Loss and Restoration of Photoconductivity in Red Mercuric Iodide

FOSTER C. NIX, *Bell Telephone Laboratories*

Single crystals of red mercuric iodide, which normally display photosensitivity when precipitated, lose their photosensitivity on aging. This loss is accompanied by a change from the mono- to the polycrystalline fibrous state with considerable randomness of orientation of the individual crystallites. The nonsensitive crystals can be resensitized by subjecting them to an electric field for a time of the order of a few minutes. The increase in photosensitivity is accompanied by a decrease in the dark current. These correlated phenomena may not occur till after the lapse of an appreciable time after the field is first applied. The rate of decrease of the dark current with time is greater the lower the temperature. The data also suggest, but do not conclusively demonstrate, that the dark current increases with decreasing temperature. The rate of resensitization and the magnitude of the attained photosensitivity are found to increase with (a) increase in applied field strength and (b) decrease in temperature. When the light is turned on the photoelectric current is found, under certain circumstances, to rise briefly to a maximum and then descend to a permanent value at which the total current is equal to the value of the dark current prevailing when the voltage was first applied.

CRYSTALLINE materials exhibiting internal photosensitivity have been divided by Gudden and Pohl[1,2] into two arbitrary classes, designated as "idiochromatic" and "allochromatic." The former are photosensitive in their initial and pure state while the latter acquire their photosensitivity through special treatments which (with one exception) disturb the stoichiometric chemical equilibrium.

The reaction products of these treatments are essentially the same, i.e., the photoactive centers are thought to consist of a quasi-neutral alkali atom with the valence electron more or less loosely bound. This loose binding is evident from the fact that electrons can be elicited either by heat, or light of suitable wave-length (for the most part, light of the visible spectrum possesses sufficient energy for the alkali halide crystals). Stasiw[3] has shown that the active centers when acted upon by the above agents elicit negative carriers which then move toward the anode under the influence of an applied potential. On reversal of potential the "electron cloud" reverses its direction of propagation.

Stasiw[4] and Pohl[5] were able to produce the active centers in a most ingenious way. This scheme consisted essentially in allowing electrons to enter the crystal from a pointed cathode. The electrodes of a KCl crystal consisted of a platinum foil fused onto the end of the crystal which served as an anode, while the cathode consisted of a pointed platinum wire. On impressing a potential of a few hundred volts across the crystal, when the latter was heated to a temperature of two or three hundred degrees, there resulted the flow of electrons out of the cathode into the crystal. This was accompanied by a pronounced discoloration of the crystal as could easily be seen with the unaided eye. For KCl the crystal appears violet in color. The process is though by Pohl and his collaborators to consist in the diffusion of anions out of the crystal to be replaced by electrons emerging from the pointed electrode. This process would result in an electrically neutral crystal with an anion deficit. However, it is difficult to understand how this proposed process could account for the phenomenon since numerous experiments indicate that cations[6] are the carrier of the electrolytic current in the alkali-halide crystals at temperatures up to *ca.* 500°C.

The "additive" method as introduced by Siedentopf[7] and Giesel[8] consists in heating a non-sensitive alkali-halide crystal in a closed vessel containing alkali vapor. The vapor need not necessarily be the metal forming the cation of

[1] B. Gudden, *Lichtelektrische Erscheinung* (Julius Springer) (1928).

[2] F. C. Nix, Rev. Mod. Phy. **4**, 723 (1932).

[3] O. Stasiw, Nachr. d. Ges. d. Wiss. z. Göttingen Math.-Phy. Kl. 1 (1932).

[4] O. Stasiw, Nachr. d. Ges. d. Wiss. z. Göttingen Math.-Phy. Kl. 387 (1933).

[5] R. W. Pohl, Phys. Zeits. **35**, 107 (1934).

[6] C. Tubandt, Handbuch d. Exp. Physik **12**, Part 1, Akadem. Verlags. Leipsig (1932).

[7] H. Siedentopf, Phys. Zeits. **6**, 855 (1905).

