

of this polarization has been worked out by Percival and Seaton.⁷⁶

In conclusion, this survey of atomic scattering processes, being mainly concerned with our progress in understanding them, has made almost no reference to their applications, which are myriad. Many illustrative applications can be found in the reviews cited. A relatively brief discussion of collision theory containing numerous astrophysical applications has been given

⁷⁶ I. C. Percival and M. J. Seaton, *Phil. Trans. Roy. Soc. London*, **A251**, 113 (1958).

by Seaton,⁷⁷ Knorr,⁷⁸ and McWhirter⁷⁹ have written brief and readable papers illustrating the importance of atomic scattering processes in establishing and maintaining the high temperature plasmas required for controlled fusion.

⁷⁷ M. J. Seaton, *Revs. Modern Phys.* **30**, 979 (1958).

⁷⁸ G. Knorr, *Z. Naturforsch.* **13a**, 941 (1958).

⁷⁹ R. W. P. McWhirter, "Atomic collision processes in low density plasma," United Kingdom Atomic Energy Authority Research Group, Harwell, England, Rept. AERE-R2890 (1959).

Persistent Internal Polarization

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A. MODEL OF POLARIZATION

1. Introduction

THIS paper discusses persistent internal polarization (PIP) effects in photoconductive materials. Such an electric polarization is due to an inhomogeneous charge distribution brought about by an external electric field acting on free carriers. Subsequent trapping of these carriers within the photoconductor gives a persistence to this distribution.

From the earliest studies of the photoconductive behavior of solid matter, the influence of internal space charge distributions upon allied phenomena has been recognized. But apparently the extremely long persistence and magnitude of space charge distributions has only recently been realized.¹ For example, persistences of hundreds of hours and charge densities of 10^{-8} to 10^{-7} coul/cm² confined to a 10μ layer of the sample's total thickness are readily detected. Furthermore, one has not known very precisely the actual distribution of the space charges within the material which give rise to this long persistence. This paper considers these problems in detail. Experimental evidence is presented on the magnitude, distribution, and discharge of PIP in relation to the structure of the solid material and type of excitation. In addition, models are developed incorporating the main features of internal polarization charge distributions.

The necessity of free charges in the generation of internal polarization, the release of PIP by subsequent irradiation, and its close connection to photoconduc-

tivity proves that this phenomenon is quite different from the well-known polarizability of dielectric media and from ferro-electric polarization.² In these cases, the electric polarization vector \mathbf{P} is produced by an alignment of dipoles having molecular dimensions or the displacement of certain sublattices. \mathbf{P} may be parallel to the external field or, in ferroelectric materials, dependent upon the field direction in discrete domains. In this paper the polarizing of photoconductors stems from a true separation of positive and negative charge carriers in the bulk of the material. Such a polarization differs from electret effect in waxes³ where the alignment of polarizable molecules of the material and their freezing-in seem to play an important role. One of the most characteristic features of internal polarization is the ease with which it can be released or shifted by subsequent excitation of the sample with light or with any kind of ionizing radiation in the absence of an external field.

An important aspect of this research is the comparison of internal polarization effects in inorganic and organic photoconductors. One finds that in such different substances as anthracene and ZnCdS, there are remarkable similarities in the nature of the polarization distributions. Hence PIP is brought about by properties which are common to quite different types of materials as, for example, high resistivity layers at the electrodes and the capability of strong trapping of one type of charge carriers. In organic materials the positive charges are the more mobile carriers, whereas in inorganic materials the negative ones are more mobile. One sees quite clearly the interchange in the

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¹ H. Kallmann and B. Rosenberg, *Phys. Rev.* **97**, 1596 (1955).

² C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956).

³ F. Gutmann, *Revs. Modern Phys.* **20**, 457 (1948).

TABLE I. Formation of barrier and bulk polarization.

Excitation	Nature of barriers	Direction of carrier motion	Type of polarization
1. Uniformly or nonuniformly absorbed	R_I and $R_{II} < R_s$	Any direction	Barrier
2. Uniformly absorbed	R_I and $R_{II} < R_s$	Any direction	Barrier
3. Maximum absorption at R_I	R_I and $R_{II} > R_s$	Less mobile carriers towards R_I	Bulk
4. Maximum absorption at R_I	R_I and $R_{II} < R_s$	Less mobile carriers towards R_I	Barrier
5. Maximum absorption at R_I	R_{II} small	Less mobile carriers towards R_I	Bulk

role of positive and negative carriers in PIP measurements. Although ZnCdS powder phosphors and crystalline anthracene layers have been chosen as typical examples for the inorganic and organic materials, PIP is found to occur in all types of materials; that is, powdered, semicrystalline and single crystal photoconductors, both of the organic and inorganic families. Section E presents a brief summary of polarization effects in single crystals both of CdS and anthracene.

