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Persistent Internal Polarization*

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Studies are reported on persistent internal polarization effects. This polarization can be produced, particularly in photoconductive, fluorescent substances of high dark resistance, by the action of various kinds of radiation in the presence of a dc electric field. It has been found that such polarizations, of more than 10 000 volts/cm, will persist for many days if kept in the dark after field removal. A material so polarized is in many ways a photosensitive electret. Among the substances tested, a [Zn:Cd]S phosphor and anthracene were used most extensively. Measurements are reported on the effect of ultraviolet, visible, and infrared light, gamma and beta rays on the production and removal of polarization. The increase of polarization with time is initially rapid and then shows saturation. It is almost a logarithmic function of the exciting radiation intensity, and a linear function of the polarizing voltage over a wide range. It is found that the equilibrium values of polarization are essentially determined by the applied voltage, and one parameter specific to the substance. Data are given on the long-time storage of polarization. It is shown that this polarization is due to a partial separation by the applied field of free mobile charges produced by the radiation inside the material and their localization in traps. It is not a charge injection-ejection phenomenon at the electrodes since it occurs just as well in samples insulated from the electrodes. In powders at least, the polarization is distributed throughout the entire sample and is not a charge accumulation near the surfaces. A correlation is established between these phenomena and the mechanism assumed for these substances to explain photoconductivity and fluorescence. A phenomenological model is presented which quantitatively describes many of the results of these experiments. This polarization effect provides a new method to detect and study energy storage in crystals.

I. INTRODUCTION

SINCE the earliest days of research on photoconductivity it has been recognized that a space charge type of polarization occurs in insulating photoconductive substances and persists after field removal.[1] Generally it was believed to arise out of the immobility of the positive charges and the trapping of electrons moving in the conduction band, or their actual removal from the crystal by the field without a sufficient supply of new charges from the electrodes. The classical method of detecting and measuring polarization was to remove the applied field and flood the crystal with red or infrared light. If the crystal had been polarized, a reverse current (to the normal photocurrent) would flow.[1] The magnitude of this reverse current was taken as a measure of the extent of polarization in the sample.

The effect of primary interest in those investigations was photoconductivity. It was natural, therefore, that polarization and the change in effective field strength due to it was considered an inherent interfering effect. Much of the current work[2] on this subject is pointed towards accurately evaluating the influence of polarization on photocurrents in order to subtract the change it introduced in the measurements[3,4]; or to perform the experiments in such a manner that the deviations due to polarization were minimized, for instance by flooding the sample with red or infrared light concomitant with the exciting radiation, or to make the measurements of photocurrents using either short-time flash illumination[5] or short-time, low-intensity radiation.[6]

Experiments of more recent vintage in the field of crystal conduction counters have encountered polarization in the form of a progressive deterioration of pulse heights with increasing number of counts. This was ascribed to the decrease in effective field strength as the polarization builds up.[7]

Three major methods have been employed to determine polarization: the measurements of a reversed current with various modifications, the use of a potential probe moved over the lateral surfaces of the crystals,[8,9] and the observation of the movement of color center clouds.[6,10]

This paper presents an investigation of the internal polarization effect itself, especially of that portion which persists for long periods of time, without any view to its special impeding effects on current flow; indeed, it will be shown, that the formation of the polarization is largely independent of the flow of an actual body photocurrent and can be performed to the same extent with the sample between insulating sheets of mica, which, while displaying the well-known dielectric charging, blocks a steady state photocurrent. It deals with the formation and removal of polarization by various kinds of radiation; with its persistence, and its natural decay. The main result is that this persistent internal polarization is a much more important and outstanding effect than anticipated up to now. Some materials are actually equivalent to the well-known

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[1] E.g., R. Hilsch and R. W. Pohl, Z. Physik **87**, 78 (1933). (For early experiments see references in 10.)

[2] E.g., A. Rose, R.C.A. Rev. **12**, 362 (1951).

[3] R. C. Herman and R. Hofstadter, Phys. Rev. **59**, 79 (1941).

[4] J. J. Dropkin (unpublished thesis, June, 1947).

[5] N. F. Mott, Proc. Phys. Soc. (London) **50**, 200 (1938).

[6] M. F. Manning and M. E. Bell, Revs. Modern Phys. **12**, 215 (1940), p. 226.

[7] R. Hofstadter, Nucleonics **4**, 11 (1949); H. Kallmann and R. Warminsky, Ann. Physik **6**, 4 (1948).

[8] R. H. Bube, Phys. Rev. **83**, 393 (1951).

[9] R. W. Smith, R. C. A. Rev. **12**, 352 (1951).

[10] A. L. Hughes, Revs. Modern Phys. **8**, 300 (1936).

electrets[11] and display polarization charges up to 10^{-8} coulombs/cm^2. The best of these materials were a (Zn:Cd)S phosphor (henceforth referred to as K) and anthracene. They are both capable of sustaining polarization field gradients of more than 10 000 volts/cm for long periods of time (see Sec. VII) and furnish output potentials far above 100 volts. The creation and discharge of these polarizations are highly radiation-sensitive.

The measurements reported are preliminary and the work of collecting new data is still in progress. They already indicate that much insight into the nature of the electrical, optical, and storage properties of photosensitive insulators can be gained from such an approach.

II. EXPERIMENTAL METHODS AND APPARATUS

Two methods have been used to measure the persistent internal polarization in a sample: the radiation discharge method, which is a nonrepeatable procedure, destroying the polarization at least partially, and the lifted electrode method which permits repeated measurements without appreciably disturbing the polarization.

After a thin (0.1 mm thick) sample of the material to be investigated has been polarized (as indicated in Fig. 1) and both its surfaces grounded thereafter, an internal potential in the sample exists which is balanced by a voltage drop of opposite direction between the polarization charges and the image charges at the surfaces of the electrodes; the total voltage drop across the electrodes is zero. If one electrode is then attached to the grid of an electrometer tube, the ground connection removed, and the sample irradiated with various kinds of radiation, a decrease of the polarization occurs and a portion of the image charges will be freed. Thus a voltage increase $\bar{V}$ (termed the radiation discharge voltage) is produced at the grid of the electrometer, and from $\bar{V}$ the total polarization stored in the powder can be computed (see Sec. VIII). Thus by measuring $\bar{V}$, the build up, the decay and the discharge of polarization can be determined. Since the radiation discharge method, however, destroys the polarization of the sample, the build up and particularly the decay of polarization can be determined by this method if, after each $\bar{V}$ reading, the sample is thoroughly depolarized and then polarized again in the same manner as before. The results of such measurements are reproducible to within less than 5 percent.

The second method, derived from electret work, uses a brass electrode (1 cm^2 area) on the sample surface which can be lifted away from the surface after the grid is connected and the ground removed. The image charges (Q) induced on the electrode by the polarization across the sample will all appear across the grid capacitance (C_e) if the electrode is lifted (C_p, the capacitance of the unpolarized sample, goes to zero), and will produce a voltage (V_e) on the grid. Then we have the relation, $Q=C_eV_e$, or

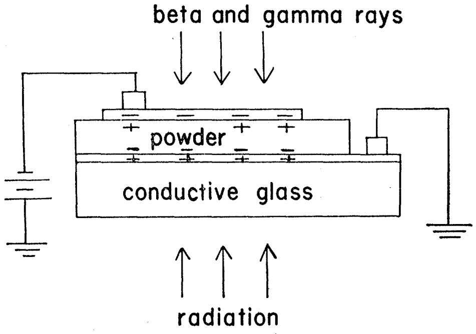

FIG. 1. Electrode and radiation arrangement of sample, showing direction of applied and polarization fields.

$$V_p=(C_e/C_p)V_e, \tag{a}$$

where V_p is an equivalent potential which would appear across the sample if only the sample itself and the charges Q were involved. We define V_p by Eq. (a) since the charge Q appears only across C_p and not also across C_e when the electrode is in contact with the sample.

Extensive measurements have shown that the field changes during the lifting process does not appreciably affect the polarizations investigated, and that the results obtained with both methods are equivalent.

For substances in the form of fine powder the samples were prepared in the manner previously described[12] but with a larger amount of Duco cement. When a sufficient thickness (5 to 50 mg/cm^2) was deposited, it was dried by an infrared baking lamp and was, when cooled, uniform and compact.

In the case of anthracene (scintillation-grade flakes obtained from the Reilly Tar Company), fused solid samples and single crystals of thicknesses between 0.05 and 0.3 mm were tested in addition to powdered samples.

The samples were placed between two electrodes; one was the conducting coat of a Nesa[13] glass plate and the second was a small square of flexible aluminum leaf in the center of the surface of the substance. A small brass weight was placed over this. When a voltage was applied across the sample, the aluminum leaf was drawn tightly down making intimate contact with the surface. Normally a dc field (termed polarizing voltage) is applied with concomitant radiation to polarize the sample. After a given period of time the radiation is removed, and then the field is turned off. The two electrodes are put to ground for various lengths of time and

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[11] G. Nadjakoff [Compt. rend. **204**, 1865 (1937)] describes a photoelectret effect in sulfur, similar to the phenomena described in this paper.

[12] See H. Kallmann and B. Kramer, Phys. Rev. **87**, 91 (1952), p. 93.

[13] Commercial form of glass plate with evaporated transparent conductive coating obtained from Pittsburgh Plate Glass Company.

TABLE I. Radiation sources.

