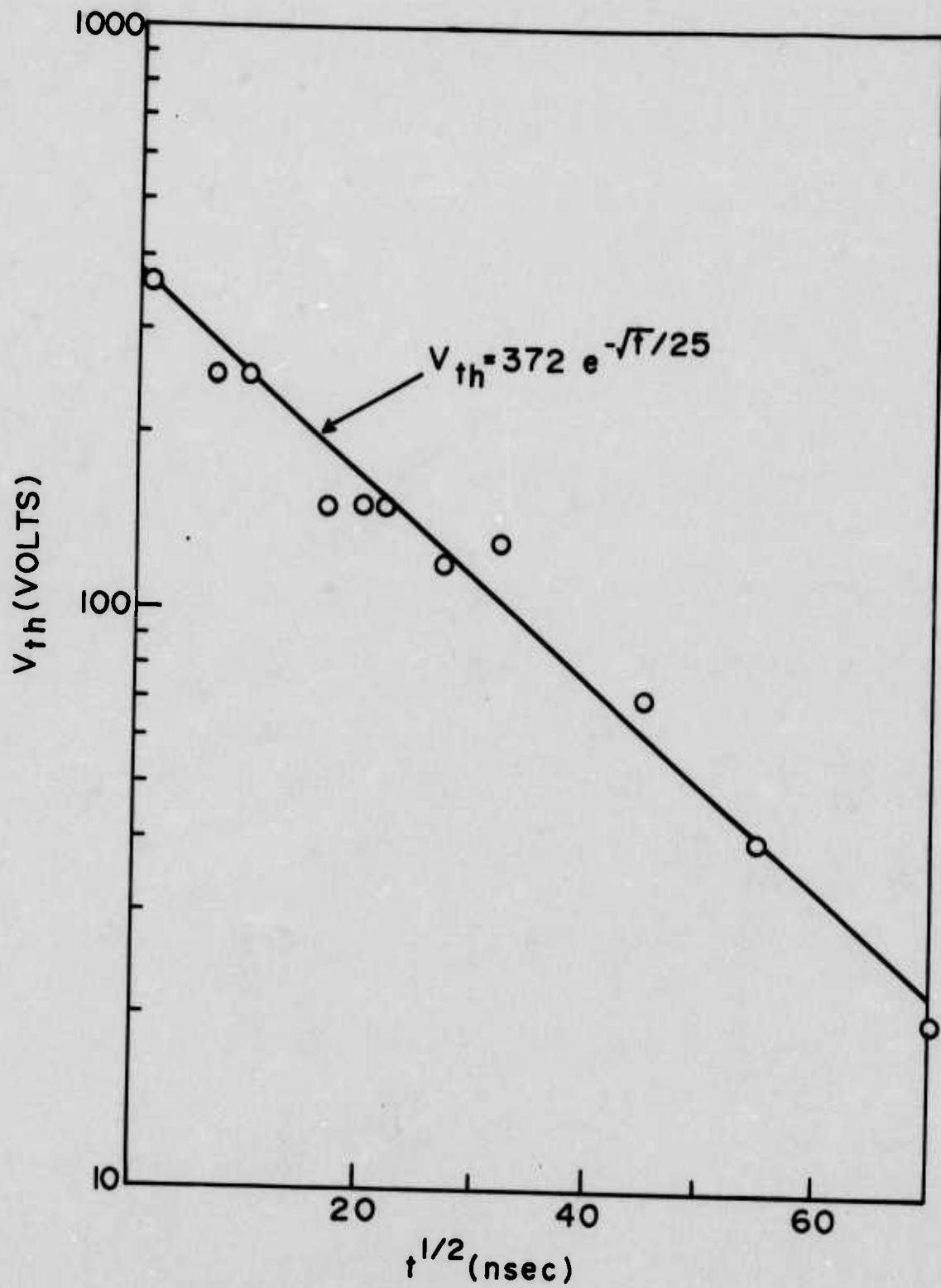


Fig. VI - 5

Threshold voltage (V_{th}) vs. $t^{\frac{1}{2}}(\text{nsec})$

3) This switching behavior is quite similar to a semiconductor-to-metallic transition at a threshold voltage V_{th} which decreases with increasing pulse width. For pulse duration $\tau \gtrsim 10 \mu\text{sec}$, the switching is suppressed for this typical device.

4) Inspection shows that in the metallic region, the resistivity under the various pulse duration closely coincide, and the device voltage reduces to about 20-25 volts after switching.

This device behavior under long pulse duration is quite different from that under short pulses ($\sim \leq 5 \text{ ns}$) described later in detail.

Since we experienced that threshold voltage change with the pulse duration, device characteristics should be examined with fast risetime and high current pulse. They were tested at USAECOM, Fort Monmouth, N.J., using a 50Ω cable discharge pulser capable of 700 ps risetime resolution, output voltage up to 2 KV (80 Amp) and a nanosecond pulse width. The typical I-V characteristic provided by Capt Laplante is shown in Fig. VI-7.

The difference of the results obtained when compared with the long pulse measurements is remarkable, as can be seen by comparing the I-V curves as shown in Fig VI-1 and Fig VI-2. Fig VI-7 demonstrates that in the high conduction state, the resistivity under the various pulse duration ($\tau \leq 5 \text{ ns}$) does not coincide at all and the threshold voltage is reduced to significantly lower values with increasing time. However, in all the cases described above, the devices show again some common characteristics, such as electrical switching, negative resistance and nonohmic electrical conduction.