In order for polarization to occur at least one type of carrier must be trapped strongly in the material, otherwise the charges would either move out of the sample after termination of the excitation or recombine after removal of the external field. In all cases investigated it is found that the carriers generally considered to be less mobile encounter a much stronger trapping than the mobile ones. It may be that this apparent smaller mobility is simply due to their stronger trapping. In any case, the different mobilities of the carriers result in different internal charge distributions under varying polarizing conditions. Experiments show that two fundamentally different internal charge distributions can develop, *barrier and bulk polarization*. In the former, the free positive and negative carriers accumulate near the electrodes because of high resistive layers at the photoconductor-electrode interfaces. If these two resistive layers are of the same magnitude, then barrier polarization leaves the sample electrically neutral. In bulk polarization the more mobile carriers are at least partially removed from the sample with the less mobile carriers remaining in a fairly uniform distribution over the bulk of the sample. The phosphor now has a net charge whose sign is that of the less mobile carriers.

The conditions necessary for these two types of polarization to occur can be stated in the following terms. Barrier polarization requires resistive layers at the electrodes, the resistances of which are higher than the resistance of the sample for the less mobile charges. Bulk polarization occurs when this condition is not satisfied, and additionally, the sample is nonuniformly excited. Table I summarizes the conditions necessary for these two types of polarization. In Table I R_I and R_{II} are the resistivities of the two phosphor-electrode interfaces and R_s is that of the sample for the slow carrier.

Internal polarization effects are described in terms of the frozen-in charge distributions. The buildup of polarization (separation of charges) occurs during external field application while the sample is in a state of excitation. This separation persists after excitation and field removal because of trapping processes. For these frozen-in charge distributions, static models are developed in detail. One finds that under certain conditions, a strong separation of charges occurs with even the less mobile charges accumulating in a thin layer. Such a possibility can exist even if the charge carriers of one sign display no mobility at all. The reason is as follows: During the buildup of polarization, a recombination of plus and minus charges occurs with a rate which is proportional to the product $n^- n^+$. During excitation, for instance, one has $\beta n^- n^+ = \alpha I$ where β determines the recombination rate and αI is the number of charges excited per sec per unit volume with the exciting intensity I . Because of this recombination, one type of carrier decreases where the other is abundant and vice versa. As a consequence, when polarization equilibrium is reached, a sheetlike distribution may develop even for those carriers which have no mobility at all.

2. Charge Layer Model of Polarization

The barrier model of polarization is described first to facilitate the understanding of the experimental results. There are a variety of approaches which one can use to describe space charge phenomena in solids. Perhaps the most well known is that in which the photoconductor is replaced by a suitable capacitor-resistance system as described for example by von Hippel.⁴ Such a system is assumed to go from an initial state of purely series capacitance to a final equilibrium state of pure series resistance. Such an approach does not shed any light on the spatial distribution and persistence of the space charge, yet these are the important quantities which distinguish the various types of internal polarization. One could also describe the polarization of photoconductors in terms of dielectric relaxation phenomena, but again the actual variation in the space distribution remains unspecified.

⁴ A. R. von Hippel, *Dielectrics and Waves* (John Wiley & Sons, Inc., New York, 1954).

The approach used here is a macroscopic model consisting of localized charge layers which may not be infinitesimally narrow; indeed the whole picture of bulk polarization is built upon a charge layer of one sign which may extend across a greater part of the sample. The models assume that the nature of the charge distribution is determined to a large extent by high resistive layers; in the case of barrier polarization by those near the electrodes. Under the latter conditions with many free charges available throughout the whole sample, the polarizing field will tend to produce charge accumulations near the electrodes in rather narrow layers. The net charge of the sample then depends solely upon the relative strength of these resistive layers.

The model used is of a macroscopic nature. The corresponding atomistic picture has been developed by B. Jaffe.⁵ According to his calculations the layer thicknesses are much smaller than those derived from the experiments, particularly for such high field strength as used in PIP work. This is probably due to the grainy structure of the surfaces employed; only with very good single crystal, the layers may approach the thickness predicted by the atomistic picture.