[8] F. Giesel, Ber. d. Deutsch Chem. Ges. **30**, 156 (1897).

the crystal in question; e.g., alkali vapors other than sodium can provoke discoloration and sensitization of rocksalt. This discoloration of the clear rocksalt was thought by Siedentopf to consist of a diffusion of the alkali metal atoms into the crystals; principally through places of imperfections such as holes, fissures, etc.

Still a third and important method of producing internal photosensitivity (Goldstein,[9] Röntgen and Joffé[10]) consists in the irradiation of nonsensitive crystals with light of sufficiently short wave-length (gamma-rays, x-rays and ultraviolet). This photochemical process is thought to evoke an electron transfer from anion to cation, thus producing quasi-neutral alkali and halogen atoms. The allochromatic crystals suffer a discoloration by the above treatments. Clear rocksalt becomes a yellow, while KBr becomes bluish-violet.

The concentration of the photoactive centers is found to vary from 10^{15} to 10^{17} per cubic centimeter. However, the concentration can be influenced by the past history of the material; e.g., greater concentration of centers can be obtained in materials which have been rapidly cooled or in crystals which have remained in a strained state after formation from the melt.

On plotting the velocity of propagation of the slowest of an isolated group of electrons under the influence of an applied electric field as a function of temperature, it is found that a striking similarity exists to a similar plot of electrolytic conductivity vs. temperature for KCl.[4, 5] At temperatures in the range of the lower branch of the curve the electrons have a velocity distribution, the spread of which decreases with increasing temperature, becoming uniform at ca. 670°C and remaining so for the range of still higher temperatures studied.

The agreement as to slope and point of change of slope between the two different sets of data lends strong evidence to support the contention of Pohl[5] and his collaborators, concerning the relationship existing between electrolytic dark current and emanation of electrons out of the pointed electrode, as expressed above. At least it must be admitted that there is a close con-

nection between the electrolytic dark conduction and the velocity of propagation of the "electron cloud" under the influence of an applied electric field.

In the processes described in the foregoing paragraphs the mechanisms of sensitization have all dealt with the production of a discoloration and consequent photosensitization by either allowing foreign bodies to diffuse into the "nonsensitive" material, or by photochemical means. In the following we will describe the discovery of *loss* of internal photoelectric sensitivity with time in inherently sensitive single crystals of red mercuric iodide and with detail studies of the factors involved in their resensitization.

During the course of a study of the photoconductivity of extremely pure single crystals of red mercuric iodide, which were prepared by slow precipitation of purified material from ethyl alcohol, we observed that *after the lapse of one and one-half years of undisturbed rest the crystals had lost a considerable portion or even the whole of their photosensitivity*. During the course of a series of measurements made to ascertain the nature of the current-voltage curve (readings being taken at random in order to eliminate any effects which might result from the order in which the measurements were made) an increase in sensitivity was observed at lower voltages after readings had been made at higher voltages. We were able to obtain reproducible results in these measurements only after we had allowed the highest voltage which was used to remain impressed across the crystal for several hours. *In other words, the impressed voltage resensitized the previously desensitized crystals*. We found further that many crystals had *completely lost* their inherent photosensitive properties. These completely desensitized crystals could then be sensitized by allowing a sufficiently high voltage to remain impressed across the crystal for times comparable to those required to resensitize the partially sensitive crystals. The data used in plotting the following curves were taken on sensitization studies of crystals which had become completely nonsensitive.

These nonsensitive crystals have continued to change as regards the rate of resensitization, magnitude of the dark current, etc., ever since

[9] E. Goldstein, Zeits. f. Inst.-Kunde **16**, 211 (1896); Berl. Ber. 222 (1901).
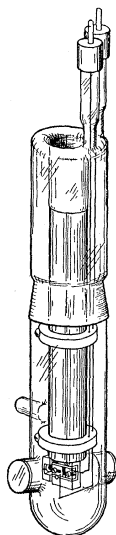[10] W. C. Röntgen, Ann. d. Physik **64**, 1 (1921).

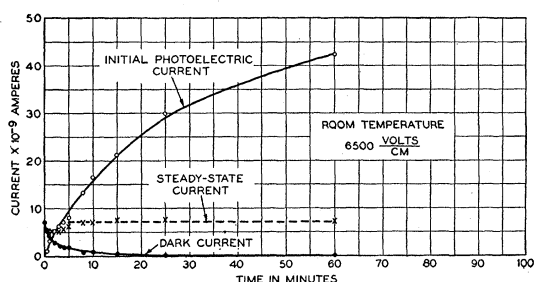FIG. 1. Experimental glass tube with amber insulation.