Radiation region	Source	Wavelengths (or energy)	Intensity[a]
Ultraviolet light	Mercury discharge bulb	3660 A	15 microwatts/cm^2 [b]
Visible light	3-volt tungsten bulb	4000–7000 A	*ca* 1 milliwatt/cm^2 [b]
Infrared light	250-watt heating lamp	0.8 to 2 microns	15 milliwatt/cm^2 [b]
Mercury flash tube	FT-214 tube	uv—visible-infrared	5×10^4 ergs/cm^2 [b]
Gamma rays	Radium	2 Mev	1 millicurie
Beta rays	Strontium 90	*ca* 1 Mev	10 millicuries

[a] Geometry factor different for each source.
[b] At the sample surface.

then a polarization measurement is performed as described above. The polarizing process can also be performed between insulating sheets; the determining factor is the external field across the sample. In this case after polarizing, for the purpose of measurement, one or both insulating sheets are removed when the lifted electrode method is used.

Exciting or releasing radiations in the form of ultraviolet (3660 A), visible and infrared (up to 2 microns) light were incident on the sample through the transparent glass side and high energy radiations (gamma and beta rays) impinged on the sample through the thin aluminum foil as shown in Fig. 1. The various radiation sources are tabulated in Table I.

The electrometer system used to measure polarization voltages is shown in Fig. 2. It should be noted that no external grid resistor is used. The cathode is biased positive with respect to ground so that the grid floats at ground with a minimum grid current being drawn (*ca* 10^{-14} amp). To this system, one of the electrodes (usually the metal electrode) was connected, whereas the other electrodes (Nesa glass) was kept at ground. Since the maximum polarization voltages to be measured are well above 100 volts and since the cut-off voltage of the tube is about 6 volts, it was necessary to introduce two variable air condensers as voltage dividers. The entire grid input assembly was enveloped in a grounded electrostatic shield. All parts of the apparatus exposed to higher voltages were made of polyethylene. Therefore, it was the Nesa glass that was usually kept at ground to avoid leakage across the glass sides. Using usual precautions the apparatus was free of drift, kept a negative applied voltage long enough for accurate measurements, was easily calibrated and held its calibration for many months of operation. The minimum detectable voltage is 10 millivolts; the maximum voltage capable of being registered is 150 volts.

The substances tested up to now are described in Table II. No polarization means that the persistent effect was not detectable with described methods. These scanty results indicate that the substances show either both noticeable photoconduction and polarization or neither. This means that the production of mobile charge by exciting radiation is necessary for polarization; but obviously, this is not a sufficient condition. This can be seen from the results with pure ZnS and CdS. Both show little photoconductivity, but one knows from conduction counting experiments with pure CdS that various kinds of radiations produce mobile charges in unactivated CdS.[14] The small photoconductivity in these substances is attributed to the lack of localized charge (and consequently a small carrier lifetime); i.e., they contain no activators to make the positive charge remain fixed in the substance. Therefore no photoconductivity and also no persistent polarization can develop. For high photoconductivity at least a partial localization of one kind of charge is necessary, but it is not enough to bring about persistent polarization. For this a partial localization or trapping of both charges is imperative since otherwise the kind of charge which is not trapped at all could always recombine with the localized charge when the external field is removed. From this viewpoint it would be interesting to see whether substances with long time storage properties display an exceptionally high polarization. Our investigations already show that the reverse does not hold. The phosphorescence of anthracene, which was specially tested, is extremely poor compared to that of the (Zn:Cd)S phosphors, and in spite of this it displays a very strong persistent polarization. The reason for this lack of correlation probably originates in the small number of displaced charges required to bring about a very appreciable polarization. Not more than 10^{12} (+) and (−) trapped charges per cm^2 in a layer of $\frac{1}{10}$-mm thickness are sufficient to produce a polarization voltage of 100 volts.

It appears obvious that in order for polarization to persist, the number of mobile charges after the removal of the exciting source must decay fast to a low value. Thus in all substances without a very high dark re-

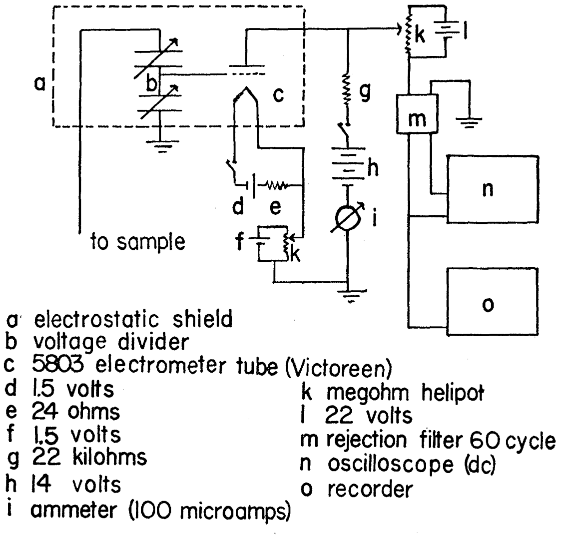

FIG. 2. Schematic diagram of the measuring and recording system.

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[14] H. Kallmann and R. Warminsky, Ann. Physik 6, 4 (1948).

sistance, polarization may occur under an applied field, but will not persist after field removal. The high dark resistance of the (Zn:Cd)S phosphors and of the organic phosphors is thus essential for the long persistent polarization.

It may be that some of the substances showing no polarization under ultraviolet excitation can be polarized with higher excitation energies. This is however, doubtful since anthracene, with a long wave absorption cut off at 3900 A, can still be polarized with light beyond 5000 A. A more detailed investigation of the polarization, of its build up, its decay, removal, and its persistence was primarily studied in the substances *K* and anthracene.

III. POLARIZATION AS FUNCTION OF EXPERIMENTAL VARIABLES

A. Polarization as a Function of Polarizing Voltage and Polarizing Time

Most of the evidence accumulated to the present indicates that the internal polarization in a sample increases fairly linearly with the applied polarizing voltage; but such a dependence is only sensible when the dependence of the polarization of the polarizing time is taken into account. This buildup of polarization with time is characterized by an initial rapid increase followed by a gradual slowing down of the rate of increase until an equilibrium value is reached and no further increase occurs. This build up is of the form $P=P_{\max}[1-\exp(-t/\tau)]$. This slowing down of the rate of increase probably results from the fact that as the polarization builds up, the effective polarizing field on mobile charges decreases. (See Sec. VIII.) This type of rise of polarization is illustrated in Figs. 3 and 4 for anthracene and *K* respectively. These data were taken using a fairly high intensity light source of excitation (*ca* 15 microwatts/cm^2). If the exciting intensity is reduced, the time to reach the maximum polarization increases. A series of measurements on anthracene shows this quite clearly; the applied field was kept constant, while for several intensities of exciting radiation, the polarization build up *versus* time was determined. The results are plotted in Fig. 5. For very low intensities the slope is small and almost linear in time. As the intensities increase, the initial slope increases (though at a much slower rate and the linear portion of the curve is limited to smaller periods of time. It may be assumed that if the polarizing time was increased indefinitely for each curve, the final equilibrium values of the polarization would be identical regardless of the intensity of excitation.

TABLE II. Materials tested for persistent internal polarization (P.I.P.).

Substance	Physical state	Exhibits pronounced P.I.P.	Exhibits pronounced photoconductivity	Exhibits pronounced fluorescence
1. *K* (Zn:CdS)	Powder	X	X	X
2. *M* (ZnS)	Powder	X	X	X
3. *N* (ZnS)	Powder	X	X	X
4. *L* (Zn:CdS)	Powder	X	X	X
5. *LG*2150 (ZnS)	Powder	X	X	X
6. Anthracene	Powder	X	X	X
7. Anthracene	Fused polycrystal	X	X	X
8. Anthracene	Single small crystal	X	X	X
9. Fluoranthene	Fused polycrystal	No	No	X
10. Chrysene	Powder	X	X	X
11. 9-Bromoanthracene	Powder	X	X	No
12. *Trans*-stilbene	Single large crystal	X	X	X
13. ZnS—nonactivated	Powder	No	No	No
14. CdS—nonactivated	Powder	No	No	No
15. Paraffin	Fused sample (thin)	No	No	No

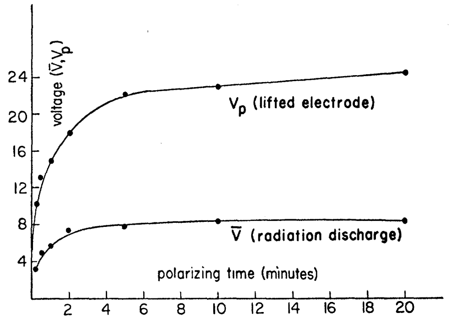

FIG. 3. Lifted electrode and radiation discharge voltages in anthracene as function of the polarizing time (polarizing voltage $=20$ volts; ultraviolet intensity $=15$ microwatts/cm^2).

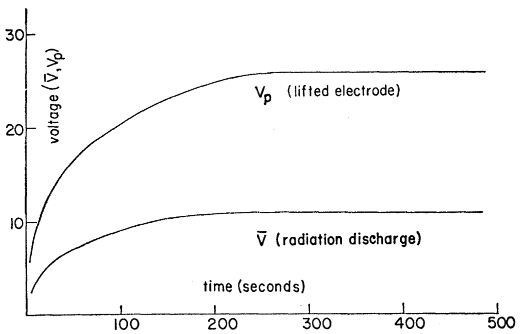

FIG. 4. Lifted electrode and radiation discharge voltages in *K* as function of the polarizing time: (a) radiation discharge voltage; (b) lifted electrode voltage (polarizing voltage $=100$ volts; ultraviolet intensity $=15$ microwatts/cm^2).

