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Development of high voltages in potassium dihydrogen phosphate irradiated by γ rays

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The ferroelectrics Rochelle salt and guanidinium sulfate hexahydrate, when irradiated by γ rays, were found by Gilliland and Yockey to exhibit intense scintillations during a temperature ramp. Yockey found the same effect in potassium dihydrogen phosphate and triglycine sulfate. Robertson and Baily, Schmidt and Peterson, and Zerem and Halperin confirmed these results and identified the spectrum as that of the second positive system of N_2 or the first negative system of N_2^+. These bands are excited by electric discharges in the ambient gas. We have improved the time resolution of the scintillation by use of an RCA C31024 and found a rise time of about 1.5 nsec. Nine lines have been found which are all identified only with the second positive system of N_2. The 391.4-nm line of N_2^+ is not found and therefore the electron energy spectrum does not extend much above 19 eV. A few of the light pulses are partially polarized and therefore come from internal breakdown inside the crystal. Voltage differences of about 13 kV must exist across the crystal or to ground. The scintillations are not seen if the crystal is not in the ferroelectric phase when irradiated. The model of Zerem and Halperin is replaced by the suggestion that real charge liberated in the crystal by the absorbed dose, is trapped at domain boundaries and is freed during the temperature ramp. The effect is not associated with thermoluminescence as was formerly believed. Some crystals are not active but are activated by exposure overnight to 8000-psi N_2 at 50 °C.

I. INTRODUCTION

In the course of a study of the thermoluminescence of the ferroelectrics, Rochelle salt, and guanidinium aluminum sulfate hexahydrate (GASH) Gilliland and Yockey[1] discovered that intense scintillations appear during the temperature ramp. Later, the same effect was found by Yockey[2] in potassium dihydrogen phosphate (KDP) and in triglycine sulfate (TGS). The pulses were reported to be 40 msec in duration and to contain at least 1.5×10^5 eV.

Bettinali and Ferraresso[3] studied thermoluminescence in KDP but did not report scintillations. The pulses are of such magnitude that they can drive a chart recorder off scale, so that this effect is manifest with the usual equipment used in thermoluminescent research. These authors did not give the total absorbed dose, but if it was 1 Mrad or higher, the effect might not have been seen.

Robertson and Baily[4] reported similar pulses in both irradiated and unirradiated TGS. They obtained a spectrum in which they identified five lines with those of the second positive band system of N_2. On this basis and for other reasons they ascribed the effect to electric discharges in the ambient N_2 gas. Their experiments were repeated by Schmidt and Petersson[5] and the results were confirmed. Zerem and Halperin[6] studied the scintillations from KDP exposed to x rays. They proposed a process by which the high voltage is developed. According to their model the charges induced on that crystal surface which is perpendicular to the polarization are partially compensated by ions settling on the surface. The domain structure forms a matrix of small capacitors. As the temperature ramp proceeds the dielectric constant in the direction parallel to the Z axis falls rapidly and high voltages are thereby generated.

In this work we have obtained the optical spectrum of the pulses in two independent ways, one by photography with the aid of an image intensifier, and one by counting pulses while scanning the spectrum with a monochromator. In this way we have extended the identification to nine lines belonging to the second positive system of N_2. The lines reported by Baily and Robertson[4] and Schmidt and Petersson[5] could also be associated with the first negative N_2^+ bands. We find the band at 391.4 nm to be undetected, and therefore we conclude that N_2^+ bands are not excited. Consequently, the electron energy spectrum in the discharge must not extend appreciably above 19 eV.

Oscillograms of the pulses previously obtained were system-rise-time limited.[2,4–6] We have used a newly available and very fast rise-time photomultiplier and a fast rise-time oscilloscope to obtain a reasonably faithful picture of the time resolution of the pulses. We have also photographed the individual discharges on the crystal face directly by the use of the image intensifier. These photographs exhibit Lichtenberg figures which show clearly that most of the discharges are in the ambient N_2 gas. However, the fact that the light of some pulses is partially polarized indicates that such pulses come from inside the crystal. The application of Paschen's law to published values[7,8] of sparking potentials in N_2 indicates that voltage differences of 13 kV or more are present on the crystal surface or from the crystal surface to ground.

The scintillations appear in a much wider temperature range than is consistent with the model of Zerem and Halperin.[6] We suggest that real charge has been liberated in the crystal by the ionizing radiation and it is not all available at the Curie temperature. Most of it is probably trapped at domain boundaries which, in irradiated ferroelectrics, persist above the Curie point. These domains anneal, coalesce, and disappear over a broad temperature range and release real charge to the surface of the crystal.

This effect was discovered in the course of research on thermoluminescence[1,2] and it was thought that thermoluminescence accompanied the scintillations. We find, however, that there is no background thermoluminescent glow in KDP during the scintillation display. It is necessary for the crystal to be in the ferroelectric phase during irradiation. The scintillations are found only in ferroelectrics and we believe this effect is peculiar to such substances.

II. EXPERIMENTAL PROCEDURE

A. Preparation of crystals

The experimental apparatus is shown in Fig. 1. The sample may be a single crystal of KDP, *X* or *Z* cut and carefully oriented with the polished faces perpendicular to the axis of the lens and mirror system. The sample may also consist of a few grams of small reagent-grade crystallites placed in the sample heater. The samples were irradiated at liquid-nitrogen temperature. This is well below the Curie point of KDP at 122 °K. An atmosphere of dry nitrogen is maintained in the system at all times to avoid formation of ice on the sample and on optical surfaces. A helium atmosphere must be avoided since electrical breakdown will occur in the photomultiplier high-voltage string, and also because helium will diffuse through the photomultiplier-tube envelope.