FIG. 2. Curves showing the rate of resensitization and decrease of dark current with time: Steady-state current is depicted by the dashed line. Applied electrostatic field strength 6500 volts/cm.

the effect was discovered about two years ago. In general: the older the nonsensitive crystal, the larger the dark current, the slower the rate of resensitization and the more rapid the rate of loss of photosensitivity after resensitization. The resensitized crystals lose their photosensitivity after a certain length of time. In the early stages of these studies crystals were observed to lose their photosensitivity only after many days, whereas they now lose it completely in some ten or twelve hours after resensitization. The time necessary for the disappearance of the photosensitivity after resensitization can be substantially shortened, by impressing potential of opposite polarity to that used during the resensitization, also, in the early stages of the

resensitization, by irradiation with light from a tungsten lamp. We have been unsuccessful up to the present time in finding any factors which can influence the rate of loss of the original intrinsic photosensitivity.

The data to be presented in the following pages cannot be considered as quantitative. However, we have selected data made from studies on one particular crystal in a space of time small enough to permit comparable measurements to be made. Comparison of Figs. 2 and 6 will show some of the general changes that have taken place over a period of two months.

For the purpose of resensitization, the de-sensitized single crystal was placed between two smooth platinum-faced electrodes. The electrodes were firmly pressed against the smooth crystal faces by means of finely adjustable jaws. The amber-insulated crystal holder was mounted on the end of a re-entrant hollow copper tube which was sealed to the outer walls of the Pyrex glass tube (Fig. 1). Amber insulation was used throughout the tube. All measurements were made with the tube evacuated to a pressure less than 10^{-3} mm of Hg. The currents were measured by means of a string electrometer which registered the drop of potential across a sputtered carbon film, of 10^9 ohms resistance. The crystal was connected in a simple series circuit containing large heavy duty "B" batteries and the high resistance. The voltage was applied continuously, unless otherwise stated, during the course of the measurements. Measurements were made at temperatures ($+23°C$, $0°C$, $-33°C$, $-79°C$, $-183°C$). The procedure consisted in observing (a) the dark current at the moment when the voltage was applied (hereafter to be called $t=0$) and at various times t thereafter; (b) the result of illuminating the crystal for various time-intervals beginning at various times t. In what follows, we denote the dark current by i_t^D; its value just after the voltage is applied ($t=0$) by i_0^D; the total current just after the light is turned on at instant t by $(i_t^D+i_0^\phi)$; the total current after the light has been shining for a while (see below) by i_s. We apply the name "initial photoelectric current" to i_0^ϕ (i.e., the augmentation of current occurring as soon as
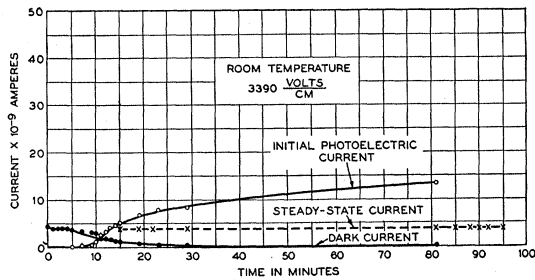
FIG. 3. Curves depicting the same relationship between decrease in dark current, rate of resensitization, with time as Fig. 2 at a lower field strength. Field strength 3390 volts/cm.

the light[11] is turned on), and the name "steady-state current" to i_s.

In Figs. 2 and 3 are plotted the values of $i_t{}^D$, $i_0{}^\phi$ and i_s observed with our crystal while the voltages there indicated were being continuously applied from $t=0$ over a period of 60 or 80 minutes, and light was being turned on occasionally for short intervals of time. It is seen that the dark current decreases steadily from $i_0{}^D$, while the initial photoelectric current increases steadily from zero.