Further, experiments with very short excitation times were carried out with both *K* and anthracene. For anthracene, 300 volts was applied for 15 seconds. During this time a light flash from a FT-214 mercury flash tube was incident on the sample which was otherwise kept in complete darkness. The flash time is of the order of 1/2000 second and the energy incident on the sample was 5.3×10^4 ergs/cm^2. The voltage V_e amounted to slightly more than 70 volts. This is smaller than that obtained if the same total amount of energy would be applied during a longer period. With a quenched sample of *K* and an applied field of 200 volts the same experiment also produced a polarization larger than 70 volts. This shows that even with short excitation periods rather large polarization voltages can be produced. Anthracene was also polarized with an exposure to 15

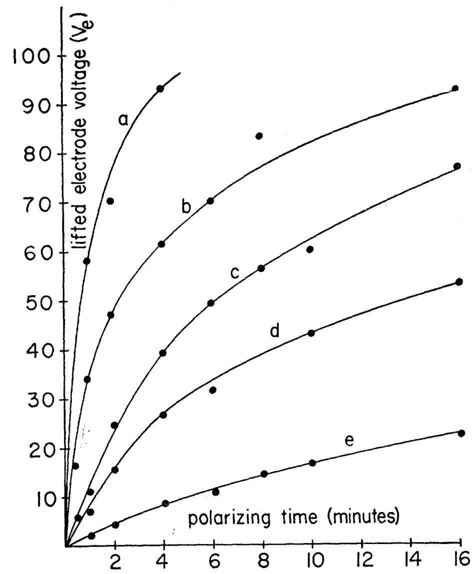

FIG. 5. Polarization in anthracene as function of polarizing time for various ultraviolet intensities: (a) 2.2×10^{-8} watt/cm^2; (b) 4×10^{-9} watt/cm^2; (c) 7.3×10^{-10} watt/cm^2; (d) 1.3×10^{-10} watt/cm^2; (e) 1.4×10^{-11} watt/cm^2 (polarizing voltage$\sim$300 volts).

microwatts/cm^2 of ultraviolet radiation for 1/25 second. A voltage of 300 volts was again applied for 15 seconds. This yielded a voltage V_e of 37 volts. The energy absorbed by the 1/25-second exposure is less than the energy absorbed by the 1/2000 second flash by a factor of about 1000, and yet the polarizations produced differ by a factor of only 2 or 3. This is roughly in agreement with the curves of Fig. 5 if the much smaller absorption of the energy emitted by the flash bulb than that of the ultraviolet radiation is taken into account. It should also be taken into account that the polarization obtained depends not only on the time of irradiation but also on the period of time the field is applied; for the same periods of irradiation the polarization would be larger when the field is applied for longer periods due to retrapping. The relationship between the intensity of the exciting radiation and polarization will be more fully discussed in the next part.

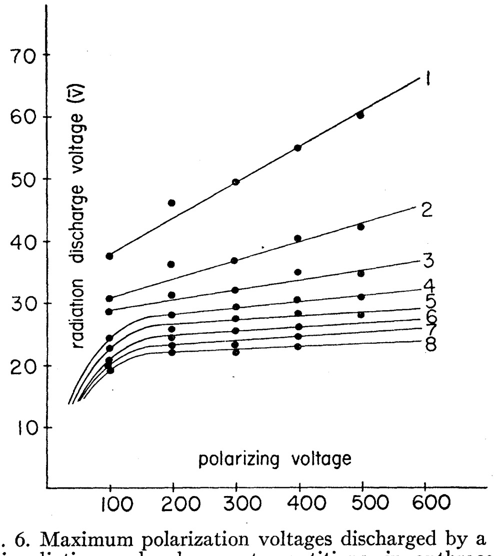

FIG. 6. Maximum polarization voltages discharged by a single light irradiation and subsequent repetitions, in anthracene as function of the polarizing voltage. (Polarizing time = 1 minute; ultraviolet intensity = 15 microwatts/cm^2.)

To determine the dependence of the polarization on the polarizing voltage, all measurements should be made for equilibrium polarization. But it was observed that the results are not too different if instead one compares polarization values taken after a definite shorter polarizing time.

Figures 6 and 7 present ($\bar{V}$), Figs. 8 and 9, V_p, and Fig. 10, V_e *versus* polarizing voltage. Figure 10 departs from the usual linearity and shows a parabolic shape. This special shape may be due to the much lower intensity of ultraviolet used in this case. Figure 9 shows that at low polarizing voltages V_p equals or even exceeds the polarizing voltage.

The results should not be intercompared since they differ by different ratios of C_e/C_p for V_p in different samples. Generally V_e and V_p are of the same order of magnitude. It should be further mentioned that the absolute polarization values may also depend upon the thickness of the samples. The voltages $\bar{V}$ are usually 2 or 3 times smaller than V_p. It is to be expected that at very high voltages the polarization increase will be slowed down because of the saturation of the number of traps available for polarization. This may be true for anthracene, but for inorganic substances a simple calculation shows that saturation should not be expected at the polarizing voltages used in these experiments since the number of traps is of the order of 10^{16} per unit volume which is much more than the number of charges required for polarizing.

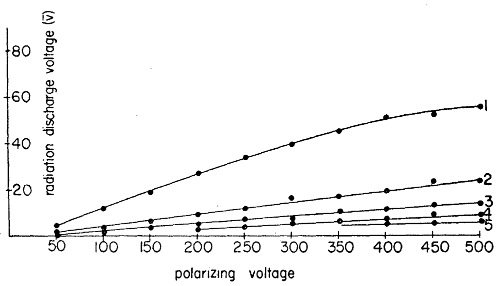

FIG. 7. Maximum polarization voltages discharged by a single light irradiation and subsequent repetitions, in K as function of the polarizing voltage. (Polarizing time = 1 minute; ultraviolet intensity = 15 microwatts/cm^2.)

B. Polarization as Function of the Intensity of Various Exciting Radiations

The voltage, V_e, in anthracene as a function of the exciting intensity is given in Fig. 11 for a range of polarizing times and for excitation with 3660 A, which is strongly absorbed by the bulk material. The following major results were obtained: (1) polarization of the order of volts can be created with exceedingly low intensities of ultraviolet radiation (10^{-11} watt/cm^2 and less); (2) the polarization is a very slow (almost logarithmic) function of the exciting intensity; (3) a reciprocity law does not hold for this case, which implies that the absorbed energy is not equally well utilized for producing polarization at different intensities.

Light of wavelengths longer than the absorption edge of the substances (3900 A in anthracene and 4200 A in *K*) is also capable of producing polarization. The excitation by visible light may be at first sight astonishing for anthracene since no excitation to fluorescence has been reported in this instance. However, it was found that visible light is also capable of exciting phosphorescence and even a small photoconductivity in anthracene. For *K* the polarizing effect of visible light is probably due to the absorption of this light by the activator atoms and a production of mobile electrons. In both substances the amount of visible light necessary to produce polarizations comparable to ultraviolet polarization is much larger than that of the ultraviolet because of the much smaller absorption of this light. But these small amounts of light absorbed are sufficient to produce polarization. Measurements were further performed to determine up to which wavelengths polarization can still be produced. For this purpose a sample of *K* was first thoroughly de-excited with infrared light for 20 minutes to avoid any noticeable dark polarization and then polarized under visible light using various filters to cut off the radiation at progressively longer wavelengths with each succeeding measurement. The results are given in Table III. With increasing wavelengths the polarization decreases, but is still considerable at 6100 A and vanishes only beyond 7000 A. Since *K* has a fluorescent spectrum which reaches beyond 6000 A, this supports the idea that this polarization is due to an absorption in activator levels. It will be shown in Sec. VI that visible light is also effective in discharging the polarization with an efficiency of about 10 percent of that of ultraviolet light due to the smaller absorption coefficient for visible light.

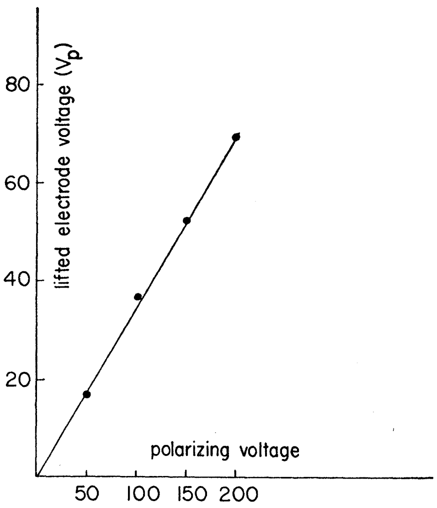

FIG. 8. Lifted electrode voltage in *K* as function of the polarizing voltage (polarizing time = 5 minutes; ultraviolet intensity = microwatts/cm^2).