Single crystals which were grown before 1964 were obtained from the Clevite Corporation. These single crystals were cylinders 12.7 mm in diam and from 9 to 25 mm in length. Some of the crystals were cut and polished optically flat within one wavelength at 546.1 nm. In other cases the crystals were cut with a jeweler's saw and sanded flat with kerosene as a lubricant. They were then ground in succession with 17- and 9.5-μ Al_2O_3 polishing powder. The ends of the crystals were parallel to better than 50 μ, as determined by a micrometer. In some cases the lower end was aluminized. In other cases the upper surface of the crystal was aluminized by a partially transmitting coating and the lower surface was fully reflecting.

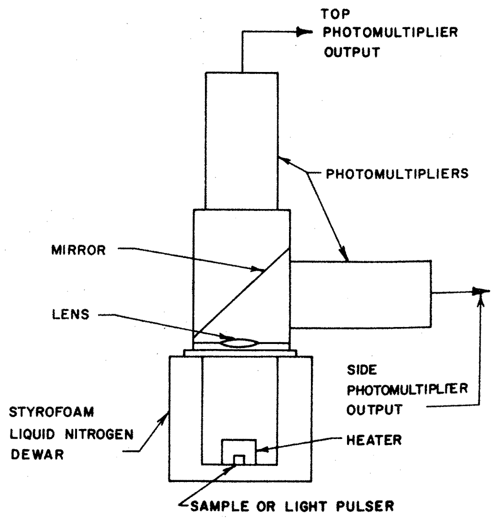

FIG. 1. Experimental apparatus.

It was found that some samples were not active but became so if heated to 50 °C under high pressure of N_2. Ar and He did not activate the crystals. The samples were placed in a styrofoam plug located at the top of an American Instrument Company Model 46-14615SP Reaction Vessel. Pressures up to 2500 psi were obtained by using a standard gas bottle coupled to the vessel. N_2 and Ar pressures greater than 2500 psi were obtained in the following way: The liquified gas of interest was placed in a thin-wall styrofoam container. The liquid almost completely filled the reaction vessel. The sample was placed in a styrofoam case and the vessel sealed quickly. The valve on the gas bottle was opened to charge the system to approximately 2500 psi and all valves were then closed. The pressure in the vessel rose to approximately 8000 psi as the liquified gas evaporated. The maximum pressure was controlled by the amount of liquid initially placed in the styrofoam container.

B. Irradiation procedure

In a typical experiment the following procedures were carried out. The crystal was located in the sample heater and the proper optical alignment was obtained. The system was then flushed with dry nitrogen. Liquid nitrogen was placed in the space provided and the sample was cooled slowly. The top photomultiplier and lens-mirror support assembly was removed and a cover with thermal insulation was placed on the irradiation chamber. The irradiation chamber was released by a quick release clamp and a cap placed on the chamber.

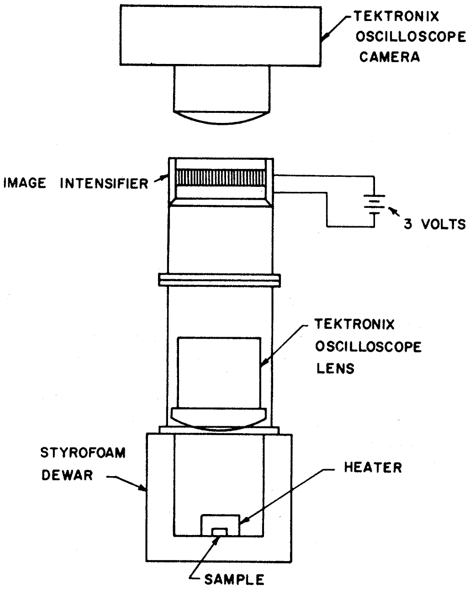

FIG. 2. Image-intensifier camera and sample chamber.

The irradiation chamber was placed in a ^{60}Co irradiator. The sample was exposed to 300 krad (tissue) per h for 2 min. Upon completion of the irradiation the process was reversed and the irradiated sample was ready for study. The sample was heated at rates varying from 7 to 12 °K per min.

C. Physical characteristics of light pulses

1. Pulse-shape and rise-time measurements

The pulse-shape and rise-time measurements were performed by removing the mirror in Fig. 1 and permitting the light to reach the top photomultiplier only. The pulse-shape and rise-time measurements were done with an RCA photomultiplier tube type C31024 which, according to the manufacturer, has a rise time of 1 nsec; see also a report by Stevens and Hocker.[9] The signal cable from the photomultiplier was connected to a GR-874-T Tee, then to a GR 874-K coupling capacitor, and finally to a Tektronix Model T50N125 termination. A GR 874-X insertion unit containing a 1-kΩ resistor was placed on one branch of the tee and allowed a positive bias to be applied to the anode of the photomultiplier. The resulting signal was photographed as displayed on the screen of a Tektronix 519 oscilloscope which has a deflection sensitivity of 8.6 V/cm. Yockey's previous work[2] was done with an EMI 6256S and a Tektronix 555 oscilloscope. The rise time of that system was about 15 nsec. The system was tested with an ORTEC Model 921-00 nanosecond light pulser.