Two cases are to be distinguished:

(I) If the light is turned on after the lapse of some minutes, $i_0{}^\phi$ is so large that in spite of the diminution of i^D, their sum is greater than $i_0{}^D$. Under these circumstances *the total current* does not remain equal to $(i_t{}^D+i_0{}^\phi)$ but *rapidly declines to a value i_s not very different from $i_0{}^D$, at which it remains constant so long as the light continues to shine.* This remarkable fact (further illustrated in Fig. 4 and further discussed) has been established for room-temperature. At lower temperatures we observe the constant value i_s, but cannot compare it with the value of $i_0{}^D$, because of the extremely rapid decrease in i^D, thus preventing reliable values of $i_0{}^D$ to be obtained.

(II) For small values of t such that the sum of $i_t{}^D$ and $i_0{}^\phi$ is smaller than $i_0{}^D$, the total current remains constant throughout the illumination at the value—i.e., $(i_t{}^D+i_0{}^\phi)$—which it assumes as soon as the light is turned on.

---

[11] The data presented were obtained with general radiation from a tungsten lamp. From numerous measurements made with monochromatic radiation from various parts of the spectral sensitive domain of red mercuric iodide it has been definitely established that the behavior described is independent of the character of the light used so long as it falls in a spectral region to which the crystal is photoelectrically sensitive.
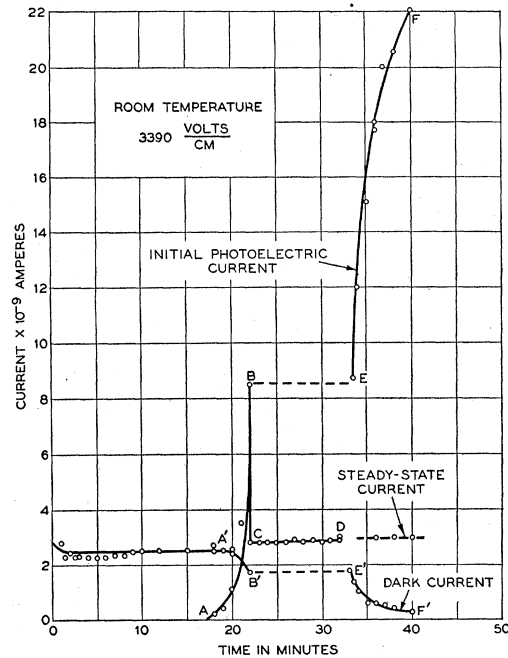

FIG. 4. Curves showing the constancy with time of the dark current during the incubation period and effect of constant illumination on the rates of change of photoelectric and dark currents.

It is seen in Fig. 3 that there is no perceptible photoelectric current for an appreciable time T after the voltage is applied; and that then there occurs an apparently simultaneous decrease in the dark current and increase of the photoelectric current. We call the period T the "incubation period." It varies in duration from zero (or a length too small to observe) up to several hours. We have not been able to obtain any data concerning the factors controlling the lengths of these incubation periods. Attempts to correlate crystallographic directions and incubation periods have proved to be futile. However, it is clear that *there exists an intimate relationship between the decrease in dark current and the resensitization process.* It is a rule illustrated in Figs. 2 and 3, that the higher the applied field the more rapid the decrease in dark current and increase in photoelectric current with lapse of time after the incubation period ends. (Note that in the case of Fig. 2, T is imperceptibly short.) It is also seen that the higher the voltage the larger the final sensitivity attained, with an accompanying increase in steady-state current (i_s) and value of the dark current at $t=0$ $(i_0{}^D)$.
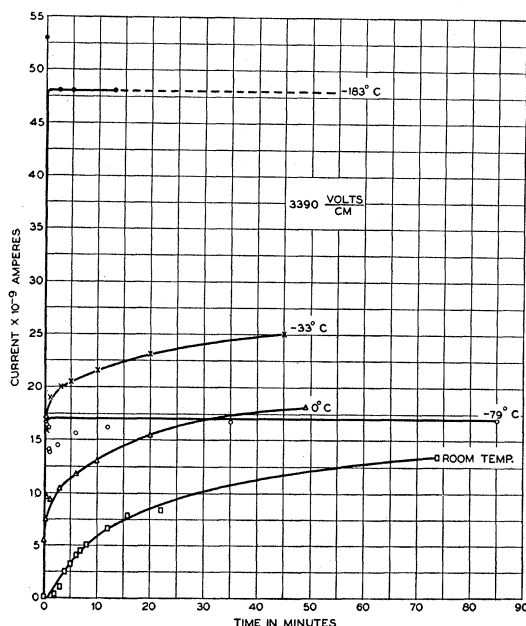
FIG. 5. Curves depicting the rate of resensitization at temperatures between and including room and liquid air temperatures.