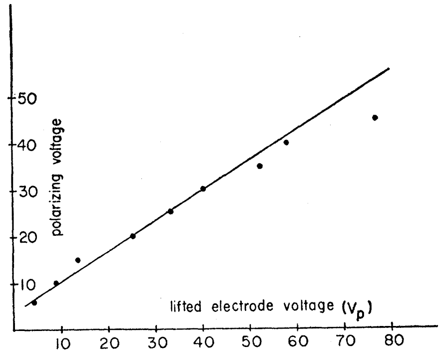

FIG. 9. Lifted electrode voltage in anthracene as function of the polarizing voltage (polarizing time = 1 minute; ultraviolet intensity = 15 microwatts/cm^2).

Polarization can also be produced in both substances using high energy radiation, e.g., 1-Mev electrons as an excitation source. The irradiation was equivalent to about 1 r/sec or 2 erg/sec energy absorbed in the sample. With a polarizing voltage of 200 volts applied to *K* for 10 and then for 20 minutes, V_e voltages of 64.1 and 93.5 volts respectively were obtained. Under ultra-

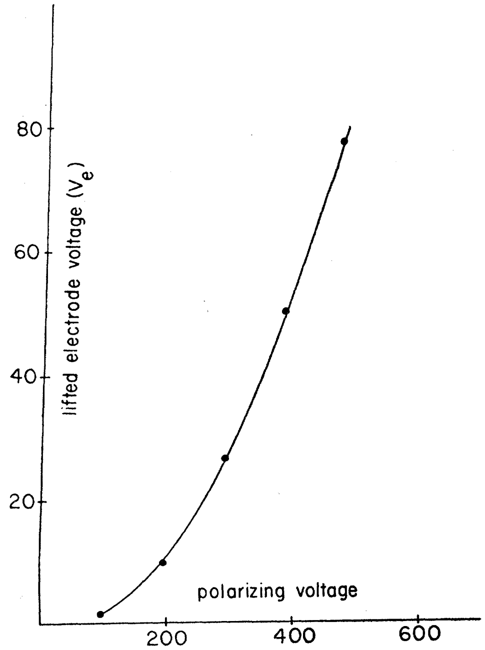

FIG. 10. Lifted electrode voltage in anthracene as function of polarizing voltage for low ultraviolet exciting intensity (polarizing time = 5 minutes; ultraviolet intensity = 4×10^{-9} watt/cm^2).

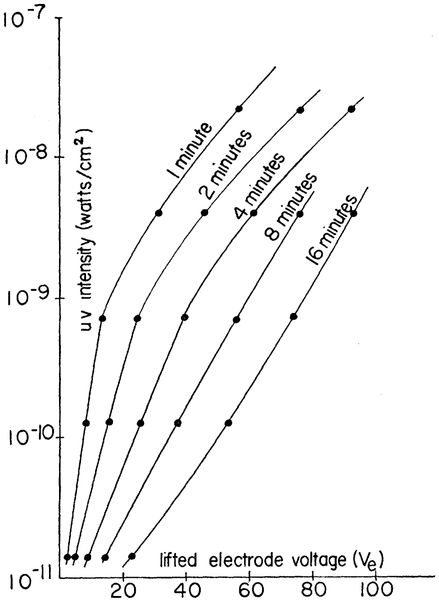

FIG. 11. Lifted electrode voltage in polycrystalline anthracene as a function of the exciting ultraviolet intensity for different polarizing periods. (Polarizing voltage *ca* 300 volts.)

violet irradiation of 150 ergs/sec absorbed, polarizations slightly over 100 volts in a 5-minute polarizing time resulted.

With K, the increase of polarization by fast electrons with polarizing time was measured by both methods. In Table IV the results are given for polarizing periods of 1, 5, and 10 minutes. Column 2 of the table shows a larger increase in polarization for the 5 to 10 minute period than the 1 to 5 minute period. This is unusual and has not recurred. The meaning of the fourth column will be explained in Sec. VIII; the results indicate that a polarizing time of 10 minutes is sufficient to produce an equilibrium polarization value with this exciting intensity. Fast electrons are also very effective in discharging polarization, as is indicated in Table V.

Since both substances show large polarizations under visible light excitation and both are highly fluorescent (blue in anthracene; yellow in K), it seemed possible that this fluorescent light is to some extent reabsorbed and contributes considerably to the observed polarization. The experiments have verified this idea. Two fused samples of anthracene were used. One was placed directly above the ultraviolet lamp. Between it and the second sample a Corning glass 3-73 filter was interposed which cut out any ultraviolet not absorbed by the first sample and transmits only the fluorescent light excited in the first sample. A polarizing voltage was applied to the second sample. Figure 12 is a curve of V_e as a function of the polarizing time. The polarization voltages obtained in this manner are a large portion of those produced by direct ultraviolet irradiation. Experiments of the same type were performed on quenched samples of K. The effect is exactly the same; irradiating the sample with the fluorescent light from a second sample produced a V_e voltage well above 100 volts after 3 minutes polarizing time with a polarizing voltage of 200 volts; again a considerable portion of the polarization obtained by direct ultraviolet irradiation. The intensity of the exciting ultraviolet source was 15 microwatts/cm$_2$ at the site of the first sample.

TABLE III. Visible light polarization in quenched sample K. Source of light—tungsten bulb. Polarizing time = 5.0 minutes. Polarizing voltage = 50.0 volts.

Filter (Corning glass)	Cutoff wavelength (short wavelength end)	Polarization (V_e)
3–70	4900 A	33.0 units
3–67	5350 A	31.8 units
2–60	6100 A	22.0 units
	Dark polarization	2.6 units

These experiments indicate further that the observed slow increase of polarization observed in a thick sample with polarizing time is due to the absorption in the rear portions of the inhomogeneously excited sample of the fluorescent light emitted from the excited portion. This was tested in the following manner: two quenched samples of powder K, one of the thickness 0.44 millimeter and the other of 0.055 millimeter were placed face to face and pressed together and irradiated with ultraviolet light through the thicker sample, which completely absorbed the ultraviolet light. The two samples were polarized for 10 minutes and then separated after removal of the light and field, and grounding, and the polarization was measured in the thick sample. The measurement was repeated with the ultraviolet light incident through the thin sample. The polarization in the thick sample was again determined. The ratio of the polarization voltages in the thick sample for the irradiation through the two different sides was 1.1. Both measurements were repeated with a 1 minute polarizing period. The corresponding ratio in this case was 5.4. The higher polarization in both cases occurred with the ultraviolet incident through the thick sample.

TABLE IV. Beta-ray polarization *vs* time of polarization. Powder K. Strontium 90 source. Polarizing voltage = 200 volts.

Time of polarization (minutes)	Lifted electrode voltage (V_p) (volts)	Radiation discharge voltage ($\bar{V}$) (volts)	Ratio $\frac{\bar{V}\text{ cal}}{\bar{V}\text{ meas}}$
1.0	41.2	21.8	1.11
5.0	54.3	29.3	1.045
10.0	82.0	43.1	0.996

This experiment shows that for short polarizing periods, the polarization is mainly restricted to the region of direct excitation. For longer polarizing periods, the increase in polarization is mostly due to those regions only indirectly excited. It may be pointed out, however, that even with uniformly excited powders the equilibrium value of the polarization is only gradually approached even under strong, homogeneously absorbed, radiation in both substances; this is due to the gradual decrease of the effective polarizing field.

IV. NATURE AND DISTRIBUTION OF POLARIZATION

Up to now no complete concept has been presented as to how polarization is established. The most obvious process for producing polarization is a displacement of the free electrons in the conduction band, while the positive charge is localized in activators. This inhomogeneous charge distribution of free electrons, which may be subsequently trapped, also produces an inhomogeneous distribution of the localized positive charge because of the equilibrium established between positive and negative charges as a consequence of recombinations. Thus the final persistent polarization consists of electrons in traps, eventually inhomogeneously distributed, and of an inhomogeneous positive charge distribution. Thus even when the traps are filled almost to saturation (homogeneously) polarization occurs as a consequence of the inhomogeneous positive charge distribution. The persistence of the polarization will, in any case, depend on the persistence of the electrons in the traps. That inhomogeneous distribution of electrons in traps is not imperative for polarization is evidenced by the following experiments: a quenched sample of *K* was polarized with field and concomitant ultraviolet radiation. It was then thoroughly quenched so that no dark polarization occurred and irradiated with ultraviolet (*ca* 20 microwatts/cm^2) for a period of two hours with both electrodes at ground. The total energy absorbed per unit area in this time is 1.4×10^6 ergs/cm^2. This is sufficient to fill most traps existing in the sample (*ca* 10^{16} per unit volume). It was then ultraviolet polarized under exactly the same conditions as the previous case. The polarization observed in these two measurements are given in Table VI. The same type of experiment was repeated using fast electrons as the exciting and pre-exciting source. This was done to preclude any interference in the previous measurements because of the inhomogeneous absorption of ultraviolet light. It is apparent from the data that pre-excitation has little effect upon the value of polarization under ultraviolet light or fast electrons, showing that an inhomogeneous distribution of electrons in traps is not necessary for strong persistent polarization. A few further measurements have been made for shorter polarizing periods and these agree with the aforementioned long-time results.

TABLE V. Preliminary measurement of sensitivity of discharge of polarization in *K* with various radiations.