2. Photography of scintillations

An image-intensifier camera system (shown in Fig. 2) was utilized to observe the surface of the crystal during the experiment. The lenses used in the system were Tektronix short focal length *f* 1.4 and *f* 1.3 with 1:1 and 1:0.5 magnification, respectively. The image intensifier was a specially fabricated Bendix microchannel plate image-intensifier tube with integral power supply. The gain of the image tube was adjustable up to 500 000. The samples were treated in the manner described above and observed during the temperature ramp.

D. Spectroscopy

Two methods were used to investigate the spectroscopy of these highly individualized light pulses. The intensity was below that needed for photography and therefore the use of more sensitive detectors was required.

In the first method, a Jarrel-Ash $\frac{1}{4}$-m Ebert monochromator was placed in the optical path of the side photomultiplier tube (see Fig. 1; monochromator not shown). The light from the exit slit fell on an RCA C31024. In order to obtain two signals for coincidence logic processing a beam splitter was placed in the mirror holder shown in Fig. 1. This was a quartz plate partially aluminized on the front surface. Most of the light was reflected to the side tube, where a cylindrical quartz lens focused the light on the entrance slit of the monochromator. Sufficient light reached the top tube (EMI 9594QUB) to generate a signal for the coincidence logic shown in Fig. 3. The signal from each photomultiplier was amplified and then differentiated by a Tennelec TC-200 pulse-shaping amplifier. The partially shaped signals were then extracted and routed through a Tektronix Type O plug-in with a log adaptor. The logarithm of the pulse amplitude was then returned to the TC-200, where it was integrated and then

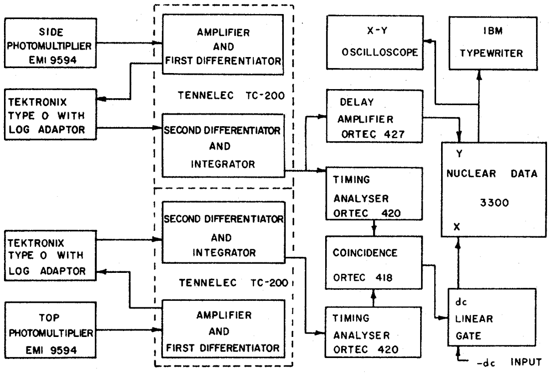

FIG. 3. Block diagram of pulse amplification, shaping, and coincidence system.

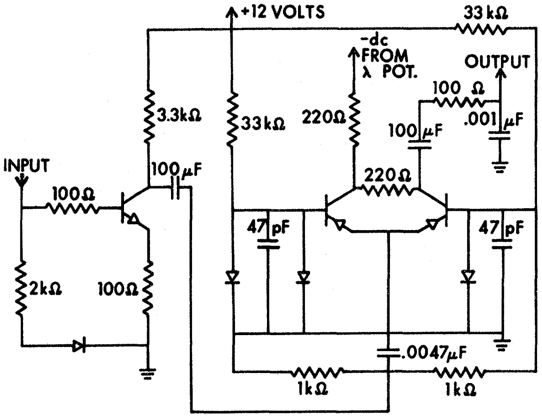

FIG. 4. Schematic diagram of dc linear gate designed for use in spectroscopy studies.

differentiated again to provide the correct pulse shape for the Nuclear Data 3300. The log manipulation was utilized since the amplitude of the pulses spanned several decades. The log amplifiers were easily switched out of the circuit when not needed. The signal from the side photomultiplier was stored in the Y-axis memory of a Nuclear Data 3300 pulse-height analyzer operating in the X-Y mode. A signal indicating the wavelength was stored in the X-axis memory. It was obtained as follows. A 20-turn potentiometer was attached to the wavelength drive mechanism and a negative dc potential of adjustable magnitude was applied to the potentiometer from a Power Design Model 2005 supply. As shown in Fig. 3, the outputs from the two linear amplifiers were coupled to Ortec timing analyzers which were in turn coupled to an Ortec universal coincidence unit. Resolving time was set for 0.1 μsec. The coincidence pulse was applied to the control gate of a dc linear gate (see Fig. 4) which sampled the magnitude of the dc potential at the monochromator wavelength potentiometer and generated a pulse whose amplitude was equal to this potential. In this way, when a pulse occurred, the total energy and the wavelength were stored in the pulse-height-analyzer memory. The spectrum was obtained by scanning back and forth at a uniform rate between two predetermined wavelengths during the temperature ramp.

In the second method, the image intensifier was used to photograph the spectral lines. The image tube was fastened directly to the monochromator from which the exit slit had been removed. The output of the intensifier was photographed using a Tektronix oscilloscope camera. The experiment was performed in a darkened room. The iris of the camera remained open so that each event was recorded when it occurred. The film was removed immediately and the camera was ready for the next event.

Optical interference filters were also used to study amplitude fluctuations. A different filter was placed in front of each photomultiplier, shown in Fig. 1. These filters had bandwidths of 7.5–10.0 nm. Since the reflection coefficient of the partially aluminized mirror would depend upon the polarization direction of the incoming light beam, a Polaroid HNPB ultraviolet polarizer was placed over the lens so only one component could reach the mirror. Thus all pulses were analyzed only for amplitude at a particular wavelength.