Fig. 4 depicts the relationships between the dark, initial photoelectric and steady-state currents in a case in which an incubation period of some 17 minutes was observed. It also clearly shows the effect of steady illumination of the crystal after the incubation period is past and the photoelectric current becomes appreciable. The points A and A' mark the end of the incubation period, when the dark current begins to decrease with accompanying development of photosensitivity. Beginning at the time corresponding to BB' the crystal was irradiated continuously for 10 minutes. (Note how rapidly the photoelectric current rises to and drops from its "initial" value i_0^ϕ represented by B, and how constant it remains during the whole subsequent ten minutes at its steady-state value as shown by the points along CD.) At the time D the voltage and the light were cut off simultaneously. The voltage was then re-impressed across the crystal at the time corresponding to EE' and the light turned on again immediately for a brief flash, whereupon the initial photoelectric current (i_0^ϕ) and dark current (i_t^D) were found to be equal to E and E', respectively. The sensitization was then allowed to proceed in the normal

manner—voltage applied continuously, with occasional flashes of light to establish the degree of photosensitivity. *It is to be noted that constant illumination during the time interval B–D had no detectable effect on the subsequent trend of the curves depicting dark current (i_t^D) and photoelectric current (i_0^ϕ).* The sensitization appears to have continued its normal course along $EF(E'F')$ accompanied by the same steady-state current, as if during the illumination it had been neither hastened nor retarded. In other words the period of constant illumination simply served to displace the extension of AB and $A'B'$ along the time axis to EF and $E'F'$. The steady-state current i_s again is equal to the value of the dark current at $t=0(i_0^D)$.

In view of the close relationship existing between the dark current and photosensitization of a desensitized crystal, it was of especial interest to study the rate of sensitization as a function of temperature. If the dark current which we measure is of an electrolytic nature we should expect it to decrease very rapidly with decreasing temperature with a consequent decrease in the rate of sensitization. However, we found the contrary to be the case. Fig. 5 shows a family of curves depicting the initial photoelectric current i_0^ϕ as function of time measured from the application of the voltage or from the end of the incubation period, at a number of temperatures between and including room and liquid air temperatures. These results show that the rate of sensitization *increases* with *decreasing* temperature. This is in strong contrast to the results of Pohl and Stasiw in which they found the "rate" of sensitization of KCl to *increase* exponentially with *increasing* temperature at a rate comparable to the increase in electrolytic conductivity with increasing temperature. At liquid air temperature the rate of sensitization is so great that the stages of the increase are not observable by the means which we have hitherto used to study the effect.

In general the lower the temperature the greater the ultimate sensitivity attainable. However, as is to be seen from Fig. 5 there exists some inconsistency in the photoresponse at CO_2 temperature $(-79°C)$ for it is somewhat less than the response at liquid ammonia temperature
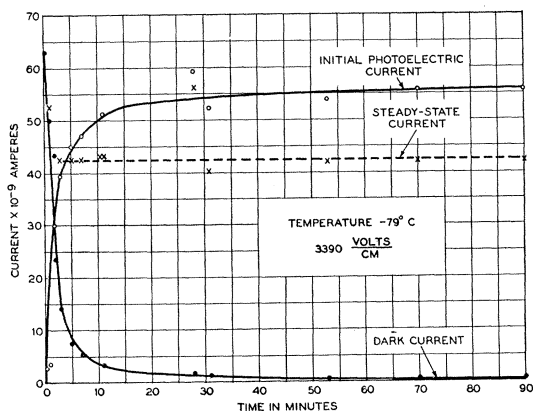
FIG. 6. Curves showing same relationships as Fig. 3 between rate of sensitization and decrease of dark current with time. These measurements were made on the same crystal as was used in Figs. 2, 3, etc. Measurements made at a date two months later.