Radiation	Radiation released voltage per unit radiation (volts/sec)/ergs/cm^2)
Ultraviolet (3660 A)	0.6
Visible light (4000 A to 7000 A)	0.06
Infrared light (0.8 to 1.5 microns)	10^{-5}
Fast electrons (10-millicurie strontium 90 source)	*ca* 1
Gamma rays (1-millicurie radium source)	*ca* 1

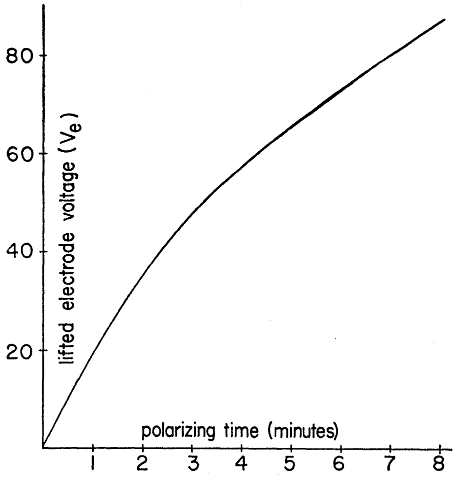

FIG. 12. Lifted electrode voltage in anthracene excited with anthracene fluorescent light as function of polarizing time. (Polarizing voltage = 200 volts.)

The previous discussions assumed that the polarization was created by a separation of charge internally and their subsequent localization. There are various other possible ways in which polarization may be established. It is possible that the sample as a whole is no longer electrically neutral due to charges removed from or injected into the sample. It was found, however, that if the polarity of the applied field was reversed the sign of the polarization voltages were also reversed. Since the signs of the charge transferred into or out of the sample should not be changed by reversing the field, the observed polarization cannot be accounted for by any charging of the sample. Measurements performed with the lifted electrode and the radiation discharge method showed no trace of an excess charge.

In a neutral sample persistent polarization can be caused either by an injection of charge of one sign from

TABLE VI. Effect of pre-excitation upon polarization in *K*.

(A) Effect of ultraviolet pre-excitation upon ultraviolet polarization in *K*. Ultraviolet excitation. Polarizing voltage = 50 volts. Polarizing time = 5.0 minutes.

Pre-excitation time (min)	Lifted electrode voltage (arbitrary units)
0.0	35.3
20	33.7
120	36.1

(B) Effect of beta-ray pre-excitation upon beta-ray polarization in *K*. Strontium 90 source. Polarizing voltage = 200 volts. Polarizing time = 10.0 minutes.

Pre-excitation (roentgens)	Lifted electrode voltage, V_e (volts)
0	92
1×10^4	88
1.7×10^5	96

one of the electrodes and a simultaneous ejection of charge of the same sign at the other electrode (see any discussion of electrets); by a separation of mobile charge and their subsequent localization; or by dipole alignment. The sign of the charge near the surface of the sample was always found to be opposite to the sign of the potential applied to the adjacent electrode during polarizing. This indicates that the polarization is due to a separation of mobile charges inside the sample, since an injection of charge would bring about the opposite sign of polarization, and dipole polarization seems unlikely because of the parallelism between these effects and those of photoconductivity.

The neutrality of a polarized sample and the exclusion of injection and ejection of charges is further confirmed by the fact that a sample can be polarized as well with contact electrodes as with both electrodes insulated from the sample by means of mica plates.

Experiments were performed to determine the distribution of polarization inside the sample. Charges may be separated into two clouds, so that in the part of the sample adjacent to the negative electrode a positive charge prevails and in the other part a negative charge, or the polarization may be uniform throughout the sample. In the first case the sample could be divided by a plane parallel to the electrodes into two parts, each of which should have an excess charge of a sign opposite to that of the adjacent electrode during the polarizing process.

To discriminate between the two possibilities, two *K* samples, both mounted on conducting glass, were pressed together with powder surfaces in contact and polarization measurements were performed. The arrangement, treated as a single sample, showed the normal polarization properties when tested with the radiation discharge method. After repolarizing, the two samples were separated. The magnitude and sign of the charge at the two interface surfaces were individually determined by the lifted electrode method. The sample that was in contact with the negative electrode during the polarizing process displayed a negative charge at the interface surface (surface in contact with the second sample). If this interface was covered with an aluminum foil electrode, the voltage released by the radiation discharge produced a positive voltage signal, in agreement with the results obtained by the lifted electrode method. The sample on the other electrode exhibited a positive surface charge on the interface surface. This indicates that both samples were similarly polarized in a local type of polarization throughout the whole sample. Such a uniform polarization distribution may be attributed to the grain structure of the samples. Inside an individual grain a true separation of space charge may occur. Hofstadter[7] and Smith[9] report a macroscopic separation in nearly ideal single crystals.

It may be noted from such measurements that removing the aluminum foil while it is strongly attracted by the field has little effect upon the persistent polarization.

V. DARK POLARIZATION

As already mentioned, some of the inorganic substances can be polarized in the dark (without concomitant radiation) to values which are not too much smaller than those obtained under light polarizing. This dark polarization occurs, with one exception (an electroluminescent ZnS powder), only after the substance was pre-excited; it increases with increasing pre-excitation and decreases with increasing time lapse between pre-excitation and polarizing, and vanishes completely only when the powder is de-excited by infrared radiation before polarizing. Whereas polarization can be discharged by any kind of ionizing radiation, the capability of being dark-polarized can be destroyed only by infrared irradiation. This is due to the fact that dark polarization comes about by the displacement of the small amount of free charge which persists in the powder as a consequence of electrons liberated from traps even long periods of time after excitation. Therefore only those radiations which empty the traps and do not excite the powder prevent dark polarization.

The appearance of such a dark polarization is closely connected to the phosphorescence and/or the slow decay of photoconductivity in these substances after excitation, which also demonstrate the presence and the creation of mobile charges from trapped electrons. The decrease in the number of free charges with increasing period of time elapsed since the removal of the exciting radiation, accounts for the fact that dark polarization performed shortly after pre-excitation is larger than when performed a long time after pre-excitation.

The following measurements on K illustrate all this behavior quite clearly. Table VII(A) describes the considerable dark polarization as a function of the duration of pre-excitation. It is, however, after 20 minutes of

TABLE VII. Dark polarization in *K*.

(A) Dark polarization as function of pre-excitation time in *K*. Ultraviolet excitation. Polarizing time = 10.0 min, performed 30 sec after pre-excitation. Polarizing voltage = 100 volts.

Pre-excitation time (min)	Lifted electrode voltage, V_e (volts)
0	1.7
10	18.3
20	27.5
Polarized with ultraviolet	64.0

(B) Dark polarization as function of time after pre-excitation in *K*. Ultraviolet excitation. Polarizing voltage = 100 volts. Polarizing time = 10.0 min.

Sample No.	Pre-excitation time (min)	Delay before polarizing	Lifted electrode voltage, V_e (volts)
1	20	30 seconds	27.5
1	20	20 hours	11.3
2	135	30 seconds	20.0
2	135	18 hours	12.2

pre-excitation, still less than half the ultraviolet polarization.

The value of the dark polarization was however not strictly proportional to the length of pre-excitation. This is to be expected since the free charge responsible for the dark polarization mostly originates in the re-emission from shallow traps. For a given intensity of pre-excitation, the population of these shallow traps does not increase with time of pre-excitation as soon as this time exceeds the trap lifetime.

Table VII(B) indicates how dark polarization diminishes if the polarizing is performed a long time after pre-excitation. This slow decrease of dark polarizability with time is closely correlated to the weak dependence of polarization by light on the light intensity. Even with a low concentration of mobile charges, polarization can be obtained if the polarizing field is applied for sufficient time, just as with extremely weak light intensities polarization can be produced.

Dark polarizability and short-time spontaneous decay of polarization are correlated. Substances with initially strong dark decays, i.e., having relatively many shallow traps, show large values of dark polarizations, those with slight initial dark decays, such as anthracene show only small values. A sample of anthracene, pre-excited with full intensity of visible light for 5 minutes, was dark-polarized one minute later, and gave a V_e voltage of 12 volts, which is small compared to the polarization voltage of over 100 volts with simultaneous excitation. Dark polarizing 9 minutes after pre-excitation produced a V_e of 5.6 volts. Quenching with infrared radiation for 5 minutes eliminates the dark polarization. Dark polarization in anthracene is much weaker and the dark polarizability decreases more rapidly with time after pre-excitation than in *K*. This shows the much smaller number of shallow traps in anthracene than in *K*.

At the other extreme are the properties of the electroluminescent ZnS powder.[15] This has an extremely fast dark decay of polarization in comparison to *K*. However, the dark polarization is at least one-third of the ultraviolet polarization, even after strong de-excitation of the sample and dark polarizability cannot be eliminated by infrared de-excitation.

Further, it was found that the time required to reach an equilibrium value is much longer for dark polarization than for polarization under strong ultraviolet, which corresponds with the finding that polarizing under weak light irradiation also requires longer times to reach equilibrium.

These dark-polarizable substances offer another method to further explore the mechanisms of polarization. The influence of a subsequent reversal of the polarizing field on the polarization can be studied. A sample was dark polarized with a given field direction; the field was removed and then reapplied in the reversed direction (this will be termed field reversal). After this, the remaining polarization was determined as a function of the duration of polarizing periods of the original and the reversed fields and as a function of the respective field strengths. The results are tabulated in Table VIII. They show that the polarization is not necessarily reversed with field reversal and that the direction of the first polarizing field is the determining factor. Considerable reduction and eventual reversal of the initial dark polarization occurs if the reversed field is of the same strength and is applied for a period much longer than the polarizing time, or if the reversed field is slightly stronger than the original one. In this latter case a reversal of the polarization occurs when the time of application of the reversed field is only slightly longer than the polarizing time. With decreasing polarizing time the time of reversed field application necessary to reverse the polarization decreases somewhat faster. In the case of the electroluminescent ZnS, the polarization was always found to be in the direction of the last polarizing field applied, contrary to the above results with *K*. This is a further indication of the large number of shallow traps in this substance and the possibility of a direct field excitation.

