PRNC 21 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 ---Page Break--- STUDY OF RADIATION DAMAGE IN ORGANIC CRYSTALS USING ELECTRICAL CONDUCTIVITY Amador Cobas and Harry Semant - Principal Investigators Conchita Zuazaga - Research Assistant Progress Report #1 Work performed at Puerto Rico Nuclear Center Rfo Piedras, P. R., under U.S. Atomic Energy Commission Contract AT(40-1)-1833 (Project 14) July 1963, ---Page Break--- TABLE OF CONTENTS Introduction Section I. Results of Preliminary Work and Discussion Section II. Radiation Damage Measurements Section III. Discussion of Radiation Damage Results BIBLIOGRAPHY ---Page Break--- 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 of 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. 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 the 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.

---Page Break--- -2- ‘The effect of neutron irradiation on anthracene has been studied previously by Komandeur (3,4), but to our best knowledge, no other work on this subject has appeared since then. Since Komendeur'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 1. RESULTS OF PRELIMINARY WORK AND DISCUSSION. Using the Kalimann-Pope technique (2), we have grown single crystals of anthracene using Eastman-Kodak anthracene X-480 and H-460. They range in thickness from 10 to 70 μm and from 0.3 mm over 1 cm. These crystals were obtained from ethylene chloride and xylene as received from the supplier (Gastman) 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. Kalimann-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 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 Kalimann-Pope cell, have shown that the electrodes are completely symmetrical, that 41 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 T. TABLE 1. SYMMETRY OF CONTACTS (Dark Current) Applied Voltage (volts) 2 s+ x 10^13 amp > x 10^13

amp: 2 8.0 P80: 10 3210 32.0 30°: 60.0 2 160.0 100 300.0 30.0 130: 400.0 2 400.0: Ho: 400.0: 00:0 We also found that the current-voltage relation (in the dark) was ohmic up to 100,000 volts/em 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). ---Page Break--- As was found by all other investigators (9,10), we observed that the photocurrent flowing when the illuminated face of the crystal was at 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 NaT saturated 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 THROUGH ANTHRACENE Applied 3650A Photocurrent Voltage (no iodine) (volts): s+ 10^10 amp tt" x 10^10 amp: at/in 2 100 29 3.6 wo: (2050 810 2 256 20 3200 110 2291 50 3300 19.0 1% +200 3500 50.0 275.0 it and 17 refer to currents measured when the polarity of the side through which the 3650A light entered was positive and negative respectively. Intensity of 3650A light: 170 pleanent ---Page Break--- -5- TABLE III HOLE INJECTION INTO ANTHRACENE Applied 4360A Photocurrent voltage (iodine electrode): s(volts): s x 10^10 amp tr x 10^10 amp sate 2: 0.33: 0.07 and was: 0.10 240 2 = 105 18 583 50: 500 oat:

12200: 2200: 2700. 2 2.0. 21350 i+ and 4° 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 360A Light: 450 44 watt/ ca? Kallman 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 a tracer of tetracene and a band of 3600-4000Å. ---Page Break--- (On the other hand, the 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 4360Å 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 non-uniformly 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-volts 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. ---Page Break--- = 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 x 10^5 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 ---Page Break--- termination 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 experimental 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. ---Page Break--- -9- 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 crystal. 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; 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 10^0 traps/cm³ escapes detection. There remains the question of the change in the saturation current as a result of 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 (T-T 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 anthracene 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 non-irradiated 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 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 the 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 ‘simply involves the relocation of the dislodged anthracene molecules to their equilibrium lattice positions with the activation energy provided by thermal neutrons or environmental temperature, ---Page Break--- -u- Finally, it can be suggested that anthracene anions, produced in accord with the first mentioned mechanism, favor the formation of an iodine charge-transfer complex more so than normal anthracene molecules. This is 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. ---Page Break--- =e BYBLIOGRAPHY (1) Lampert, M.A., Rose, A., and Smith, R.W.: J. Phys. Chem. Solids 8, 464 (1959) (2) Kallman, B., and Pope, M.: Rev. Sci. Inst. 29, 993 (1958). (3) Kommandeur, J.: Ph. D. Thesis, University of Amsterdam (1958) (4) Kommandeur, J., and Schneider, J.A.: J. Chem. Phys. 28, 590 (1958) (5) Rattnana, R. and Pope, M.: J. Chem. Phys. 32, 300 (1960) (6) Wark, P., and Helfrich, W.: J. Appl. Phys. 33, 205 (1962) (7) Many, A., and Rakawy, Acta Phys. Rev. 128, 1980 (1962) (8) Kallman, H., and Pope, M.: Rev. Sci. Int. 3 44 (1959) (9) Pope, M. and Kallman, H.: Symposium on Electrical Conductivity in Organic Solids, Interscience Publishers, New York (1961) (10) Carre, C.B., and Hanany, Y. (ed.): Semiconductors, Reinhold Publishing Corporation, New York (1959) (11) Kallman, H., and Pope, M.: Nature

186, 31 (1960) (02) Rose, Av: Phys. Rev. 97, 1538 (1955) ---Page Break--- VOLS 3 g 7 a ---Page Break--- Faked 4 7170p crv #3 Gt) vost A pioreeuRZERT TENSITY ---Page Break--- ---Page Break--- Sieg Be i Soon: anata asain cree ge ---Page Break--- VOLTS ---Page Break--- sph aad Wu) dnadiakid pobre Way >-2:00% ty Hay 6-700 AH Yas) (seed) a X10" MAPS, €) erveraL, source ---Page Break--- x doulas eevstnn, sours, ---Page Break--- ‘RAFT BOK ---Page Break--- ss) ip ibd fig Hg h-'om . Bs May 9 8:081 (oi irs EDI feg PORAL SHEILDING PAREN BOX outs ---Page Break--- Mau 13 te #160 AH 43 /aee) ewverne ooh! wounee | = wtaL, st6ionla ‘source + ~~ PHRME EIN) BOX ---Page Break--- ---Page Break---