The photoconductor is considered to be a plane, parallel slab of material having thickness d_0 sandwiched between two electrodes as shown in Fig. 1. Assume that the polarization distribution consists of two charge layers, $-Q^-$ (taking the sign out of the charge) and Q^+ situated at distances d_1 and d_3 from the positive and negative electrodes respectively. Then at equilibrium of the charge separation (i.e., when no further separation of charges due to the external field occurs) one has

$$V_0 = \sum_a E_a d_a \quad (a=1, 2, 3) \quad (1)$$

and

$$\text{div} \mathbf{D} = \text{div} k \mathbf{E} = Q, \quad (2)$$

where V_0 is the applied polarizing voltage and the surface divergence in (2) must be applied across both line charges. k is the static dielectric constant of the photoconductive material. For complete generality E_2 is expressed as

$$E_2 = (1-\gamma) E_0 = (1-\gamma) V_0/d_0, \quad (3)$$

with γ an attenuation factor. $\gamma=1$ means that the back field developed between Q^- and Q^+ exactly cancels the applied field E_0 . If such a state would be reached, no further increase of polarization can occur because the transport of charges across the region d_2 has ceased and no dc current would flow through the sample. By using (1)-(3), one obtains

$$Q^- d_1 + Q^+ d_3 = k\gamma V_0. \quad (4)$$

When the external voltage is removed and the elec-

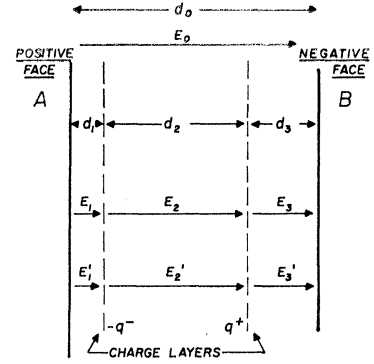


FIG. 1. The 2-layer model of barrier polarization. E' field quantities refer to the internal fields persisting upon the removal of E_0 .

trodes are grounded, relation (1) becomes

$$0 = \sum_a E'_a d_a \quad (a=1, 2, 3), \quad (5)$$

where primes will always refer to field strengths due to the polarization charges in the absence of E_0 , as shown in Fig. 1. It is assumed that Q^- and Q^+ are not significantly altered from their initial position and magnitude when the external excitation and thereafter E_0 are removed. This is true in those cases where a considerable number of deep-lying trap levels exist so that the number of free charges in the conductivity and valence bands is much smaller than the total number of separated charges present during excitation.

The densities of the image charges σ^+ and σ^- which are induced at the grounded electrodes by virtue of the frozen-in charges, Q^- and Q^+ , are given by the well-known relations

$$\sigma^+ = Q^- [(d_2 + d_3)/d_0] - Q^+ (d_3/d_0), \quad (6)$$

$$\sigma^- = Q^- (d_1/d_0) - Q^+ [(d_1 + d_2)/d_0]. \quad (7)$$

The σ 's here are the image charges on the sample in the absence of the external field. If $Q^- = Q^+ = Q_0$, then (6) and (7) reduce to

$$\sigma_0^+ = Q_0 (d_2/d_0) = -\sigma_0^-.$$

The σ 's are related to the polarizing voltage V_0 if it is assumed that the only effect of the removal of E_0 is the reduction of all field strengths by the amount E_0 . Thus $E'_a = E_a - E_0$. The assumption that the Q 's are not considerably changed by the removal of E_0 is borne out by experiments which measure the internal fields after polarizing; these experiments show that E'_2 is of the order of E_0 . Thus Eq. (4) is valid with $V_0=0$.

The deviation of charge neutrality is measured by the factor ϵ , defined by

$$Q^- = Q_0, \quad Q^+ = Q_0(1-\epsilon), \quad (8)$$

from which one obtains

$$\begin{aligned} \sigma^+ &= (k\gamma V_0/d_0) \{ (d_2 + \epsilon d_3) / [d_1 + (1-\epsilon)d_3] \}; \\ \sigma^- &= - (k\gamma V_0/d_0) \{ [d_2 - \epsilon(d_1 + d_2)] / [d_1 + (1-\epsilon)d_3] \}. \end{aligned} \quad (9)$$

⁵ B. M. Jaffe, Ph.D. thesis submitted to New York University.

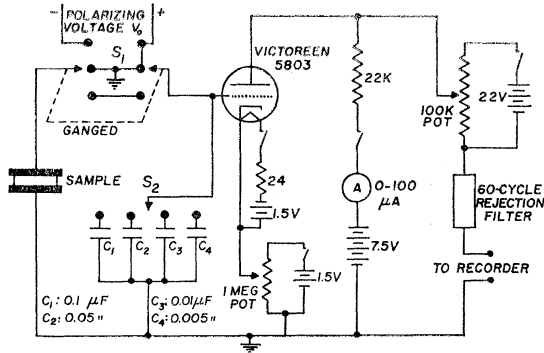


FIG. 2. The electrometer measuring circuit. The standard condensers C_1 to C_4 must be of low leakage construction. By making the standard condensers large in value compared to the quenched capacity of the sample, negligible back-fields are developed across the sample during the discharge of polarization.