TABLE VIII. Effect of polarizing field reversal on dark polarization in *K*.

Original field (volts)	Duration (sec)	Reversed field (volts)	Duration (sec)	Radiation discharge voltage (volts)
300(−)	5	...	...	19.9(−)
300(−)	5	300(+)	5	13.4(−)
300(−)	5	300(+)	10	13.1(−)
300(−)	5	300(+)	40	11.2(−)
300(−)	5	300(+)	120	7.6(−)
300(−)	5	300(+)	300	5.7(−)
300(−)	2	...	...	14.6(−)
300(−)	2	300(+)	10	8.1(−)
300(−)	2	300(+)	20	7.9(−)
300(−)	2	300(+)	40	6.0(−)
300(−)	2	300(+)	120	5.1(−)
300(−)	2	300(+)	300	(+)
300(−)	1	...	...	11.6(−)
300(−)	1	300(+)	5	4.6(−)
300(−)	1	300(+)	10	4.8(−)
300(−)	1	300(+)	20	2.7(−)
300(−)	1	300(+)	40	2.7(−)
300(−)	1	300(+)	120	(+)
300(−)	1	300(+)	300	(+)
200(−)	5	...	...	9.7(−)
200(−)	5	300(+)	5	3.4(−)
200(−)	5	300(+)	10	2.6(−)
200(−)	5	300(+)	20	(+)
200(−)	5	300(+)	40	(+)

These results could be interpreted in the following way: the observed dark polarization is not solely due to the displacement of those charges already present in the conduction band (which are in equilibrium with those found in traps) at the moment the field is applied. While the field is on, new electrons are emitted from traps at those places where the free electron density is depleted as a consequence of the field action, and these

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[15] [1V: obtained from Sylvania Electric Company.]

electrons too are displaced, increasing the polarization. With longer time lapse from the moment of field application the number of electrons available decreases constantly, and this slows down the further increase in polarization. If, after a certain time t, the reversed field is applied for the period t', in this time t' less electrons are available for displacement than in the first time interval t if t' is not much longer than t.

Thus one can understand why the subsequent application of a reversed field can annul the original polarization only if the reversed field is applied for a much longer time than the initial field, and why the action of the reversed field becomes more pronounced when t is made smaller. This picture is in agreement with the previously discussed findings, that the polarization obtained under concomitant illumination is not very dependent upon the intensity of the illumination if the polarizing time is extended enough.

VI. DISCHARGE OF POLARIZATION

Any radiation creating mobile charges will not only produce polarization when an external field is applied but will also discharge a persisting polarization in the absence of an external field. This discharge process will be theoretically discussed in Sec. VIII.

The discharge of polarization is different when it is performed with both electrodes at ground from that performed while one electrode is isolated because of the build up of an external field during the latter procedure. In the first case the polarization can be removed completely by a sufficiently long continuous irradiation.

The discharge of polarization by low-intensity radiation is described in Table V for K under various types of radiation; the voltage build up was determined with one electrode isolated and attached to the electrometer. K shows a noticeable spontaneous dark decay only up to a period of about 20 minutes after polarizing; therefore all measurements reported here were made after the polarized substance had undergone a dark decay of at least one hour. The intensity of the ultraviolet light used for the discharge was 2.4×10^{-10} watt/cm^2. This produced a discharged voltage at the grid of 1.5×10^{-3} volt in one second. This corresponds to a discharge 0.63 volt/second per erg/cm^2 (*ca* 3×10^{-11} coulomb/sec per erg/cm^2 across the 50-micromicrofarad sample) of radiation absorbed. If it is assumed that a single photon produces one mobile electron which then moves completely across the sample under the internal field, then the quantum efficiency of the discharge process is about 10^{-3}. However, if retrapping and recombination is taken into account, the quantum efficiency increases to between 10^{-1} and 1. With such low-intensity radiation the discharged voltage increases linearly with time over a very long period before it shows saturation characteristics.

In the case of low-energy radiations other than ultraviolet, the intensities required to produce a certain discharged voltage were much larger. The values given in the table are only approximate values for these cases. The absorption of visible light in K is much smaller than that of ultraviolet and this reduces the discharge rate correspondingly to about one-tenth of the value for ultraviolet. For infrared (with an intensity of about 15 milliwatts/cm^2), which is primarily absorbed by the trapped electrons or the remaining ionized activators only, the absorption coefficient is still smaller and depends moreover on the number of trapped electrons. Infrared radiation of wavelengths of 1.5 microns and longer have been found to be still effective in discharging the polarization in K. Similar wavelengths also show detectable effects on photocurrents, primarily in the form of quenching. But the effects of such long wavelengths are more pronounced in the discharge of polarization than in the conductivity investigation.

The discharge for ultraviolet, visible, and infrared radiations was determined by measuring $\bar{V}$; for high-energy radiations it was determined by measuring V_p. One such curve of the gamma-induced decay in K is shown in Fig. 13 for 5 r total irradiation. If for a given polarization V_p is measured and, thereafter, $\bar{V}$, the results differ. The reason for this difference, as already pointed out, resides in the build up of the backfield, which prevents complete discharge of polarization when the electrodes are isolated. The ratio of these two values can be obtained by comparing Eqs. (8) and (13) of Sec. VIII. This gives for the ratio, $\bar{V}/V_p=1-\epsilon$. For K, the best evidence gives a value for ϵ (determined by $\bar{V}/V_0$ ratio) of 0.30. Thus $\bar{V}/V_p=0.7$. The agreement with the value of 0.6 given in Table V is excellent, though perhaps to some extent fortuitous.

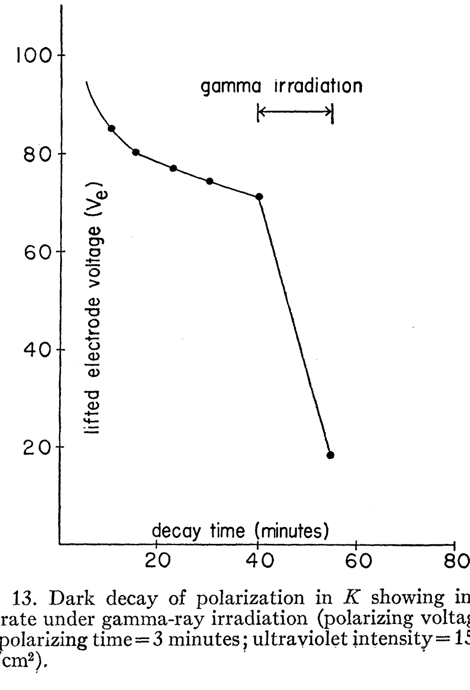

FIG. 13. Dark decay of polarization in K showing increased decay rate under gamma-ray irradiation (polarizing voltage = 200 volts; polarizing time = 3 minutes; ultraviolet intensity = 15 microwatts/cm^2).

During irradiation, $\bar{V}$ displays an increase with time given by $\bar{V}=\bar{V}_{\max}[1-\exp(-t/\tau)]$ and approaches a saturation value. When this is reached, further irradiation produces no further increment in voltage. If, after the removal of the radiation, the discharged voltage is grounded off and the radiation is reapplied, a new voltage build up begins again. This too approaches a saturation value, which is, however, smaller than the previous value and is reached after a longer period of irradiation than the first. In K this discharging process can be repeated 4 or 5 times before $\bar{V}$ drops below 5 percent of the initial $\bar{V}$. In anthracene the process can be repeated under certain conditions much more often, and still produces considerable discharge voltages after more than 10 repetitions. The values of these successive discharge voltages are plotted in Fig. 14 for each repetition for both substances. The voltage $\bar{V}$ reached in one run has been found to be independent of the kind of discharging radiation and of its intensity as should be expected. Short flashes if strong enough produce the same $\bar{V}$ as weak long time irradiation. The ultraviolet light source (*ca* 15 microwatts per square centimeter) and the visible light source were both used to discharge the polarization. In both cases the maximum voltage $\bar{V}$ reached was identical to that produced with the flash unit in 1/2000 of a second. The time of irradiation required to reach the maximum voltage was of the order of seconds for visible light and a minute for the ultraviolet, because of the several hundred times larger intensity of the visible light source.

The dependence of the saturation values for consecutive discharges upon the applied polarizing voltages is shown in Figs. 6 and 7 for anthracene and K respectively. These figures will be discussed in Sec. VIII. They show that $\bar{V}$ is proportional to the polarization and thus to V_p. It may be noted that the intensity of the discharging radiation is much more than sufficient, from an ordinary quantum efficiency standpoint, to release all the polarized charges.