The main difference between short pulse ($1 \text{ nsec} \leq \tau \leq 5 \text{ nsec}$) and long pulse measurements ($0.1 \text{ } \mu\text{sec} \leq \tau \leq 10 \text{ } \mu\text{sec.}$) should be the thermal effect in the case of a long pulse duration. For long pulses, because of temperature variation of the threshold voltage, heating effects might play a role. It was noted empirically that plots of IV vs $t^{1/3}$ yielded a straight line and compared to plotting of empirical equation of

$$IV = 825 \exp(-0.423 t^{1/3})$$

It is remarkable that short pulse (1ns) as well as long pulse measurements up to 5 μ sec. fit extremely well on a single straight line. This indicates that the heating effect on threshold switching might be excluded up to a 17 μ sec pulse, which corresponds to the time limit of our empirical equation. The square root time dependence of threshold voltage implies that up to a 17 μ sec. pulse threshold voltage depends on pulse width, and for a longer pulse become saturated approximately less than IV depending on constant term α . We estimated I, V and R at the threshold switching point when $t = 0$ and $t = 5 \text{ } \mu\text{sec.}$ and tabulated in table VI-1. It is very interesting that the threshold current of 2.2 A when $t = 0$, drops to 0.24 A when $t = 5 \mu\text{s sec.}$

In order to understand the bulk NbO_2 switching, we have studied DC measurements using thick NbO_{2+x} single crystal specimen with $x \approx 0.1$. DC measurements were made by applying constant current to the bulk NbO_2 specimen in a series with a resistor. Figs. VI-9 and VI-10 illustrate the I - V characteristic of $\text{NbO}_{2.00}$ specimen. Specimen were cut into cubes of an approximate 1.3 mm thickness and contact was made by platinum foil between sample and screw.

There are three well defined regions for each specimen with different stoichiometry. For the low current region ($i \lesssim 10^{-5} \text{ A}$) the resistance of the specimen was almost independent of current. Therefore in this region

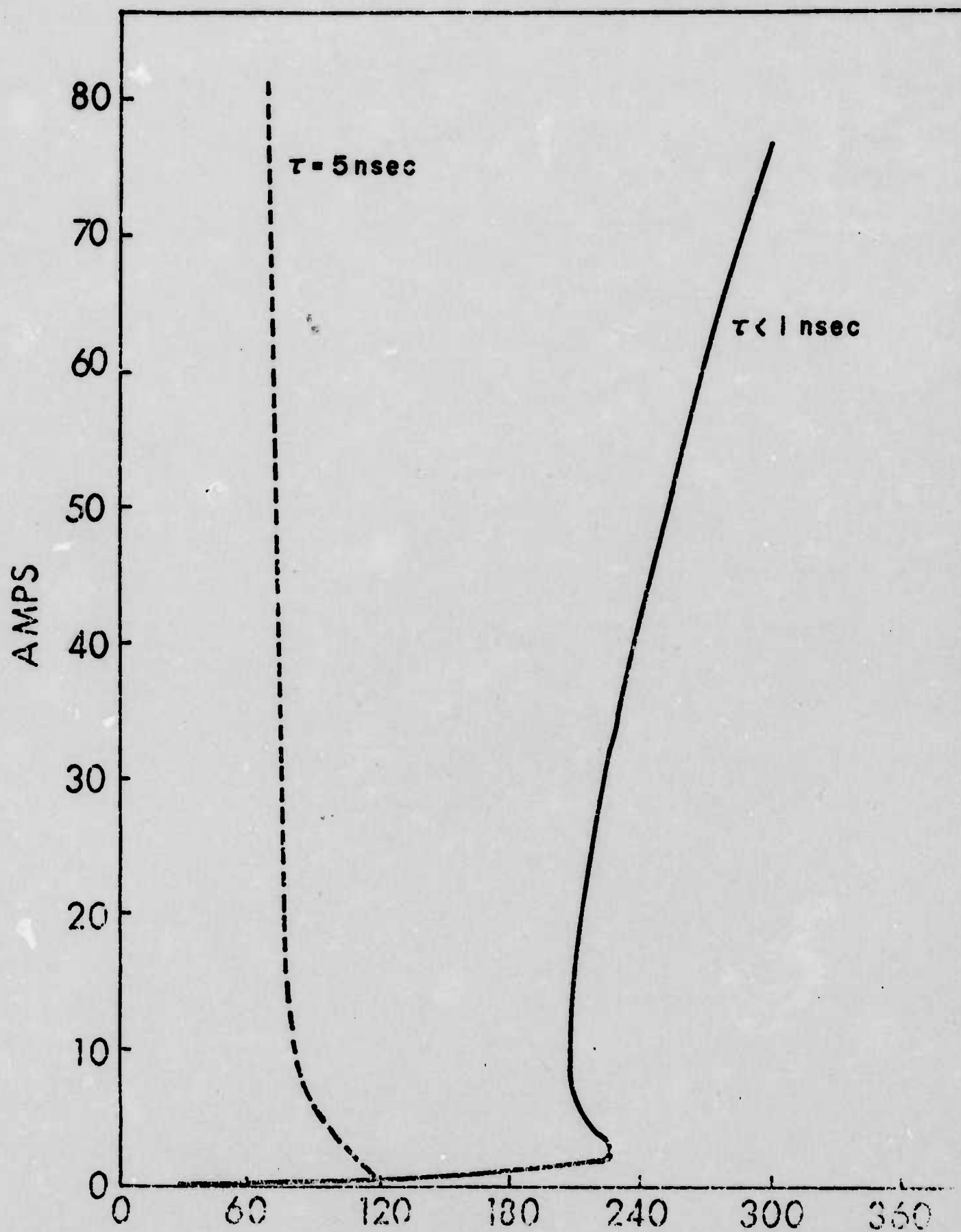


Fig. VI - 6

Current-voltage characteristic of NbO_2/NbO device
under fast pulse condition ($\tau = 5 \text{ nsec}$)