$(-33°C)$. Nevertheless we feel justified in concluding from numerous experiments that in general *the lower the temperature the greater the photoelectric sensitivity attainable.*

In view of the fact that the electrolytic dark current in inorganic salts, e.g., KCl, decreases exponentially with decreasing temperature, it appears improbable that the observed dark currents are of this character.

Fig. 6 shows the relations between dark (i_t^D) steady-state and initial photoelectric (i_0^ϕ) currents as a function of time for $-79°C$. The same general behavior was found as in the experiments conducted at room temperature. These data were obtained some two months later on the same crystal as was used for the series of experiments given in Figs. 2 to 5. Comparison between the $-79°C$ curve in Fig. 5 with the photoelectric current curve in Fig. 6 shows some of the effect of increase in age on the properties of the crystals. It has been generally observed that the dark conductivity tends to increase with increasing age of the crystals.

Comparison of x-ray patterns made of intrinsically sensitive (i.e., freshly-made) and desensitized crystals shows a marked difference in the physical state of the crystal: the sensitive crystals are found to be monocrystalline, whereas the desensitized ones show a polycrystalline fiber structure with considerable scattering.
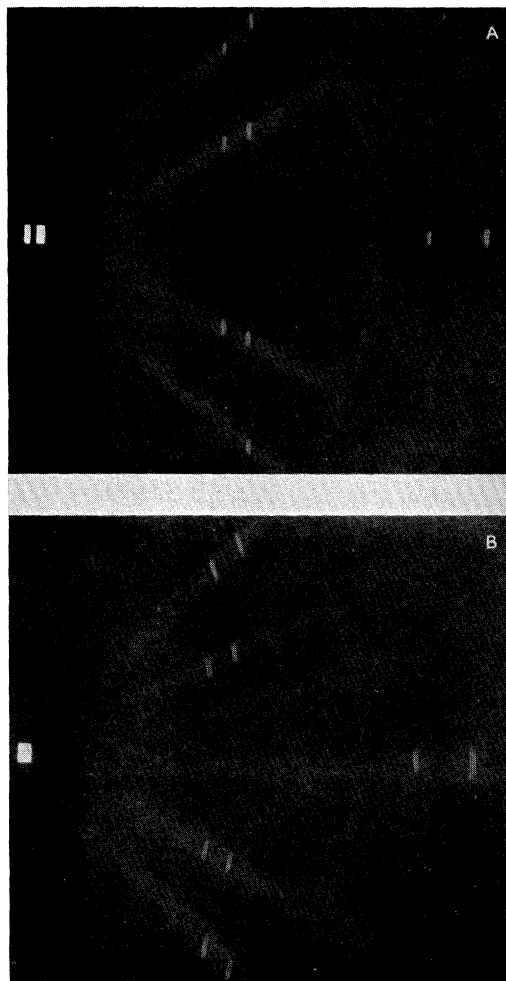

FIG. 7. X-ray diffraction patterns of (A) sensitive and (B) desensitized crystals. Retouched to bring out contrast.

Fig. 7A shows a typical x-ray diffraction pattern of a freshly-made sensitive crystal, while Fig. 7B is representative of the desensitized crystals. The lattice constants of the sensitive and desensitized crystals were found to be identical, with no detectable change in relative intensity of spots and without the appearance of new lines. The x-ray patterns of resensitized crystals were found to be identical with those of the desensitized ones, i.e., Fig. 7B.

It does not seem probable that the mechanism of sensitization used in the present work is identical with that which was used in the Stasiw and Pohl experiments; for: (1) the rate of sensitization does not increase exponentially

with increasing temperature as in the Stasiw and Pohl experiments, but on the contrary decreases with increasing temperature; (2) sensitization does not necessarily result merely from the passage of a dark current through the crystal but commences only when the dark current begins to decrease with time; (3) the

dark current does not decrease exponentially with decreasing temperature but remains comparatively large at low temperatures.

In conclusion we wish to thank Dr. K. K. Darrow and Mr. E. J. Murphy for many stimulating and helpful discussions during the preparation of this manuscript.