III. EXPERIMENTAL RESULTS

A. General behavior of crystals

Initially a radiation exposure of 100 krad (tissue) was used. However, the total number of pulses in the second exposure was $\frac{1}{10}-\frac{1}{20}$ that of the first. A reduction in numbers occured after each irradiation until after five or six runs only a few pulses were observed. For this reason, 10 krad (tissue) was chosen as a workable exposure which provided good results. The amplitudes of the pulses appeared to be independent of dose. Only the total number of pulses was affected. We attempted to anneal samples which had received sufficient accumulated dose to reduce the output efficiency. Annealing for 24 h near the melting point had no effect. However, it was found that a "rest" period of two days at room temperature between low-dose irradiations produced an extended useful life of the sample.

We obtained Z-cut single crystals grown by the same supplier in 1969 and found them to be less active. In fact, many of these crystals were completely inactive. The supplier had changed his source of KDP and believes his crystals are purer than those grown prior to 1964. It was found that inactive crystals could be activated by exposure of the inactive samples to high N_2 pressures at slightly elevated temperatures. Presumably this treatment caused the crystals to absorb some N_2. The activity was not permanent and it disappeared after a week at STP. An N_2 pressure as high as 9500 psi was utilized. However, no increase in activity was noted for pressures exceeding 5000 psi. At room temperatures the length of time required to activate the crystals was several days, but at 50 °C they became very active overnight. Exposure to high pressures of argon and helium had no effect on the samples.

After irradiation at 77 °K the samples had a definite violet color, as reported also by Tokumaru and Abe,[10] and a domain pattern appeared on the surface of the crystal. A photograph of a typical pattern is shown in Fig. 5. The shaded area of

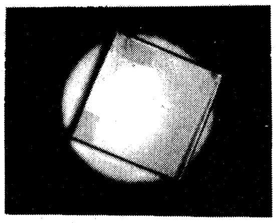

FIG. 5. Photograph of the crystal surface at 77 °K, showing domain patterns.

the crystal corresponds to the light-emitting regions discussed below.

Photographs were taken of the surface of the crystal, which is perpendicular to the ferroelectric axis during the temperature ramp. A sample of these photographs is shown in Fig. 6. The white spot seen in the upper right quadrant is a defect in the image-intensifier screen. This defect was used to orient the pictures. The complexity of the light emission ranges from a single point shown by the arrows in Figs. 6(a) and 6(b) to large discharges involving the entire cyrstal. The pattern in Fig. 6(c) shows a number of discharges across a domain pattern which extended the width of the crystal. This domain pattern was observed visually before the temperature ramp was started. We pointed out above that the film was always changed immediately when a flash was seen on image-intensifier screen. This is not a composite picture of a series of scintillations. Such discharges may correlate with the multiple spike oscillograms shown in Fig. 7. The lens magnification in Figs. 6(c), 6(e), and 6(f) is twice that in Figs. 6(a), 6(b), and 6(d), as discussed above. Discharges to the holder at ground potential can be seen in Figs. 6(d) and 6(f). In Figs. 6(a) and 6(b) the crystal was placed on top of a nylon nut. The lens was focused on the upper surface of the crystal and, because the depth of focus was small, the nylon nut is out of focus. Nevertheless it is visible through the KDP crystal by its thermoluminescent light. The small circular dark area near the center of the picture is the hole in the nut. Figure 6(e) shows a Lichtenberg figure playing over the surface of the crystal. Figures 8(a) and 8(b) show a side view. The ferroelectric axis runs in the page from the upper left quadrant to the lower right quadrant. Figure 8(a) shows a prominent discharge from the crystal face to the grounded holder. Also seen in Figs. 8(a) and 8(b) are discharges between different parts of the crystal surface. The white spot showing the defect in the image-intensifier screen is in the lower right quadrant in Figs. 8(a) and 8(b).

B. Spectroscopy

We have located, using the first experimental method described above, lines or bands at 313.6, 315.5, 337.0, 353.0, 357.5, 375.5, 379.5, 399.8, and 405.9 nm. Pulses appeared at these wavelengths but not between them. The width of the bands was about 2.0 nm. In order to establish experimentally that our apparatus truly eliminates random coincidences, we set the wavelength dial at 297.7, 322.5, 371.0, 391.4, and 403.0 nm for a complete heating cycle and found no pulses registered.

The image intensifier was used to study the relative intensity of the observed lines in one pulse. Figure 8 shows a typical photograph of the image-intensifier output screen when a pulse is recorded. No major fluctuations in line intensity were observed. These results were verified by use of the optical interference filters. A scatter of data points similar to that found with the Ortec pulser was observed.

Each of the nine bands found by the two experimental methods described above can be identified with the more intense bands of the second positive system of N_2. Some also correspond to the first negative system of N_2^+. Robertson and Baily[11] reported three lines, two of which could be from either system and one, namely, 403.0 nm, which corresponds to neither but which might be due to NO. In a second paper[4] they report five lines, but do not cite the wavelengths. Schmidt and

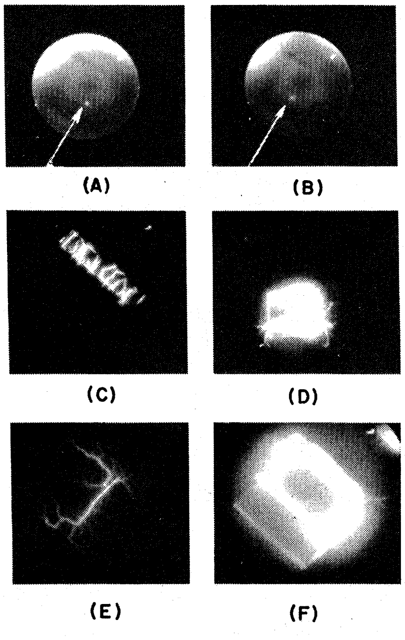

FIG. 6. Typical electrical discharges from KDP as photographed by image-intensifier camera.