Here the image charges are given in terms of the two parameters γ and ϵ if the positions of the charge layers are fixed. For a neutral sample ($\epsilon=0$), one obtains

$$\sigma_0^+ = (k\gamma V_0 / [d_2/d_0] / (d_1 + d_3)), \quad (9a)$$

which is the most useful expression in the discussion of barrier polarization.

In Sec. D, relations (6), (7), and (9) are considered in more detail. For example, if the polarization consists of only one negative layer ($\epsilon=1$), (9a) gives the correct σ^+ with $d_3=0$ and $\sigma^- = k\gamma V_0/d_0$. For $Q^-=0$ the formulas are just reversed. The formulas (9) are quite general as long as the charge layers are thin. When this is not the case, the d_1 and d_3 positions are taken as suitable average positions of the charges.

When the polarization distribution consists of two charge layers there is no ambiguity as to the field associated with the γ factor; this is always the field between the polarization charges. When only one charge layer is present however, it must be remembered that γ always refers to that region of the sample in which the internal field is attenuated to a value γE_0 while V_0 is applied.

If one uses formula (9a) for a polarized sample, one may ask why charges accumulate near the electrodes when the whole sample is known to display a photoconductive current under dc voltage. Such charge layers can, of course, only develop when layers of higher resistivity than that of the bulk material exist at the electrodes. These resistive layers reduce the photocurrent considerably but do not make it zero. At the same time they produce charge accumulations which can be determined solely by considering the resistances across the layers d_1 , d_2 , and d_3 . This approach to the polarization problem must lead to formula (9) or (9a). For simplicity let the conductivity of the d_1 and d_3 regions of Fig. 1 be κ_1 , and that of the d_2 region κ_2 , with $\kappa_1 \ll \kappa_2$. This assumption automatically introduces neutrality of the sample. With an external voltage V_0 applied, a current flows through the sample which is the same in

each layer at equilibrium. For $\gamma \approx 1$ this current would be very small.

$$i_{\text{equi}} = \kappa_1 E_1 = \kappa_2 E_2 = \kappa_1 E_1 \quad (10)$$

The difference between the internal fields implies that charges are accumulated at the interfaces. σ_0 is now readily determined to be

$$\sigma_0 = \left(\frac{kV_0}{d_0} \right) \frac{1 - \kappa_1/\kappa_2}{(\kappa_1/\kappa_2) [d_2/(d_1+d_3)] + 1} \cdot \frac{d_2}{d_1+d_3}, \quad (11)$$

again assuming that the Q 's are unaffected by the removal of E_0 . Equation (11) is identical with (9a) when γ is given by

$$\gamma = \frac{1 - \kappa_1/\kappa_2}{(\kappa_1/\kappa_2) [d_2/(d_1+d_3)] + 1}, \quad (12)$$

which approaches unity with $\kappa_1(d_1+d_3) \ll \kappa_2/d_2$. This means that the resistances of the d_1 plus d_3 layer must be large compared to that of the d_2 layer, to cancel the external field in the interior of the sample. With the conductivities in the d_1 and d_3 regions different, one can also describe the case of a nonneutral sample.

B. MEASURING METHODS

1. Observable Quantities

The above discussion shows that the polarization distribution is strongly influenced by conductivity changes in the sample. For this reason precise measurements of the charge distributions cannot be made using split samples¹ since the transition layer introduces a new region of high resistivity. This in itself brings about a charge distribution different from that of a uniform sample, as was found by comparing split samples with uniform ones. For the same reason probes are also unsatisfactory. One must resort, therefore, to radiation discharge methods which alter the original internal charge distribution and thus bring about a change of the image charges σ^+ and σ^- . From these changes in σ conclusions can be drawn upon the original charge distribution.

One can also obtain information on the nature of the polarization distribution by examining the nature of the buildup of polarization under different types of excitation.

2. The Electrometer Circuit

Polarization is measured by collecting freed image charges across a standard condenser C_K which is incorporated into the electrometer circuit shown in Fig. 2. One can determine either the total charge accumulation σ_{max} across C_K for the complete depolarization of the sample, or the rate of charge accumulation $d\sigma/dt$, the latter yielding the direction and magnitude of induced depolarizing currents.