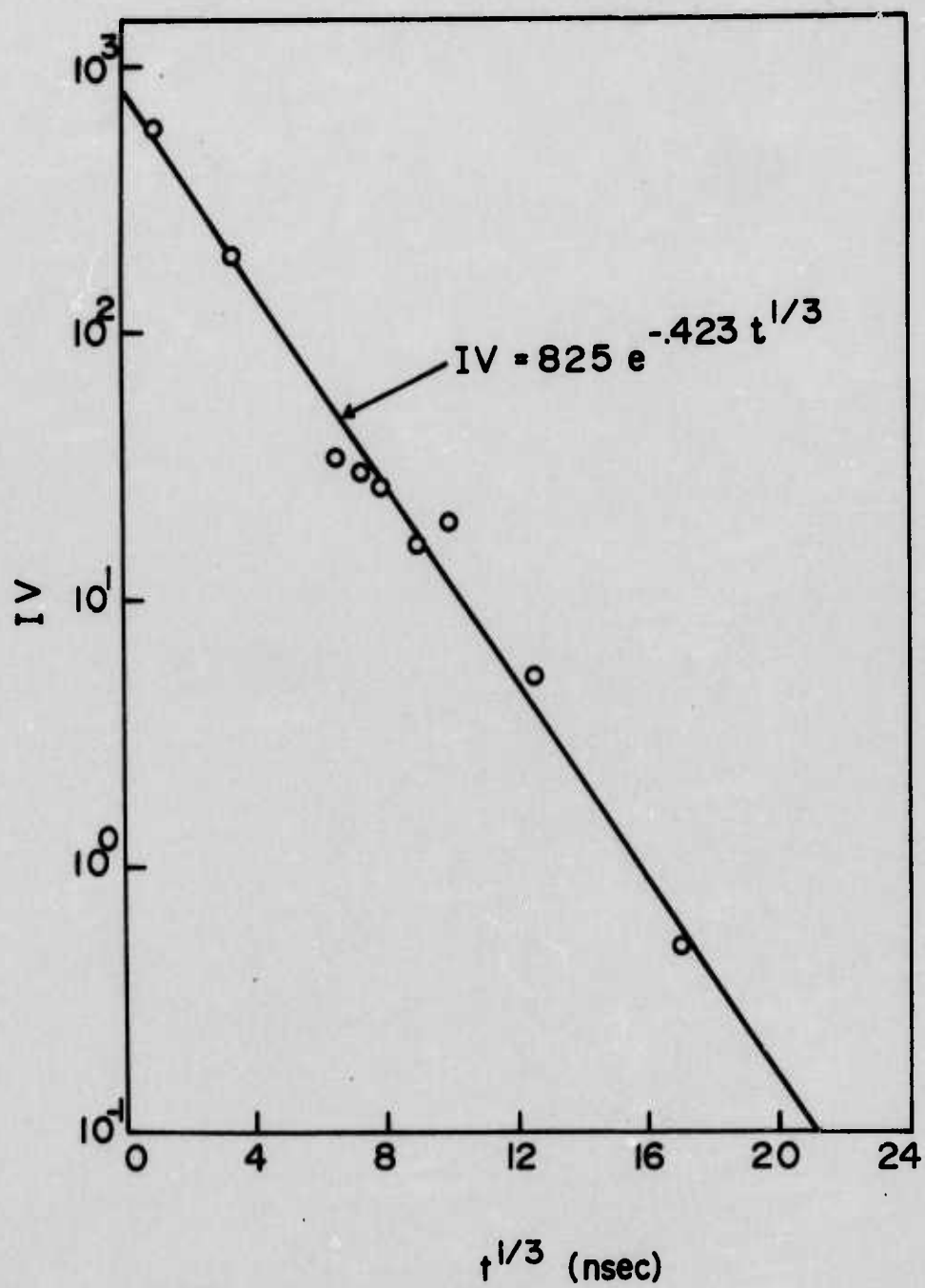


Fig. VI - 7

IV vs $t^{1/3}$ (nsec)

TABLE VI-1.

The estimated current, voltage and resistance of a NbO_2/NbO
at threshold switching point.

	$t = 0$	$t = 5 \mu \text{ sec.}$
I (Amp)	2.2	0.04
V (Volt)	372	22
R (Ohm)	1678	550