TABLE I. Summary of spectroscopy results.

Present paper	Baily and Robertson (Refs. 4 and 11)	Schmidt and Petersson (Ref. 5)	First negative (Ref. 12) system of N_2^+
313.6			none
315.5		315	none
337.0		337	338.1
353.0			none
357.5	357	357	358.2
375.5	375		376.16
379.5		380	378.3
399.8			391.4
	403	403	none; line due to NO 4027.8
405.9			

Petersson[5] report five lines, three of which could be due to either system. These results are displayed in Table I. We have looked very carefully a number of times for the strong first negative line of N_2^+ at 391.4 nm without finding it. From this evidence it may now be concluded that all bands are in the second positive system of N_2 and that the first negative system of N_2^+ is not excited.

We repeated this experiment using liquid Ar for the cooling agent with the hope of photographing Ar lines. Thus the ambient gas was Ar which had boiled off. The N_2 second positive lines are so persistent that we were never able to exclude them. A discussion of this phenomenon is given by Pearse and Gaydon.[12] Our apparatus was not designed to be evacuated and so perhaps very small amounts of N_2 diffused in. We did not observe Ar lines.

C. Pulse shape and rise-time observations

When the samples of irradiated KDP reached a temperature of 123 °K, pulses were observed at a maximum rate of approximately five per sec. These pulses appear with decreasing frequency until a temperature of 220 °K was reached, although occasionally some were observed near room temperature. When deuterated KDP was utilized the pulses did not appear until a temperature of 223 °K was reached. The scintillations behaved very much like those from ordinary KDP otherwise. Figure 7 illustrates typical oscilloscope traces. The photomultiplier rise time of 1 nsec reflects the capability of the electronic system. The observed rise time of the pulses similar to that in Fig. 7(a1) was about 1.5 nsec and so the electronic system was sufficiently

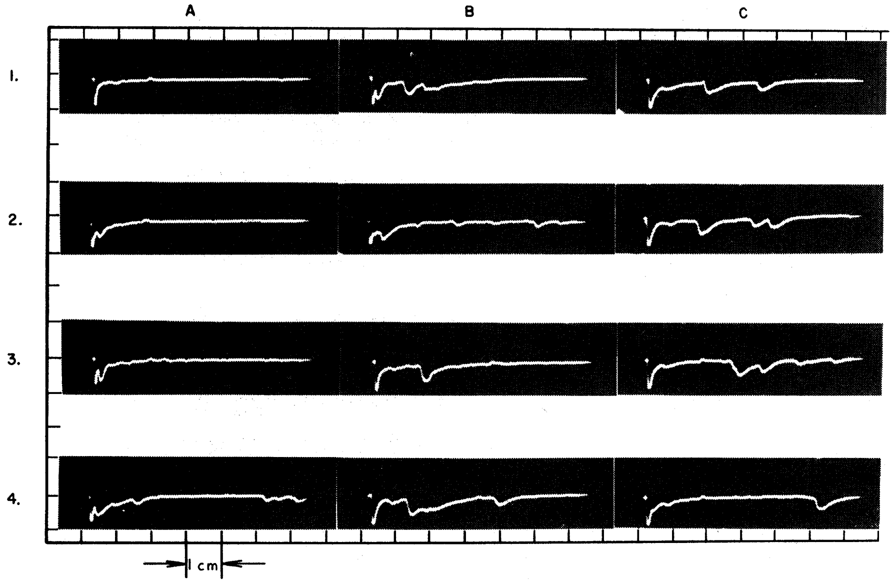

Fig. 7. Typical pulse shapes photographed as displayed on oscilloscope (sweep speed = 20 nsec/cm).

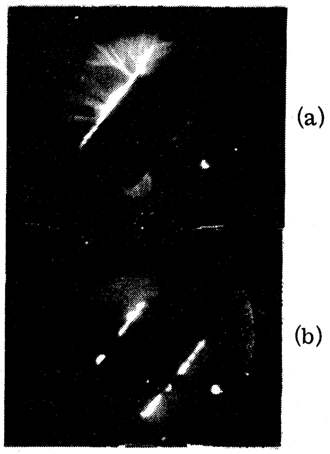

Fig. 8. Typical electrical discharges from KDP at the crystal surfaces and to ground.

fast to record the pulse with reasonable fidelity. The decay time (90 to 10%) of such single pulses varied from 15 to 30 nsec. Pulse ringing was negligible because of the coaxial output of the RCA C31024 tube. Only a small negative pulse, due to reflection, and a small positive pulse, presumably from ions striking the anode, were observed after the main pulse [see Fig. 7(a1)].