3. Lifting Electrode Method

The total polarization in the sample can be determined by the lifting electrode method similar to that used in electret work.³ For this, a movable electrode replaces one or both of the contacts on the photoconductor so that when the electrode is lifted the initially bound image charge appears across C_K . Suitable corrections must be made to compensate for the change in sample-electrode contact under successive liftings.⁶

4. Dark and Radiation Release Methods

Any change in the internal distribution of polarization charges will produce a change in the image charges σ . Connecting the polarized sample to C_K and noting the accumulation of charges on this standard condenser ($C_K \gg C_s$), yields some information about the total change of the internal charge distribution. Such changes can occur either by dark decay or radiation release.

A polarized sample decays in the absence of external radiation through the thermal release of trapped polarization charges. For a polarized sample having charge layers near the electrodes as shown in Fig. 1, one would expect that upon removal of the polarizing excitation and field the thermally released polarization charges would show a tendency either to recombine directly across d_2 or move out of the sample across d_1 and d_3 . If one assumes that the number of charges moving in one or the other direction is solely determined by the prevalent internal electric fields and that the resistivities are the same in the d_1 , d_2 and d_3 regions, the dark decay of the polarization will not produce any charge accumulation on C_K since its change with time equals the sum of the currents in all three regions. With equal resistivity in these regions, this sum will be proportional to the total voltage which is zero, according to Eq. (5). If the resistivity of the layers were not different, polarization could not have developed in the first place. In addition, if polarization had been developed because of different resistivities, no depolarization discharge would be measured if these resistivities are made equal during the discharge.

Since it is found that considerable charges do accumulate on C_K during the decay, there must be differences in resistivity for the various regions. Furthermore, one must conclude that the charge accumulation on C_K is predominantly due to thermally released charges moving in the d_2 region since *the dark decay discharge current is always of opposite direction to the charging current*. There are, of course, currents in d_1 and d_3 but these are smaller than the current in d_2 , because of the higher resistivities of d_1 and d_3 .

The dark decay of polarization is observed in three ways, as indicated in Fig. 3, depending upon the interval which has elapsed since the removal of the polarizing field and excitation. For very short intervals, one meas-

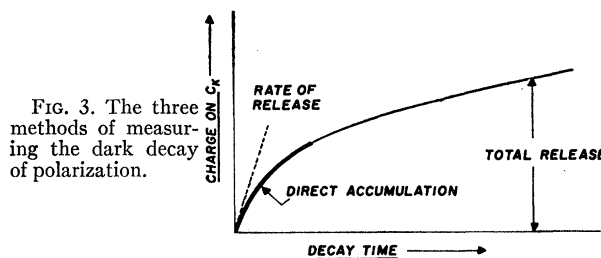


FIG. 3. The three methods of measuring the dark decay of polarization.

ures the rate of dark decay directly; for longer intervals, the total charge accumulation on C_K is measured in a definitive time interval. Eventually as the dark decay is prolonged to very long intervals, one must perform a total release of polarization by radiation to determine the amount of polarization left in the sample.

It is common practice in photoconductive measurements to remove space charges by irradiation with infrared wavelengths, as such radiation releases trapped charges. A much more effective method is to irradiate the sample with wavelengths that amply produce free charges in the bulk; these charges move under the influence of the internal fields to neutralize the space charge accumulations. Again, with uniformly absorbed radiation, the discharge current is found to be opposite in direction to the polarizing current because of the high resistivities of the d_1 and d_3 layers.

When nonuniformly absorbed radiation (i.e., narrow band excitation) is used in the release of polarization, the situation can be quite different. One may produce the majority of the free charges either in d_1 or d_3 . This is found to be true in bulk polarization. The consequence of such irradiation is that the release current i_1 or i_3 can be made to exceed i_2 in magnitude so that the net current *will be in the same direction as the polarizing current* during a portion of the release.

The basic importances of the radiation release method are that one measures not only the magnitude of polarization (by driving free charges across d_2) but that one can also obtain a detailed examination of the internal charge distribution by generating release currents in discrete regions of the sample. For example, in the case of a neutral sample with charge layers Q_0 at d_1 and d_3 , and with the resistance of these layers very large, the charge accumulated at the condenser after complete release by uniform irradiation is $Q_0 d_2 / d_0$. If the complete release would be performed by irradiating only the layers d_1 and d_3 (by excitation on both sides of the sample), the charge release into the condenser would be $Q_0 [(d_1 + d_3) / d_0]$ which is a charge not only of opposite sign but much smaller than that obtained under uniform excitation. In both cases the neutral sample is completely depolarized.