$$V_{th} = 372 \exp(-\sqrt{t}/25)$$

$$IV = 825 \exp(-0.425 t^{1/3})$$

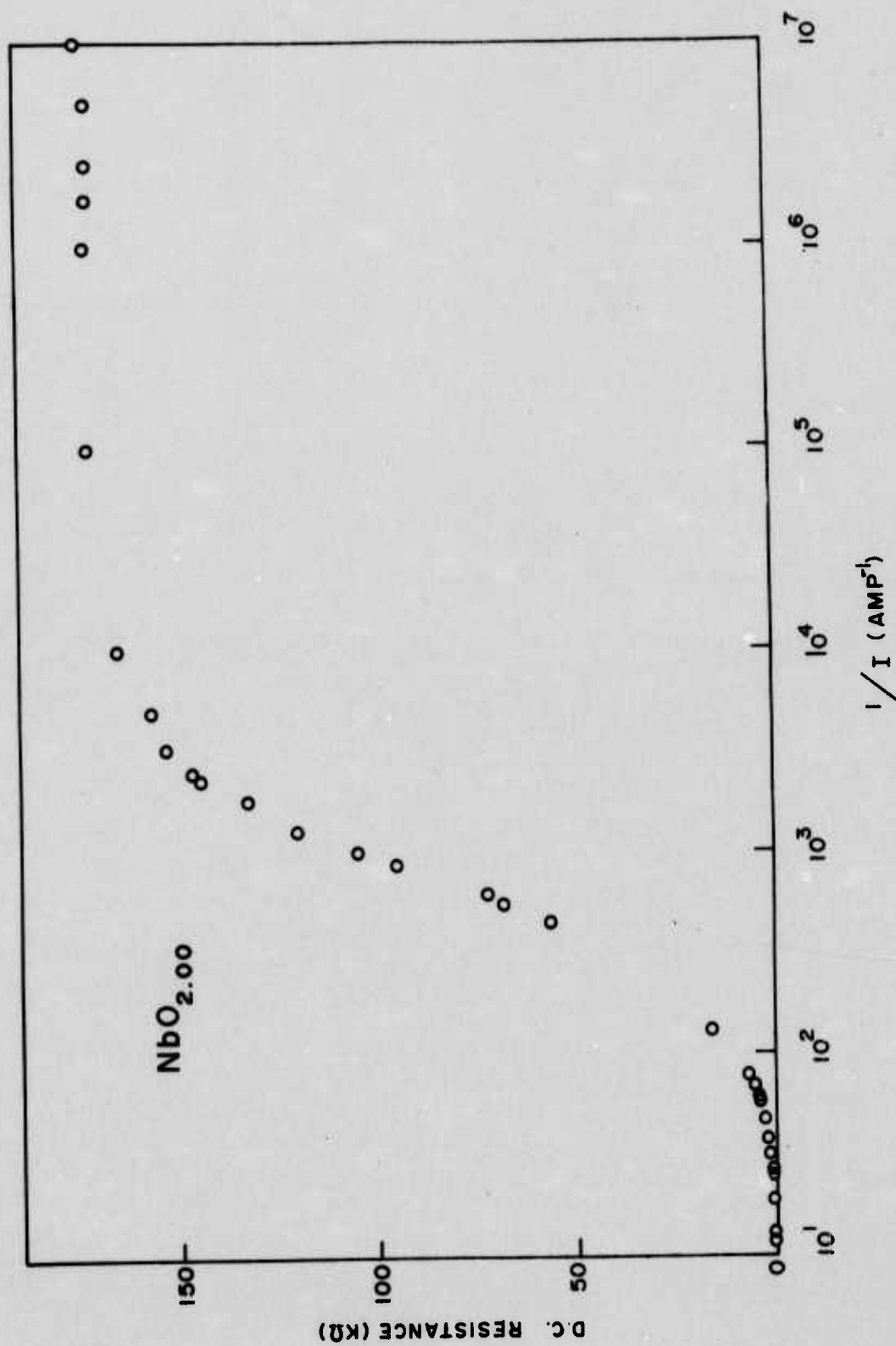


Fig. VI - 8
 R_{DC} vs $1/I$ (AMP⁻¹) for NbO_{2.00} single crystal

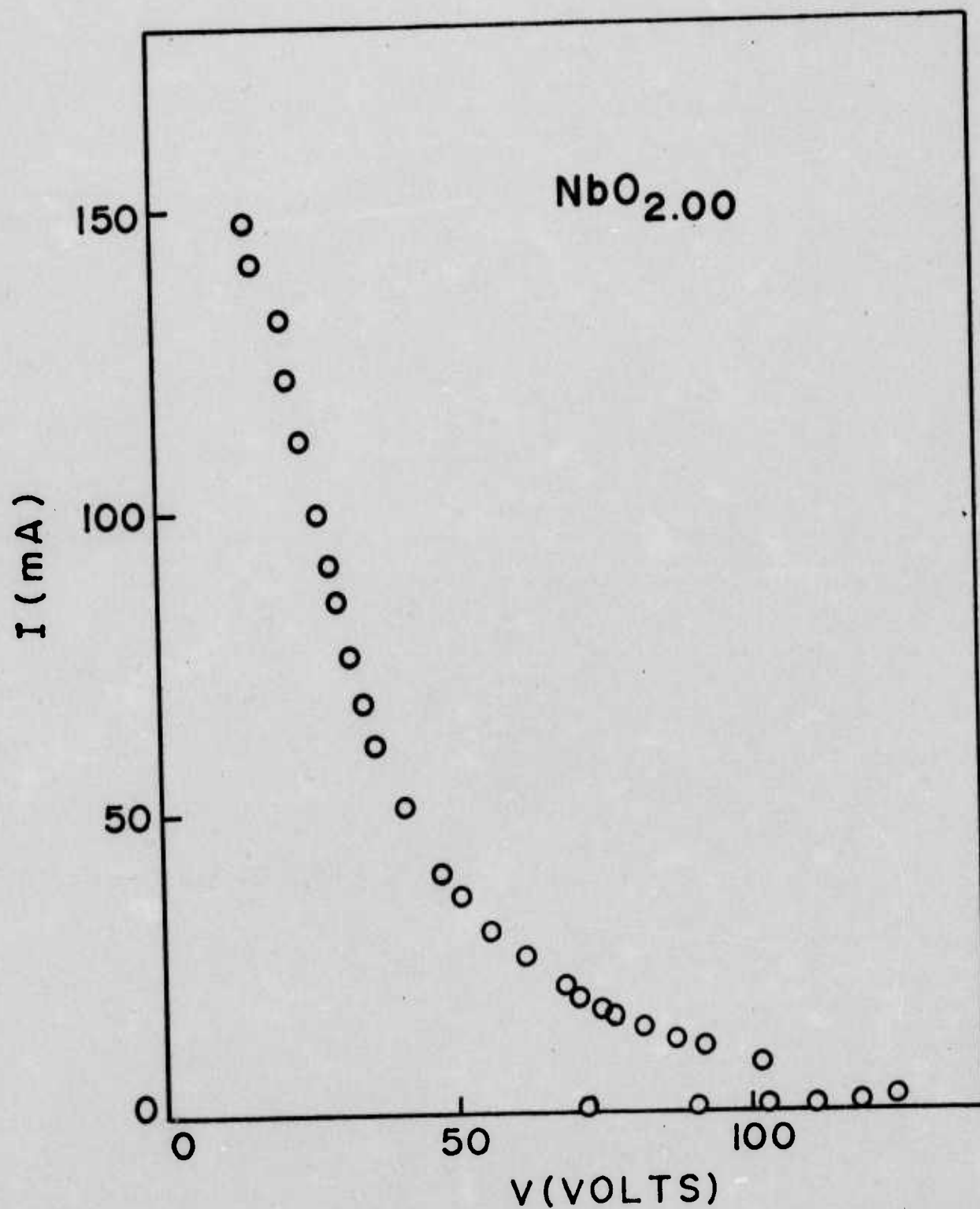


Fig. VI - 9

DC current-voltage characteristic of bulk NbO₂
single crystal

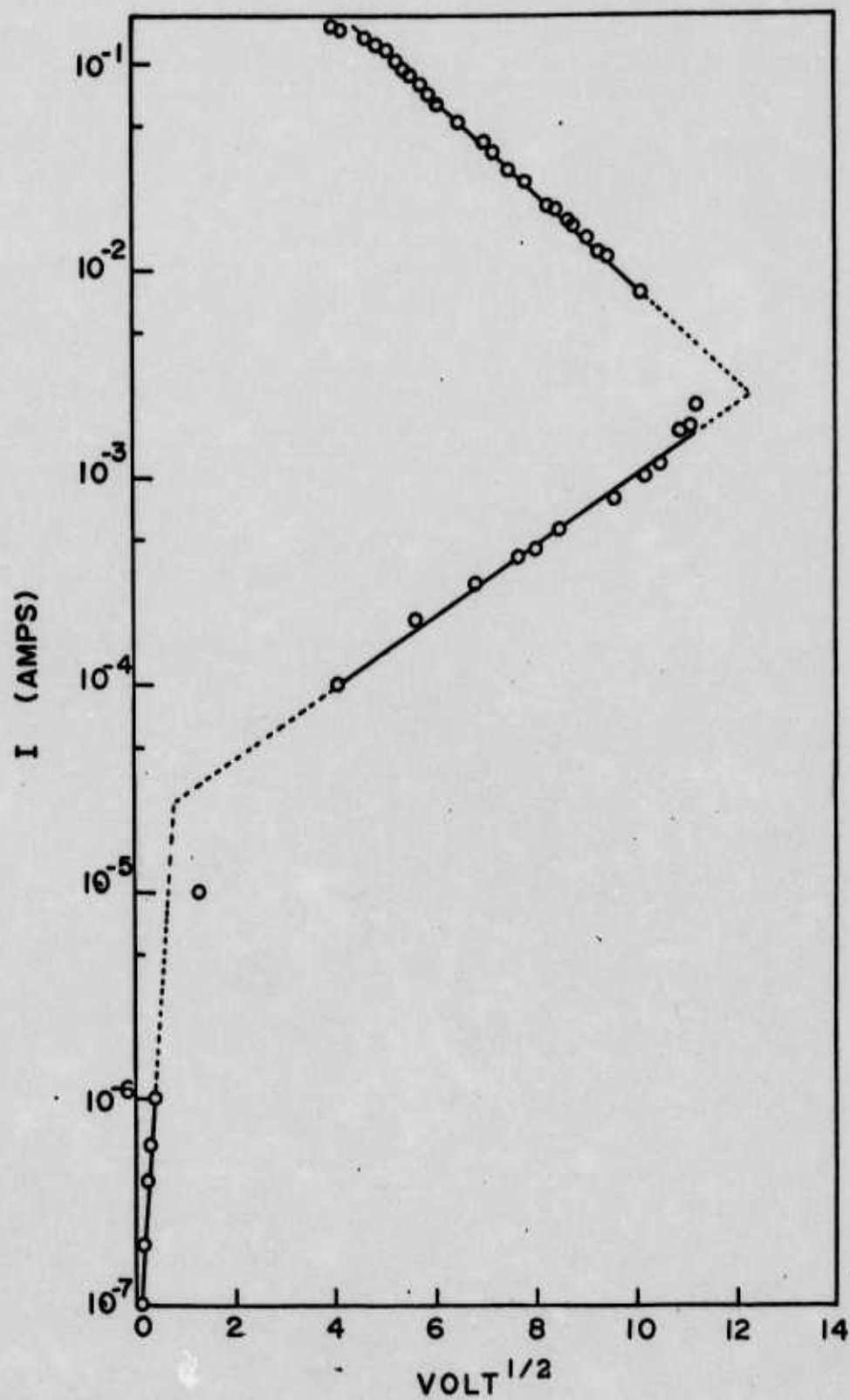


Fig. VI - 10

Linear dependence of $\log I$ vs $V^{1/2}$ on NbO_2 single crystal

the voltage across the specimen was following the ohmic law. For the intermediate current region (from 10^{-5} to 10^{-2} A), the voltage across the specimen increased rapidly, the resistance decreased exponentially and then switched to a high conduction state in I-V characteristic shown in Fig. VI-9. For higher current ($i \gtrsim 10^{-2}$ A to 1.4 A) the resistance decreases slowly and asymptotically approaches a limiting value (less than 8 ohm-cm) and then becomes a high conduction state. Fig. VI-10 shows a plot of I vs V for $\text{NbO}_{2.00}$ specimen. The data used in this figure are the same as the one used before in Fig. VI-9.

The graph clearly shows the similarity obtained by pulse measurements on NbO_2 film devices. The point at which switching occurred did not coincide with the starting point for decreasing resistance, and it corresponds to the minimum point of the linear portion in Fig. VI-9. This indicates that exponential decrease of resistance is followed by the electrical switching. Therefore, a nonohmic behavior was observed before the switching (definition of pre-switching).

Similar measurements have been done for non-stoichiometric NbO_2 , such as $\text{NbO}_{1.90}$ and $\text{NbO}_{2.10}$, and presented in Figs. VI-12 and VI-13. All the results are summarized in Table VI-2.