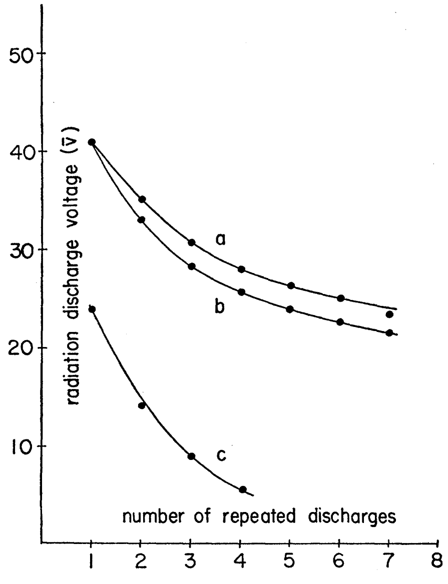

FIG. 14. Maximum radiation discharge voltages as function of the number of discharge repetitions. (A) experimental values in anthracene; (B) theoretical values for anthracene; (C) experimental values in K. (Polarizing voltage=400 volts; polarizing time=1 minute; ultraviolet intensity=15 microwatts/cm^2.)

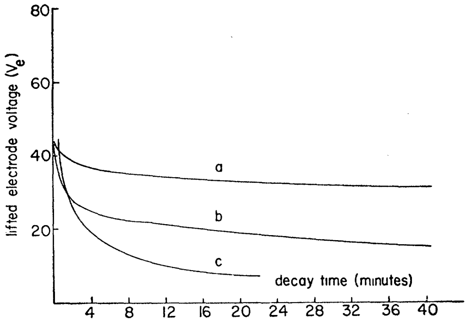

FIG. 15. Typical polarization dark decay curves in: (a) anthracene; (b) K; (c) electroluminescent ZnS powder.

That ultraviolet radiation is a very effective discharging agent is due to its strong absorption and the fact that practically each absorbed quantum creates a free electron, which moves in the interior polarization field in such a way as to compensate the existing polarization. Thus the discharge of polarization in this case is not so much due to a removal of the trapped charges as to a canceling out of the prevailing inhomogeneous charge distribution. Only infrared radiation effects the trapped charges themselves. One would expect a smaller efficiency for the same amount of absorbed energy of high energy radiation than for ultraviolet radiation, since the energy consumption for creating one free electron by high-energy radiations is larger than for ultraviolet radiations. The measurements in Table V show, however, that both efficiencies are of the same order of magnitude. This is probably due to the inhomogeneous absorption of the ultraviolet. It was found, that ultraviolet light discharges the polarization mostly in the region where it is mainly absorbed and only slightly in the rest of the sample. High-energy radiation excites, and therefore discharges, the sample uniformly.

If the electrodes are kept at ground during the first discharging irradiation, there will be no field buildup to restrict the polarization discharge. The amount of polarization discharged by this first irradiation will then be larger than with isolated electrodes, and a second irradiation with the electrode now isolated, will furnish a $\bar{V}$ smaller by about a factor of 2 than if the first irradiation was given with the electrode isolated, because of the smaller residue of polarization.

VII. ELECTRICAL STORAGE AND ITS DECAY

The spontaneous decay of the polarization consists of two relatively distinct portions; a fast decay during the first 20 minutes, followed by a very slow decay over a very long period of time. This is illustrated in Fig. 15,

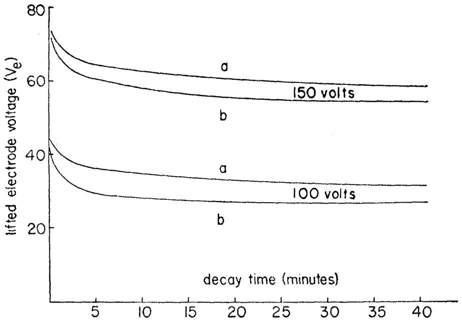

FIG. 16. Dark decay of polarization in anthracene for two polarizing voltages, 100 and 150 volts, with: (a) ultraviolet and (b) visible light excitation at each voltage (polarizing time = 5 minutes).

which describes V_p as a function of time, for anthracene, K, and an electroluminescent ZnS. Such curves are characteristic for a given substance but their exact shape depends upon the polarizing voltage, the thickness of the sample and the polarizing radiation used as well as the ambient temperature (not yet investigated in detail). If the curves of Figs. 15 and 16 are extrapolated to longer times it is seen that the further decay of polarization is very slow. This was experimentally verified by measuring the decay of polarization in K and anthracene. In K, after 100 hours, the polarization was still 60 percent of the short time value. In anthracene large values were measured after a month of dark decay. $\bar{V}$, V_p, and the corresponding Q, for three particular cases are given in Table IX, for different decay times. These values are comparable to those obtained in electret work. Figure 16 presents the curves for ultraviolet and visible light polarization which noticeably differ from each other although they display the same initial polarization. The latter polarization displays a lower value of the long persistent part and the initial decay is faster for both substances. The persistent part of the polarization increases percentage-wise with increasing voltage and increasing thickness for both powders. Experiments are now in progress to determine more accurately the actual connection between the shape of the decay curve and the occupation of the traps. Recent experiments (to be reported in a subsequent paper) indicate methods whereby the rate of decay can be substantially reduced.

The short-time dark decay was measured most accurately from 30 seconds to 20 minutes by connecting the sample to the electrometer immediately after being polarized. The electrodes were at ground except for the brief period of the measuring times. dP/dt, the rate of decay of polarization, for a thin sample of K, was found to decrease with time approximately as c/t, where c is a constant. After 20 minutes the rate decreased to a value below the present apparatus sensitivity.

If, a sufficient time after the sample shows no further detectable short time decay, a strong shot of light is given and the resulting voltage is grounded off, then an appreciable short-time dark decay occurs again. This too disappears after several minutes. Such a behavior strongly resembles the behavior of storage phosphors when they are light stimulated. The discharging radiation produces mobile charge which is partially retrapped in shallow levels and produces the new short time decay.

It has been found that in conditions of even moderate humidity, the polarization decay in powders is abnormally rapid. Therefore, all measurements were performed in a desiccated chamber.

VIII. PHENOMENOLOGICAL MECHANISM OF POLARIZATION

A detailed atomistic description of the polarization mechanism, taking into account the picture of Kallmann and Kramer[12] on the various charge transitions possible in a photoconductive substance, is in the process of preparation and will be reported in a later paper. Here a simple model for the case of equilibrium polarization will be described.

Although the polarization is distributed throughout the sample in a uniform way, it will be assumed here as a simplification that the observed polarization can be represented by two charge layers in the interior of the sample with a surface charge density σ_2^- and σ_2^+ located at distances d_1 and d_3 from the positive and negative electrodes respectively (see Fig. 17), and that $d_1=d_3$ and $|\sigma_2^-|=|\sigma_2^+|$. Then d_2, which is the separation distance of the two charge layers, is a parameter which describes the polarization and can be evaluated from the experiments.

If an external field is applied while mobile charges are being created, the field picture as shown in Fig. 17 can be described as:

$$V_0=2E_1d_1+E_2d_2. \tag{1}$$

The unknown charge density, σ_2^-, can be linked with the distance d_2 by two possible assumptions. One is that σ_2^- will show no further increase in time when the field E_2 becomes zero. The second is that the rise of σ_2^- is limited when the force on the charge layer approaches zero. Both conditions are rather artificial and it would be difficult to say which may give a better presentation. Calculations made show that the final results are identical in terms of a constant ϵ (defined below); only the meaning of ϵ is different for both assumptions. The choice in the following development will be the first assumption since this leads to $d_2=d_0$ when $\epsilon=1$, rather than $d_2=d_0/2$ when $\epsilon=1$ as results from the second assumption. This assumption that $E_2=0$ for equilibrium implies that the body photocurrents in the steady state do not essentially influence the polarization.

From elementary electrostatics, we have:

$$E_2=(V_0/d_0)-(8\pi\kappa)(d_1/d_0)\sigma_2^-, \tag{2}$$

TABLE IX. Long time persistence of P.I.P.

Substance	Polarizing voltage (volts)	Decay time	$\bar{V}$ (volts)	V_p (volts)	Q[a] (coulomb/cm²)
K	300	10 min	116.8	191	2.4×10^{-9}
K	300	60 min	103.8	159	2.0×10^{-9}
K	300	24 hr	98.3	146	1.8×10^{-9}
K	200	1 min	···	138	1.8×10^{-9}
K	200	64 hr	···	91.5	1.3×10^{-9}
Anthracene	250	1 min	93.0	···	···
Anthracene	250	10 min	80.7	···	···
Anthracene	250	41.5 hr	76.6	···	···

[a] Charge appearing across the electrometer when electrode is lifted, divided by the area of the polarized sample. (*Note added in proof.*—With better electrical contact charge densities 10 times larger have been obtained.)

and, if we use the first assumption that $E_2=0$ at equilibrium,

$$|\sigma_2^-|_{\text{eq}}=V_0\kappa/(4\pi d_0[1-\epsilon]);\quad \epsilon=d_2/d_0. \tag{3}$$

The equilibrium charge density, $|\sigma_2^-|_{\text{eq}}$, in Eq. (3) will of course be reached only if the total number of mobile charges created during the polarizing time is sufficient. If the exciting source and then the applied voltage are removed and the electrodes grounded, an image charge appears at the electrodes and the total voltage drop across the sample is zero. The new field E_2' is not zero, but there is only very little charge motion since most of the charges are frozen in traps. The new field distribution is then:

$$2E_1'd_1+E_2'd_2=0. \tag{4}$$

The image charge density on the electrodes is given by:

$$|\sigma_0|=V_0\kappa\epsilon/[4\pi d_0(1-\epsilon)]. \tag{5}$$

The direction of the new field, E_2' is the reverse of the original direction when the applied field was on, and thus would tend to decrease the polarization if mobile charges are present. This is the meaning of the negative signs in the expressions for E_2':

$$E_2'=-(4\pi/\kappa)|\sigma_2^-|_{\text{eq}}(1-\epsilon). \tag{6}$$

Under the influence of this field the small number of mobile charges always present move constantly in a direction to decrease σ_2^-, and thus produces spontaneous decay of polarization. This shift of charges is the same as that observed in the dark-polarizing of the substance.