The following notation is used throughout this paper: P^+ refers to a polarizing of the sample with radiation incident upon the positive face. R^+ is a release with radiation at this same electrode after removal of the external field. In all notations, P^+ , P^- , R^+ , and R^- , the

⁶ J. R. Freeman, "Internal polarization in inorganic ZnCdS phosphors," Ph.D. thesis, New York University (1959).

TABLE II. Magnitude of barrier polarization.

Sample No.	Material	Sample thickness	Pol. voltage V_0	Radiation	Pol. time (min.)	Max charge (coul/cm ²)
F-38	ZnCdS	150 μ	200	Visible	2	1.5×10^{-8}
80-3	Fused anthracene	80 μ	80	Near uv	5	1.7×10^{-8}
X-10	Single CdS crystal	250 μ	200	Infrared 1 μ	5	2.5×10^{-8}

positive or negative sign refers to the original polarity of the sample during polarizing.

5. Internal Field Measurements

If a counterfield E_{ext} is applied across a polarized sample,⁷ one can attenuate either the E_1' and E_3' fields or the E_2' field depending upon the direction of E_{ext} . This forms the basis of internal field measurements.

To perform such a measurement the sample is irradiated with light flashes of small intensity and of several milliseconds duration so that each flash produces only a small number of free charges. During the flashes E_{ext} is applied and adjusted until the discharge current drops to zero. E_{ext} then measures the field strength in the region where the free charges are being produced. With a sufficiently large E_{ext} , it is possible to swing the discharge in the opposite direction to that normally associated with the internal field.

With this method one can probe the magnitudes of the internal fields. An examination of E_1' or E_3' requires radiation which is strongly absorbed in these regions so that i_2 is kept small. Conversely, the examination of E_2' requires more uniformly absorbed radiation, although there will always be some competition from the i_1 and i_3 currents. Field measurements of E_2' are most useful when only one charge layer is present in the sample, i.e., d_1 or d_3 approaches zero.

C. BARRIER POLARIZATION

1. General Remarks

Barrier polarization is produced when surface resistive layers interfere strongly with charge transport through the sample. There will be no significant departure from charge neutrality during polarizing when these barriers are roughly equal. Furthermore, it is not necessary that the sample be uniformly excited during polarizing. Even with nonuniformly absorbed radiation, barrier polarization will eventually result although the buildup rate may be much slower (i.e., when the less mobile charges are driven into the unexcited portion of the sample).

These remarks are based upon two fundamental observations that show clearly the nature of barrier polarization. With such polarization a discharge is

never observed in the d_1 or d_3 region (see Fig. 1) under any depolarizing condition. Secondly, experiments with samples of various thicknesses show that σ_{max} depends only upon V_0 , the polarizing voltage, and not E_0 . These results can only be interpreted in terms of thin charge layer accumulations. Such a definite prediction cannot be made about charge neutrality, but the model developed here is equally valid for barrier polarizations having only one charge layer.

2. Magnitude of Barrier Polarization

The magnitude of barrier polarization has been measured in various types of samples under different polarizing conditions. The time of external field application is made sufficiently long in each instance so that the polarization distribution reaches a steady value. Typical results are given in Table II.

The densities of polarization charges are of the same order in vastly different samples and the number of charges involved is rather large, since densities of 10^{-8} coul/cm² correspond to 10^{11} charge carriers. The actual number of polarization charges in the photoconductor is slightly greater than this by the ratio d_0/d_2 according to the relationship $\sigma_0 = (d_2/d_0)Q$.

The near equality of barrier polarization densities in quite different samples suggests that surface conditions control the charge separation. Direct support of this argument is seen in the following experiment. Four ZnCdS samples differing in thickness by a factor of 4 were polarized with the same V_0 and visible light excitation until the distribution of polarization reached a steady value. σ_{max} was measured in each case. The results are given in Table III.⁸ Here the polarization is essentially independent of d_0 and roughly equal in all samples.

Two possible types of charge separation can be visualized in powdered or semicrystalline samples. Either there is a polarization of single grains or across the whole sample. In the former, the separated charges are restricted to individual grains whereas in the latter, the charges move across many grains and presumably become localized near surface barriers. The derivation of σ_0 for grain polarization with 2 layers per grain can be carried out exactly as in Sec. A. For a neutral sample

⁷ M. Silver, "Persistent internal polarization in anthracene," Ph.D. thesis, New York University (1959).