It is interesting to note that if NbO_2 bulk switching is controlled by current rather than voltage switching, current of $\text{Nb}_{2.00}$ is the lowest among three different stoichiometries, and it requires less power to switch it. However, DC threshold voltage of $\text{NbO}_{2.00}$ is much higher than those of other nonstoichiometric devices. In the past we experienced difficulties with bulk NbO_2 switching, since in the case of NbO_2 threshold voltage increases with the thickness of NbO_2 . Since we are interested in low threshold voltage material, it turns out that $\text{NbO}_{1.90}$ composition is far better than the other two compositions. Still the threshold voltage of these compositions is too high to switch to a higher conductive state under applied

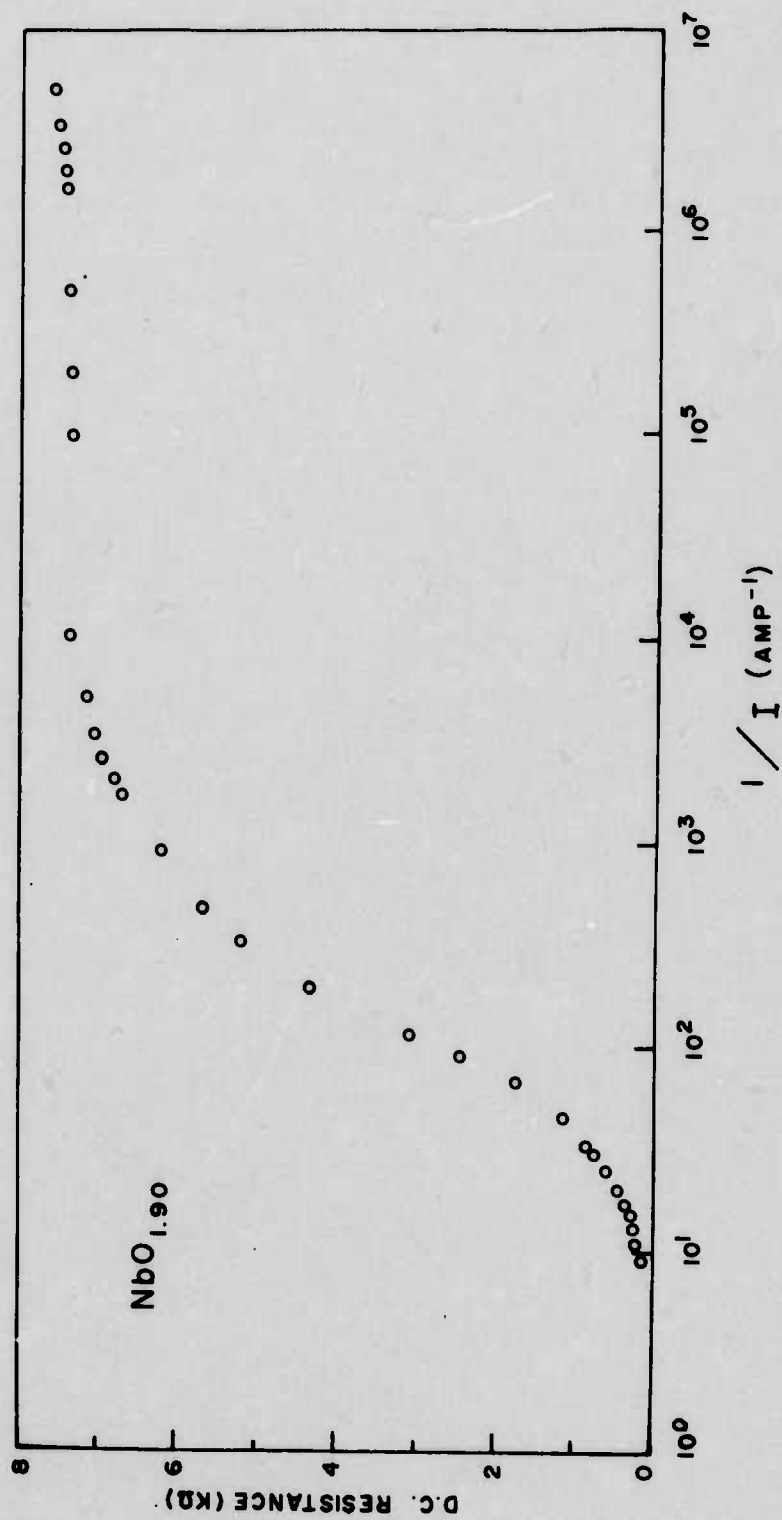
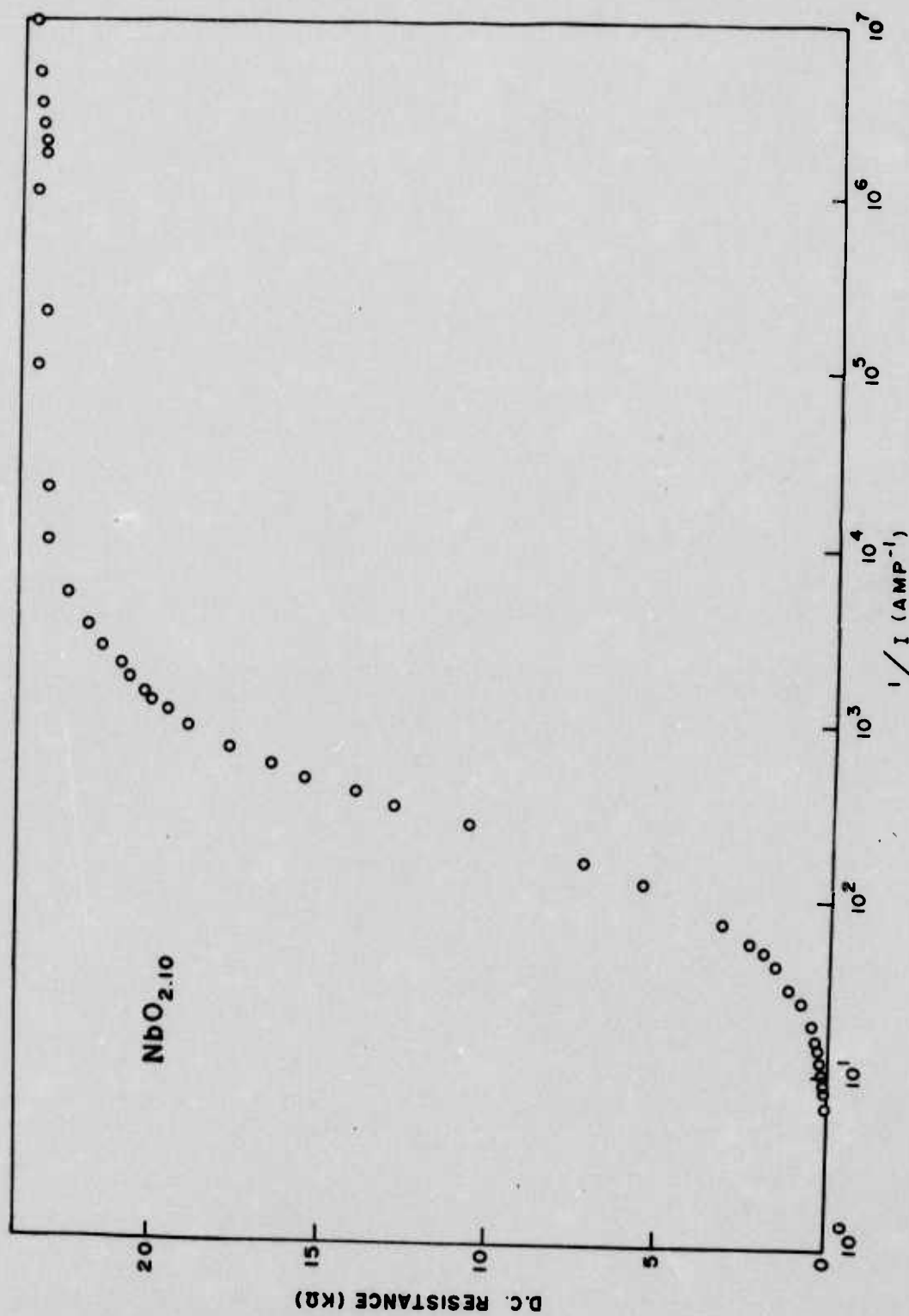