If the sample is irradiated, more mobile charges are created, and they also move in the direction of this field and decrease the polarization. In doing so, a portion of the image charge is freed, and creates an external voltage ($\bar{V}$) across the electrodes when these are isolated during the irradiation. The new field distribution during depolarization, described by barred quantities, is:

$$2\bar{E}_1d_1+\bar{E}_2d_2=\bar{V}. \tag{7}$$

This depolarization continues until again $\bar{E}_2=0$, at which time no further decrease of polarization can occur. Then $\bar{V}_{\max}$, the radiation discharge voltage described in previous sections, is given by:

$$\bar{V}_{\max}=\epsilon V_0, \tag{8}$$

since $\bar{E}_1$ $(=E_1')$ does not change during irradiation when one electrode is isolated. The calculations assume that the sample is isolated from ground during depolarization and that there is no other capacity than that of the sample itself (the grid input capacity of the electrometer is here considered negligible, though in practise this is not always so). The total released charge is given by:

$$q=V_0\kappa\epsilon A/4\pi d_0, \tag{9}$$

if one uses the unpolarized sample capacitance. $\bar{V}_{\max}$ is the maximum radiation discharge voltage that can be produced by a single irradiation of sufficient intensity. A second irradiation after grounding $\bar{V}_{\max}$ off (in the dark) would produce a new potential $\bar{V}_2=\epsilon^2V_0$, and for the nth irradiation one obtains:

$$\bar{V}_n=\epsilon^nV_0;\quad q_n=V_0\kappa\epsilon^nA/4\pi d_0. \tag{10}$$

For the sum of all the voltage maxima, one has:

$$\Sigma_n\,\bar{V}_n=V_0/(1-\epsilon). \tag{11}$$

This is larger than V_0 since $0<\epsilon<1$. The factor ϵ can be looked upon as a parameter which has to be determined from the experiments. It is assumed that ϵ is independent of the applied voltage to a first approximation.

The lifted electrode voltage V_e appearing at the electrometer when the electrode is lifted follows from the same model and is:

$$V_e=\sigma_0A/C=V_0\kappa\epsilon A/4\pi d_0C(1-\epsilon), \tag{12}$$

where C is the electrometer capacity and A is the area of the electrode. Instead of V_e it is advantageous to use V_p [defined in Eq. (a), Sec. II] since it is independent of the electrometer capacity.

$$V_p=V_eC/(\kappa A/4\pi d_0)=\epsilon V_0/(1-\epsilon), \tag{13}$$

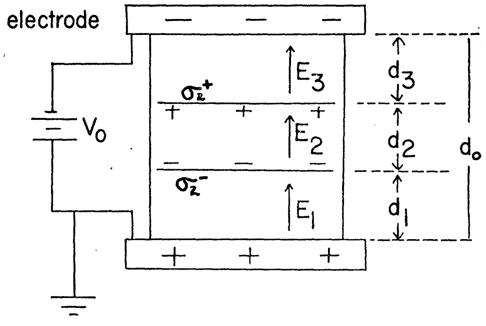

FIG. 17. Diagram of double charge layers in phenomenological model.

where $(\kappa A/4\pi d_0)$ is the capacity of the unpolarized sample. It is apparent from this that for values of ϵ larger than 0.5, the voltage V_p will be larger than V_0, the polarizing voltage. This is the case illustrated in Fig. 9, where even for low polarization times (with high intensities) this occurs.

If Eqs. (8) and (13) are used to eliminate ϵ, there results a relation between purely experimental parameters.

$$\bar{V}=V_p/(1+V_p/V_0). \tag{14}$$

These relations may be compared with the experimental data, but it should be borne in mind that all these only hold for equilibrium polarizations, whereas, for many of the data reported in this paper, such an equilibrium was only very roughly approached. The data presented in Figs. 6 and 7 were taken with a polarizing time of only 1 minute and represent polarizations well below equilibrium as can be seen from experiments with longer polarizing times and with higher polarizing intensities. However, the voltage reached in the second discharge can be considered as the equilibrium polarization for an applied voltage equal to the first radiation discharge voltage, and similarly for the subsequent discharges.

Thus, if one uses the $\bar{V}$ values of curve 1 as the V_0 values for curve 2, the calculated ϵ varies from 0.70 at $V_0=62$ to 0.82 at $V_0=38$. This indicates that ϵ varies with V_0 as $\epsilon=1-aV_0$ for these measurements. There is, however, other evidence from measurements of the ratio of $\bar{V}$ to V_0 for equilibrium polarization in anthracene which indicates that ϵ is fairly constant over a wide range of V_0 (see for example Figs. 8 and 9). This discrepancy is being investigated at present. Another method of calculating ϵ is possible from repeated discharge maxima $\bar{V}$ for a single original V_0. This is given by the vertical column of points in Fig. 6. Using the value of ϵ taken for the curves 1 and 2 of the 400-volt column, the succeeding $\bar{V}$ values are calculated using Eq. (10) and the relation of ϵ and V_0 given above. These values are plotted in Fig. 14 as the theoretical curve, b, and the actual values are given as curve a.

In Fig. 3 the voltages V_p and $\bar{V}$ are compared for various polarizing times in a thin fused anthracene sample. The curves indicate that polarization under the stated polarizing conditions approaches the equilibrium state after 200 seconds polarizing time. Both methods of measurements indicate this approach to equilibrium. This equilibrium time is shorter than for the other samples; this is probably due to the fact that this sample, thinner than usual, is more homogeneously polarized.

From the equilibrium section of the curve for V_p, a value of 0.56 is computed from Eq. (13). Putting this value into Eq. (8) yields a $\bar{V}$ of 11.2 volts. The measured value is 10.9 volts, an agreement within 3 percent of the calculated value. It may be noted that the ratio of V_p to $\bar{V}$ is only slightly dependent on the polarizing period, whereas the individual values sharply increase with increasing polarizing period. In Fig. 18 the ratio of $\bar{V}$, calculated according to Eq. (14), to the measured value of $\bar{V}$ is plotted against polarizing time. It is seen that for short polarizing periods the calculated value is higher than the measured. For

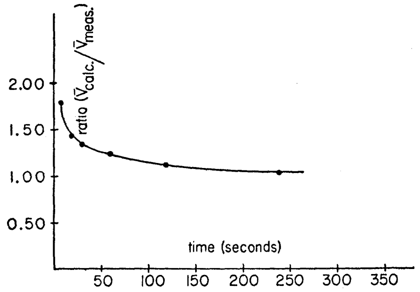

FIG. 18. Ratio of calculated maximum radiation discharge voltage to measured value (taken from the data of Fig. 11).

longer times, approaching the equilibrium period, the ratio approaches 1. This means that the ϵ calculated from Eqs. (8) and (13) agree with each other only for equilibrium polarization. A further confirmation of the equations of the model has been given in Table V for fast electron polarization in K where the final column gives the ratio of the calculated to the measured values of $\bar{V}$.

IX. SUMMARY REMARKS

Persistent internal polarization comes about by the displacement of free charges inside the material and their subsequent localization in deep traps. A requirement for persistence is that the free charges disappear fast after the polarizing field is removed, otherwise these charges would tend to discharge the produced polarization spontaneously. Thus photoconductive materials are polarizable while they are irradiated with any kind of radiation or shortly thereafter as long as free charges may exist. After removing free charges by infrared quenching the polarizability by field alone no longer exists. Electroluminescent materials are also polarizable because of the creation of free charges by the application of electrical fields. The spontaneous decay of polarization comes about by the motion of the remaining free charges in the internal polarization field. This shifts the charges in such a direction as to annul the polarization. If practically no free charges persist, polarization still decays spontaneously when charges bound in shallow traps are present which evaporate into the conductivity band. Thus a condition for strong, long persistent polarization is a large number of deep traps and only a small number of shallow traps. In agreement with these considerations, the materials K and anthracene were the best polarizable substances. They also show the fastest decay of photocurrent and light emission after the excitation is removed.

In this connection it may be realized that the total amount of charges trapped is larger than the amount necessary for maximum polarization. In our polarization measurements, we find the polarization charge to be between 10^{-10} and 10^{-8} coulombs per cm^2, that is, 10^9 to 10^{11} electrons/cm^2. Even if one assumes that each electron has a displacement of only 1/100 of the maximum displacement (*viz.*, the sample thickness) the total amount of electrons necessary to produce the polarization would range from 10^{11} to 10^{13} electrons in our layers. Since these layers are of the order of $\frac{1}{10}$ mm this number if still smaller than the number of traps usually observed in the inorganic phosphors which is of the order of 10^{16} per cubic cm. This must be also borne in mind when the decay of polarization is considered. The total amount of free charges required to cancel the polarization is larger than the polarization charge itself.

Removal of polarization occurs by the creation of free charges by any kind of radiation. They move in the internal field to cancel the polarization. This removal of polarization charge can be accelerated by the application of a reversed field.