⁸ H. Kallmann and J. R. Freeman, Phys. Rev. **109**, 1506 (1958).

having a thickness of n grains the result is

$$\sigma_0 = (\gamma k V_0 / n d_0^{(g)}) \cdot d_2^{(g)} / d_1^{(g)} + d_3^{(g)}. \quad (13)$$

where the superscript $d^{(g)}$ refers to individual grain quantities. According to (13), for constant V_0 the total polarization should vary as $n d_0^{(g)}$, the total sample thickness. Since such a dependence is not found by experiment, one must conclude that grain type polarization is not prevalent. This result further supports the assumption that the thicknesses d_1 and d_3 do not depend upon the thickness of the sample but are determined by the surface barriers alone. Physically one would expect that $(d_1 + d_3)$ increases with d_0 as a consequence of weaker polarizing fields, so that σ_0 would vary even more strongly than $1/d_0$ which is certainly not observed. In other words, the separation of charges cannot be field limited. One must conclude that $d_2 \approx d_0$ and (9a) can be written approximately as

$$\sigma_0 \approx k \gamma V_0 / (d_1 + d_3). \quad (14)$$

TABLE III. Polarization as function of d_0 .

ZnCdS		$V_0 = 200$ V, visible excitation	
Sample	d_0 (mm)	max charge (coul/cm ²)	
F-105	0.16	1.37×10^{-8}	
F-106	0.31	1.15×10^{-8}	
F-102	0.49	1.18×10^{-8}	
F-103	0.65	1.20×10^{-8}	

This relation states that the magnitude of barrier polarization depends only upon the polarizing voltage and the effectiveness of high resistivity layers at the sample's surfaces which determine, according to (12), the value of γ .

This proportionality between polarization and applied voltage was experimentally verified up to about 300 v. Above such voltages a breakdown of the sample often occurs. But by adding large amounts of a binder of higher dielectric constant to the ZnCdS material it was possible to increase the magnitude of polarization considerably. Polarizations of 16×10^{-1} coul/cm² were obtained with a 500-v polarizing in waxed samples.

3. Internal Field Strengths; γ Factor

The parameter γ not only determines the amount of polarization obtainable with E_0 applied, but also the speed of release in a subsequent discharge since the depolarization rate depends upon the internal field E_2' given by $-\gamma E_0$.

One can gain at least qualitative information on the magnitude of γ by comparing the buildup and release rates of polarization under the same intensity of optical excitation. If this excitation is so strong that there are many free carriers being produced in d_2 , the rate of

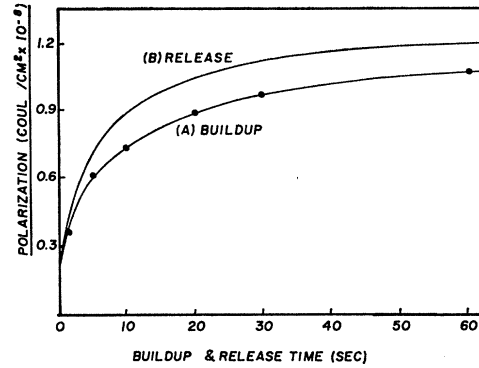


FIG. 4. The buildup and release of polarization in a ZnCdS sample. The release is given in terms of freed charge accumulation on the standard condenser C_k . For the buildup of polarization, a 200-v field with visible excitation was used. The same excitation was employed during the release.

polarization buildup and release depends essentially upon the field strengths E_2 and E_2' acting upon these carriers. Assuming that the currents in d_1 and d_3 are negligible, E_2 has the initial value E_0 and is attenuated in time as the polarization layers develop. Similarly, E_2' starts off with the value $-\gamma E_0$ and decays in time as the polarization layers are depleted. By finding that external field E_0 which produces the same rate of polarization buildup as the discharge of the same polarization, using equivalent excitation, one can determine qualitatively the initial strength of E_2' and hence γ . This approach is entirely independent of the actual details of polarization production or destruction.

Figure 4 compares the observed buildup of polarization (Curve A) with the release of the same polarization (Curve B). The sample is a ZnCdS powder polarized with visible light and a 200-v field. The release curve is the recorded accumulation of freed image charge

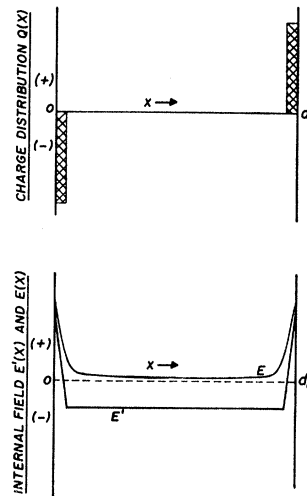


FIG. 5. The distribution of charges and the internal fields in barrier polarization upon the removal of E_0 . The negative value of $E'(x)$ corresponds to the d_2 region of the sample.