Fig. VI - 11

R_{DC} vs $1/I$ (AMP⁻¹) for NbO_{1.90} single crystal



R_{DC} vs $1/I \text{ (Amp}^{-1}\text{)}$ for $\text{NbO}_{2.10}$ single crystal

Fig. VI - 12

TABLE VI-2.

DC Measurements of $\text{NbO}_{2.00 \pm x}$ in relation to
Stoichiometry

	$\text{NbO}_{1.90}$	$\text{NbO}_{2.00}$	$\text{NbO}_{2.10}$
I_{th} (mA)	11.47	2.23	8.22
V_{th} (volt)	28	125	45.8
R_{th} (K Ω)	2.44	55.9	5.56
DC Resistance change between two regions } (K Ω)	8 - 0.15	175 ~ 0.10	24 ~ 0.12
I (at middle point of curve) (mA)	0.5	0.12	0.33

pulses. Therefore attempts were made to optimize an appropriate composition to meet the specific requirements as a transient suppressor. For the DC measurements, it is expected that thermal effects will be the most important role for the transition between two regions. We also experienced that for short pulse measurements (1 nsec) the NbO_2 layer on the NbO substrate was melted under an intense field (2 KV and 80 Amp). However, short pulse measurements at least minimize the preswitching heating and limit the temperature increase of the device. There is a strong evidence that excludes a theory of thermal switching. When a 3 mm thick $\text{NbO}_{1.87}$ sample was pulsed with 6 ns pulse width, it switched faster than that of resolution of apparatus and its threshold was more or less the same as thin NbO_2 film (1 to 10 μm). Furthermore, the DC threshold voltage increases more slowly than the thickness of the sample and tends to become almost independent of sample thickness.

Fig. VI-11 shows a plot of $\log I$ vs $V^{\frac{1}{2}}$ based on the same data as the one used for the plot of I vs. V in Fig. VI-9 and VI-10. In this figure it can be seen more clearly that all data points fall now in a successive straight line in the "off" as well as "on" state. This region again appears to be consistent with a square root voltage dependence of Schottky effects, as well as the Poole-Frenkel process. After the switching point, logarithmic current increased while the square root voltage across the device decreased. This regime appears to be consistent with a metallic state with a high conduction process.

In summary, there is some experimental evidence of a Schottky barrier as well as the combined effect of two successive regions of square root field dependence on the conduction mechanism. It is worth indicating here that NbO_2 material has a second-order semiconductor-to-metallic transition at 1070°K. According to transport measurements summarized in Table VI-3, it

Table VI - 3

Summary of low temperature transport data in niobium dioxide*

	T = 300°K	T = 435°K	Activation Energy, e.V.
<u>Current parallel to the a-axis</u>			
Resistivity, ohm-cm	3509	22.4	0.44
Hall coefficient, cm ³ /C	1377	13.6	0.40
Hall mobility, cm ² V ⁻¹ sec ⁻¹	0.40	0.60	-0.035
Drift mobility, cm ² V ⁻¹ sec ⁻¹	0.016	0.114	-0.17
$\mu_H \cdot T^{3/2}$, cm ² V ⁻¹ sec ⁻¹	2045	5365	-0.083
Polaron density, cm ⁻³	1.11×10^{17}	2.44×10^{18}	-0.27
<u>Current parallel to the c-axis</u>			
Resistivity, ohm-cm	824	11.6	0.37
Hall coefficient, cm ³ /C	517	6.7	0.38
Hall mobility, cm ² V ⁻¹ sec ⁻¹	0.63	0.58	0.007
Drift mobility, cm ² V ⁻¹ sec ⁻¹	0.068	0.22	-0.102
$\mu_H \cdot T^{3/2}$, cm ² V ⁻¹ sec ⁻¹	3270	5181	-0.040
Polaron density, cm ⁻³	1.11×10^{17}	2.44×10^{18}	-0.27

* data from Ref: 6

has low, anisotropic mobility ($\mu_d(11a) = 0.016$, $\mu_d(11c) = 0.63 \text{ cm}^2/\text{V sec}$) at room temperature and its temperature dependence is interpreted by thermal activation. Furthermore, the ratio of Hall mobility to drift mobility is much larger than one, and the drift and Hall mobilities differ also in their temperature dependence. These transport properties in NbO_2 demonstrate that the mobility in the low temperature phase can be described in terms of the small polaron picture.