Time Lags in Magneto-Optics

H. W. FARWELL AND J. B. HAWKES, *Columbia University*

A modification has been introduced in the apparatus usually employed for the time lag experiments, thereby enabling photometric measurements to be made. Minima were observed, but they were not confined to definite trolley positions. This apparatus has served to emphasize the variations in the exciting magnetic field, but has not disclosed evidence to support the view that sharp minima due to other causes are present.

THE problem of the time lag in the Faraday effect and of other possible related effects has been under examination for a long time, but within the past few years the results of Beams and Allison,[1] and particularly of Allison and his students,[2] have aroused much interest. The whole problem obviously demanded the attention of workers in numerous other laboratories, in order that the results might be checked, and if possible enough material obtained for a satisfactory basis to a theoretical treatment of the subject.

To assist in the study of this problem, the work reported in this article was begun about three years ago with the installation of apparatus substantially in accord with the descriptions in the references cited. On the first apparatus constructed the results were largely qualitative, and completely negative so far as sharp minima were concerned.

The qualitative results of the original set-up may be summarized in this way: First, the existence of the broad minimum for CS_2 in both cells was readily shown, and a satisfactory explanation in terms of the electrical constants of the circuit was demonstrated. This is in agreement with the findings of Slack and Breazeale[3] and of Webb and Morey.[4] Second, it was shown that temperature effects in the CS_2 cells were apt to be troublesome. Because of this water-cooled cells have been used since that time whenever measurements have been made. In addition the variability of the spark was clearly another hindrance to satisfactory observation.

Having failed to note definitely any sharp minima, one of us (H. W. F.) visited Dr. Allison's laboratory in August, 1933, where every courtesy was shown, and every opportunity given to study the apparatus, method of observing, as well as other details of the work. On the second day minima of the sharp type were seen in his apparatus. Minima were also seen a few days later in the laboratory of Professor F. G. Slack at Vanderbilt University.

APPARATUS

Our apparatus was then completely rebuilt in a larger room, reproducing with extreme care every essential of the apparatus seen in Alabama. In some respects minor changes were introduced. For example the sliding bridge or "trolley"

[1] Beams and Allison, Phys. Rev. **29**, 161 (1927).
[2] Allison *et al.*, J. Chem. Ed. **10**, 2 (1932).
[3] Slack and Breazeale, Phys. Rev. **42**, 305 (1932).
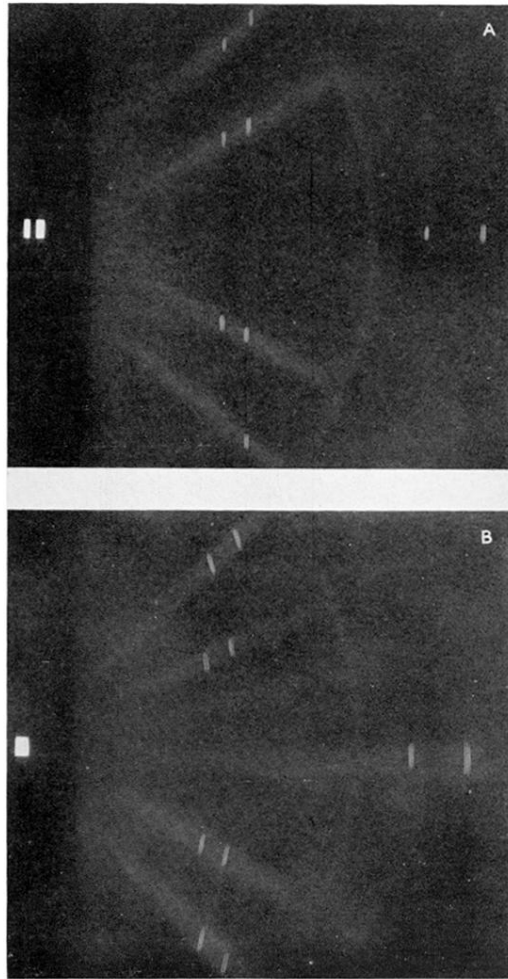[4] Webb and Morey, Phys. Rev. **44**, 589 (1933).

FIG. 7. X-ray diffraction patterns of (A) sensitive and (B) desensitized crystals. Retouched to bring out contrast.