The energy contained in the pulses similar to those of Fig. 7 was found from the calibration supplied by the manufacturer of the EMI 9594QUB, which was used in this instance, and the conversion factor of 1.6×10^{-3} A/lumen (555 nm). Most of the pulses represent at least 2500 photons. No account is made of light which does not intercept the photomultiplier. It should also be noted that the pulses were occasionally not single events, but appeared as a series of pulses or spikes. This phenomenon is shown in Fig. 7. The rise time of the spiking was never faster than 1.5 nsec but was sometimes slower. The decay times were on occasion faster than 15 nsec but were usually similar to a single event. During a pulse containing considerable spiking the decay time varied from spike to spike. The character of the time resolution is more accurately shown than previously reported by Yockey[2] and Zerem and Halperin.[6] We have looked carefully for the 1-μsec rise time and pulse width reported by Robertson and Baily[4] without finding such pulses.

D. Ferroelectric phase and relation to thermoluminescence

Experiments were performed in order to determine if crystals irradiated at temperatures above the Curie point produced the scintillations. The sample consisting of polycrystalline KDP was placed in the experimental chamber. The assembly was placed in the γ-cell drawer and the thermocouple and heater wires were brought out the top. The sample was cooled slowly until it reached a temperature of 160 °K. The drawer and the assembly containing the sample were then lowered into the γ cell. During the irradiation the heater was used intermittently to maintain a sample temperature between 140 and 160 °K. After irradiation the samples were treated two different ways. One group of samples was not allowed to cool below 140 °K. These were simply heated and the scintillations recorded. The other group was cooled to 77 °K after irradiation and then heated. Light pulses were not observed in either case. It therefore appears to be necessary that the crystal be in the ferroelectric phase when irradiated for this effect to manifest itself.

When the output of the photomultiplier is recorded on a strip chart, the pen does not return to zero between pulses. This gives the impression that the scintillations appear during a thermoluminescent glow peak. A series of experiments was done to determine whether this glow peak exists or is an artifact due to the slow return of the pen. No thermoluminescent glow was observed from the single-crystal KDP samples when photographed by means of the image intensifier as shown in Figs. 6(a) and 6(b). However, when the crystal was placed on a nylon nut the thermoluminescent glow of this nut can be seen clearly through KDP crystal. The thermoluminescent glow from the nylon nut without the KDP crystal was recorded on a strip chart and this glow peak was found to be one-tenth of the apparent glow peak under the scintillations. Any appreciable thermoluminescent glow from the KDP crystal would have rendered the nylon nut invisible in 6(a) and 6(b). We notice also that there is no thermoluminescent glow from KDP crystals in

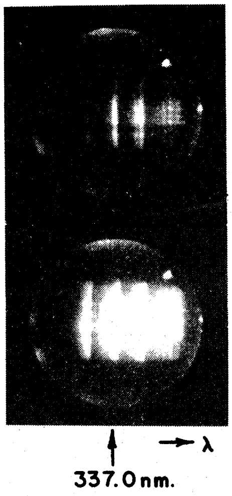

Fig. 9. Optical spectra of pulse from KDP as photographed by image-intensifier and polaroid camera.

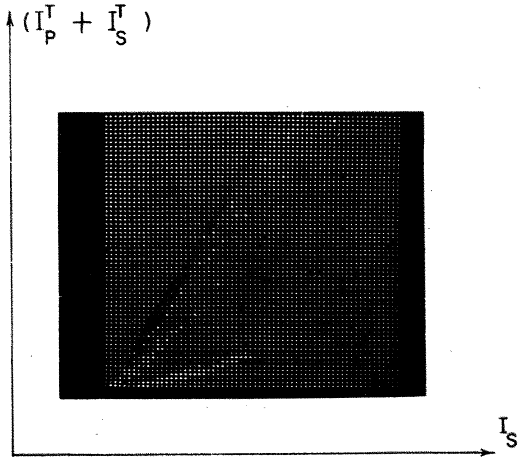

Fig. 10. Polarization data as presented by multichannel analyzer.

Figs. 6 and 8. We therefore conclude that the glow peak under scintillation is an artifact and that the previous impression that the scintillations are related to thermoluminescence[2] must be corrected.

E. Optical polarization

A test for polarization of the pulses was also performed using the arrangement described above. Figure 10 illustrates the data from the polarization experiment. Notice that in Fig. 10 a number of scintillations are recorded well below the 45° line. They are polarized to some degree. The subscripts *P* and *S* stand for the parallel and perpendicular components, while the *T* stands for the transmitted portion. Rotation of the sample and/or sample holder had no effect on the observed data.

IV. DISCUSSION

A. Processes by which surface charge and potential may be generated

Zerem and Halperin[6] and Schmidt and Petersson[5] suggested that charges which are induced on the surface of the crystals by the polarization of the medium are compensated by charged ions settling on surfaces perpendicular to the *Z* axis. Thus, according to this model, each domain is a small capacitor; above the Curie point the internal fields disappear, and only the accumulated real charges remain. At the Curie point the dielectric constant is extremely high but it decreases very rapidly as the temperature ramp proceeds. High voltages of the required value appear and the discharges result. A calculation which is more sophisticated than that of Zerem and Halperin[6] was made by Hinazumi, Hosoya, and Mitsui.[13] They applied their calculations to TGS and found that very high electric fields, which may indeed exceed the breakdown strength of air, exist on the surface of ferroelectrics.