To begin, it is noted that two successive linear relations for a plot of $\ln I$ vs $V^{\frac{1}{2}}$ is in excellent agreement with Schottky and Poole-Frenkel law. Particularly the Poole-Frenkel effect in insulators is the field lowering of a Coulombic potential barrier of traps which are positively charged when empty and neutral when occupied by an electron.

Recently Anett and Klein⁹ considered some physical origins for neutral traps, and analyzed their field lowering and high field conduction effects in terms of attractive power-law potentials and compared predictions with experimental results. Indeed small polarons provide a possible source of neutral traps. These partially localized electronic states occur under conditions of low electron mobility and strong electron-phonon interaction such that the slow moving electron polarizes the lattice to the extent that a bound state is formed.

Furthermore, Simmon pointed out that it was possible to observe an electrode limited to bulk limited transition in the conduction process if insulators contain a high density of traps.

Since the contact resistance is much higher than that of bulk NbO_2 , it follows that I-V characteristics will be virtually thickness independent and very steep, as shown in Fig. VI-11. However at some voltage, the contact

resistance falls to a value equal to that of the bulk since contact resistance decreases much more rapidly with increasing voltage than the bulk resistance. Thus at transition voltage, the combined effect of the contact and bulk resistance will appear at the actual characteristic of the junction.

Thereafter, all of the voltage in excess of about 5 volts in Fig. VI-2 (~ 1 volt in Fig VI-11) will fall across the NbO_2 layer, and finally the remaining bulk resistance decreases almost exponentially. These field lowering effects on Schottky barrier and high field conduction are then immediately followed by filamentary process thermal runaway. The fast pulse measurements indicate that for 500 V applied pulse voltage, the current rises as much as 78% within 10 ns and over 50% within 2 ns. The voltage across the device dropped from 500 to 250 V within 2 ns. However this does not indicate any time scale for switching, because our devices exhibit essentially no delay (≤ 0.7) for sufficiently high voltages (above threshold) before switching occurs. At this point, this post-switching negative resistance path with an 80% reduction in voltage in the first 10 ns would appear to correspond to a Schottky barrier breakdown and also the bulk-limited conduction process due to the Poole-Frenkel effect. In the region in which switching occurs, a power law $I \propto V^{1.0}$ is followed abruptly by $I \propto V^{-1.0}$ after switching. This sudden change in power law might be related with the collapsing of a particular gap as the field lowered the barrier. The reason for this change requires further study.

VII. Conclusion and Recommendation.

In conclusion, the polycrystalline form of devices ($\text{NbO}_{1.87}$) demonstrated experimental evidence to meet the specific requirement of radiation and thermally hardened switching material for devices. This shows a natural substitute for the more sophisticated single crystal technique and promises remarkable speed and power handling capabilities of new devices.

The switching mechanism appears to proceed in two stages which could be electrode limited Schottky barrier breakdown and bulk limited field lowering process of NbO_2 , then followed by a thermal runaway. Although the $\ln I \sim \sqrt{E}$ behavior covers the large range of current and electric field values, in the high field regime the data is fit to $\ln I \sim E$ or $\ln I \sim E^3$ behavior. The latter process is associated with the conduction mechanism of small polarons.¹⁰ Therefore, the $V_{th} \sim \exp(\sqrt{t})$ relation could be understood via frequency-dependent mobility in NbO_2 devices. However, it is somewhat uncertain whether the observed switching should be related to the avalanche breakdown or it should be due to delocalization of small polarons. Switching time of our devices is much faster than that of amorphous material switching and it exhibits essentially no delay for sufficiently high voltages above threshold voltages.³ And a sudden increase in threshold current of a device with increasing voltage cannot be due to thermal effects and necessarily has to be of an electronic nature. However, a field induced transition would not distinguish whether the transition is thermal or electronic in nature.

More work is needed in order to understand the nature of the processes taking place during switching. In particular, further attention needs to be given to the fact that carrier mobility in NbO_2 can be described in terms of small polarons. It would be very interesting to undertake a study of the mobility change as the function of a.c. frequency and electric field. Since a small polaron is due to a lattice polarization and any changes in this local polarization will greatly influence the dielectric constant, a field and temperature dependent dielectric constant might reveal much more information about the details of the mechanism. A mean free path in NbO_2 by photoemission measurements would be very useful to distinguish the possible carrier multiplication in the switching process.

References

1. T.B. Reed, Mater. Res. Bull. 2, 349 (1967).
2. G.V. Chandrashekhar, J. Mayo and J.M. Honig, J. Solid State Chem. 2, 523-530 (1970).
3. G.K. Gaule, P.R. Laplante, S.M. Shin, T. Halpern and P.M. Raccach, Metal-Oxide (MOX), Subnanosecond Transient Suppressors, IEEE Washington Component Conference, April 15, 1975.
4. T. Sakata, K. Sakata, G. Hofer and M. Mariachi, J. Crystal Growth, 12, 88 (1972).
5. S.H. Shin, F.H. Pollak and P.M. Raccach, Bull. Am. Phys. Soc. 19, 536 (1974).
6. G. Belanger, J. Destry, G. Perluzzo and P.M. Raccach, Can. J. Phys. 52, 2272 (1974).
7. R.F. Jannik and D.M. Whitmore, J. Phys. Chem. Solids 27, 1183 (1966).
8. J.G. Simmons, Phys. Rev. 166, 912 (1967).
9. P.C. Arnett and N. Klein, J. App. Phys. 46, 1399 (1975).
10. See, for example, N. Fuschillo, B. Lafevic and B. Leung, J. Appl. Phys., 46, (1975) and references therein.

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