We find a number of difficulties with this model. In the first place, if all the charge is available on the surface as the ramp passes the Curie temperature, one would expect that, because of the very steep fall of the dielectric constant, all the discharges should appear in the very narrow temperature range between 130 and 140 °K. The work of Yockey,[2] Zerem and Halperin,[6] and the present paper show that the discharges occur over a very wide temperature range, i.e., about 132–200 °K. In the second place, deuterated KDP behaves in the same way as ordinary KDP, except that discharges are initiated a few degrees above the Curie point at 222 °K. The disappearance of the discharges above the 200 °K is ascribed by Zerem and Halperin[6] to the increase in electrical conductivity in KDP above the temperature. According to the model of Zerem and Halperin,[6] deuterated KDP should be inactive. There is no reason to believe that the electrical conductivity of deuterated KDP is appreciably different from that in ordinary KDP. It is also difficult to see why some KDP crystals are inactive until receiving the pressurized N_2 treatment described above if the real surface charge comes from the ambient gas. Furthermore, we have seen light pulses from crystals with a conducting semitransparent Al film. This observation and the fact that some of the pulses are polarized proves that these particular pulses must come from breakdown inside the crystal.

We propose another model which is consistent with the literature on irradiation of ferroelectrics and with the experimental results of this paper. There are strong internal fields in ferroelectric crystals due to the polarization which exists in the ferroelectric phase. Ionizing radiation liberates electrons and holes in the conduction band. These charges will achieve a speed up to $\sim 10^7$ cm/sec and will be trapped in a few nanoseconds. They will therefore move several tenths of a millimeter. This is an appreciable separation. The domain walls are a trapping site unique to ferroelectrics in which bound electron states exist.[14] They are required to be present because, as we discussed above, the crystal must be in the ferroelectric phase during irradiation. Fousek and Janovec[15] have analyzed the kinds of domain walls which may exist. The parallel-antiparallel type of wall found in KDP and TGS may be charged or uncharged. These domains persist above the Curie point even in unirradiated ferroelectrics, as reported by Gladkii and Sidnenko.[16]

The ferroelectric effect is destroyed in Rochelle salt[17] by less than 2.6 Mrad. Nevertheless, the domain patterns are still visible long after the hystersis loop has disappeared.[14,18] We have observed the domain pattern in KDP to persist well above the Curie point. Thus the domains exist in irradiated ferroelectrics above the Curie point and they are capable of trapping electrons and holes.

The ferroelectric effect is due to the high mobility of the domain walls. The increase in the concentration of radiolytic defects is believed to contribute to blocking the motion[19–26] of the domains and freezing them in. The electrical properties of irradiated KDP anneal[24] substantially between 130 and 214 °K. We presume therefore that this behavior reflects the motion, coalescence, and disappearance of domains locked in by defects. Some domains may be freed as the pinning defects anneal. Others may be freed as they overcome the activation energy during the temperature ramp. A third factor which initiates domain-wall motion is the internal fields which are generated as charge builds up on the surface.

There will be some strain in the domain[27] because of the locking effect. When the domain wall is released it may be expected to move at the speed of sound[28] or even at supersonic velocities[29] until it is locked in by another imperfection or coalesces with another domain. Bye, Whipps, and Kene[30] have shown that the internal bias fields in ferroelectrics may actually lead to breakdown. They grew TGS crystals with a partial substitution of *L*-alanine. They found breakdown in the crystals with about 2% *L*-alanine when they attempted to obtain hysteresis loops. Bornarel and Lajerowicz[28] observed the domain velocities in unirradiated KDP. They found a distribution of velocities which had a peak at 100 m/sec and one at 900 m/sec. The domain boundary moves $\sim 10^{-4}$ cm in 10^{-9} sec. This is approximately the width of the domain. Thus ferroelectric switching-current transients should be observed in the external circuit. Such pulses were observed to be in coincidence with the light pulses by Schmidt and Petersson[5] and Zerem and Halperin.[6] The domains will release the trapped charge over a broad temperature range, as required by experiment. The mechanisms cited above may act cooperatively, resulting in a cascade of charge motion. This may be related to the oscilloscope traces A2-5 and B1-5 in Fig. 7 and the Lichtenberg figures shown in Figs. 6(c)–6(f).

Let q be the real surface charge density and ϵ_c the static dielectric constant in the Z direction. Let C be the capacitance per unit area of the condenser postulated by Zerem and Halperin[6] and V the voltage. Then

$$V = q/C \sim q\epsilon_c .$$

But ϵ_c follows the Curie-Weiss law for 50 deg or more [22] above T_0, the Curie point; therefore,

$$V \sim q(T - T_0).$$

Thus in this model V depends both on the release of trapped charge q and on $(T - T_0)$. The high voltage will be developed, as in the model of Zerem and Halperin,[6] but over a wide temperature range. One can estimate from the sparking-potential data of Allen and Philips[7] and Suleebka and Rau[8] that the voltages reached are about 13 kV. This model is also consistent with the results in deuterated KDP.

There may be some internal breakdown[30] inside the crystal. Since N_2 trapped or diffused inside the crystal has something to do with crystal activity, such internal breakdown will excite the same second positive bands in the same manner as the gaseous discharges.

It is well known that the electric fields generated by polarization in ferroelectrics are gradually compensated by conductivity. This may result in the trapping of charge at domain boundaries and explain the appearance of pulses in unirradiated TGS which has aged for a considerable time. It may be that a moisture film will increase the conduction, as discussed by Robertson and Baily.[4]

B. Crystal "burn out" above 10^5 R

Our finding that the crystal becomes "burnt out" after being exposed to a dose of 10^5 R or more is related to the effect of radiation on the domain structure. Romanyuk and Zheludev[31] have reported that doses less than or equal to 10^4 R reduce the size of the domains considerably in Rochelle salt. As the dose approaches 10^6 R the contrast in the domain structure completely disappears. This corresponds to the destruction of the ferroelectric effect reported by Krueger *et al.*[17] Tokumaru and Abe[10] irradiated KDP by ^{60}Co at liquid-N_2 temperature. No shift of the Curie point was found, but a large decrease in the dielectric constants was reported below that temperature. Burdania *et al*[21] obtained similar results in KDP irradiated by ^{60}Co γ rays at room temperature. Peshikov[22] has irradiated KDP with reactor neutrons at 70–80 °C and also found a large decrease in the dielectric constant below the Curie point. He later[24] irradiated KDP at liquid-nitrogen temperature and observed the decrease of the dielectric constants below the Curie point and their recovery with annealing. All these results show that as the dose is increased, the domain structure is altered, the dielectric constant decreases, the domains are locked more firmly, and so the process discussed above in our suggested model can no longer take place. This appears to explain the fact that crystals irradiated above $\sim 10^5$ R have a greatly reduced activity.

C. Characteristics of electric discharges

The characteristics of the discharges are typical of pre-onset or streamer formation in N_2 at atmospheric pressure. The nonconducting character of KDP plays the role of a high resistance in series with the high-voltage electrode in such studies. This prevents the discharge from proceeding beyond the streamer phase. A recent review has been given by Mesyats, Bychkov, and Kremnev.[32] The single pulse shown in Fig. 7(a1) is probably a Townsend discharge. The other pulses shown in Fig. 7 and the image-intensifier photographs in Figs. 6 and 8 are probably the development of streamers from the primary cascade. The lifetime of the $C^3\Pi_u$ metastable state is 37 nsec.[33] This is reduced to 0.5 nsec at 1 atm because of collisional deexcitation.[34] This is somewhat faster than the value of 3 nsec referenced[32] by Mesyats *et al*; this is no doubt due to the fact that very fast photomultipliers were not available at the time that work was done. The oscilloscope traces of the discharges quoted by Mesyats *et al.* and reported by Mayaux and Goldman[35] and by Palmer and House[36] resemble those in Fig. 7.

The excitation cross section for $A^3\Sigma_u^+$, $a\Pi_g$, and $C^3\Pi_a$ states of N_2 were reported by Schultz[37] and more recently by Kurzweg *et al.*[38] The onset is at 11.2 eV, according to both authors. The cross section peaks at 11.5 eV, according to Schultz, and 14 eV, according to Kurzweg, and it falls rapidly above the maximum. The ionization potential of N_2^+ is about 19 eV. Borst and Imani[39] report that the second positive bands are excited only by slow secondaries and that excitation of the 391.4-nm line requires electron energies well above 19 eV. We conclude that the electron energy spectrum is sufficiently energetic to excite $C^3\Pi_a$ and to ionize N_2, but it does not extend high enough to leave N_2^+ in an excited state.[39]

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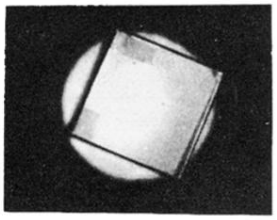

FIG. 5. Photograph of the crystal surface at 77 °K, showing domain patterns.

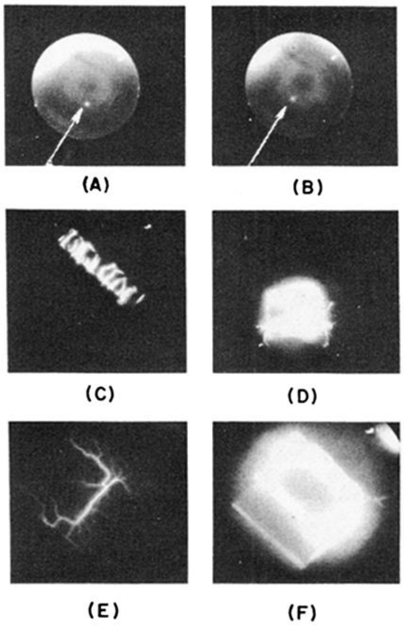

FIG. 6. Typical electrical discharges from KDP as photographed by image-intensifier camera.

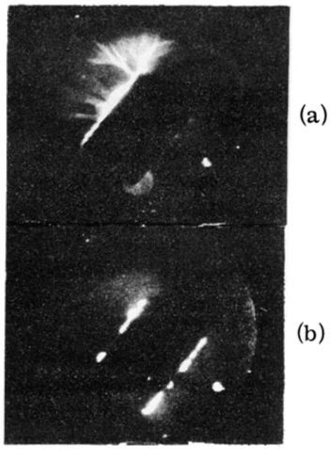

Fig. 8. Typical electrical discharges from KDP at the crystal surfaces and to ground.

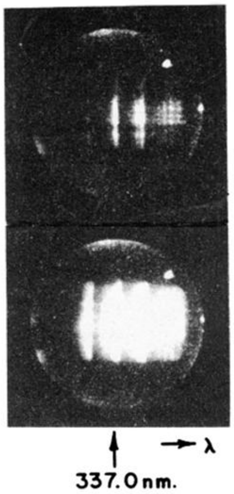

Fig. 9. Optical spectra of pulse from KDP as photographed by image-intensifier and polaroid camera.