TABLE IV. Rate of rise of polarization in anthracene.

Radiation	Initial rate of rise, excitation at positive surface (coul/sec) per (w/cm ²)	Initial rate of rise, excitation at negative surface (coul/sec) per (w/cm ²)
No excitation (dark polarized)	10 ⁻¹²	10 ⁻¹²
IR (0.8-2.0 μ)	6 \times 10 ⁻¹¹	6 \times 10 ⁻¹¹
Visible (0.48-0.7 μ)	2 \times 10 ⁻⁹	2 \times 10 ⁻⁹
Anthracene fluorescent light ($\lambda \approx 0.42\mu$)	1.4 \times 10 ⁻⁶	1.4 \times 10 ⁻⁶
UV ($\lambda \approx 0.365\mu$)	1.5 \times 10 ⁻³	4 \times 10 ⁻⁴

on C_K . The almost uniform displacement of A below B can be accounted for by the spontaneous decay which occurs in the 1 or 2 sec required to remove the external polarizing field and make a measurement. When one takes this into account, Fig. 4 shows that the internal polarization field E_2' is approximately equal in magnitude to the external field E_0 which produces this polarization. Hence $\gamma \approx 1$. Beyond this result the curves show that the release of barrier polarization is a very similar process to its buildup. Similar conclusions have been drawn from ac impedance measurements of similar samples under excitation.⁹

Another way to determine γ is through field measurements described in Sec. B. Experiments performed in this way with anthracene samples showed that the discharge current in the d_2 region is blocked by an external field which is about 75% of the magnitude of the original polarizing field. One concludes, therefore, that in anthracene samples γ is also of the order of 1.

According to Eq. (12), one expects that if (d_1+d_3) is sensibly constant, then γ must decrease with increasing thickness if it is not already close to 1. This would give σ_{\max} an even stronger d_0 dependence. Since this is not found by experiment, one must again assume that $\gamma \approx 1$. These results concerning the magnitude of γ support the basic assumption that the polarization in the interior of the sample is not essentially altered upon removal of the excitation and the polarizing field.

The charge and field distributions for barrier polarization are given in Fig. 5. E_1' and E_3' have the same values as required for a neutral sample.

Relation (14) permits a calculation of the quantity (d_1+d_3) since all other quantities are measurable. When such calculations are made assuming two symmetrically placed charge layers, it is found that for anthracene the separation distance from each electrode is of the order of 8 μ , whereas in ZnCdS samples, d_1 or d_3 has a value of 15 μ . Over these distances, at most, approximately 10¹¹ charge carriers are distributed. Hence the charge density near the electrodes is about 2 \times 10¹⁴ electrons/cm³. The difference in d_1 for anthracene and ZnCdS, even though σ_{\max} is approximately equal in both cases, has its origin in the different value of the

dielectric constant for these two materials. For anthracene, κ is taken as approximately 2, while for ZnCdS this quantity has a value of roughly 5. These are experimentally determined values from the ac capacity and sample thickness d_0 . In this way the effect of binder and included air in the sample are properly accounted for.

For the ZnCdS materials, the d_1 determined here is of the order of the grain size of the powder, so that the polarization charges are actually concentrated in a monogranular layer at the surface of the photoconductor.

4. The Buildup of Polarization: Anthracene

The initial rates of polarization buildup for various exciting wavelengths and polarity of the external field are given in Table IV.

The fluorescent light in anthracene is only weakly reabsorbed whereas radiations less than 4000 Å are very strongly absorbed in a layer less than 1 μ in thickness.¹⁰ The region of strong excitation may, however, be extended to 2 or 3 μ because of exciton diffusion and the reabsorption of some of the fluorescent radiation in the region of the absorption edge. The most striking results of Table IV are the marked differences in the initial rate of the rise of polarization through the positive and negative electrode for radiations less than 4000 Å. For radiations greater than 4000 Å, where absorption is more uniform, no such differences are observed. This difference in buildup rate is directly connected with the different trapping and apparent mobilities of the charge carriers, the positive carriers having the higher mobility and are not readily trapped. According to photoconductive measurements, the difference between positive and negative currents can be as great as 50 to 1.^{11,12}

When the anthracene sample is polarized P^+ so that the more mobile charges are drawn across the anthracene sample by the external field, the strong current of positive charge carriers produces a rapid charge separation. This is called a *fast polarizing* in which the negative charges form a layer directly at the illuminated positive electrode. For the P^- polarizing situation, the less

⁹ H. Kallmann, B. Kramer, and P. Mark, Phys. Rev. **109**, 721 (1958).

¹⁰ A. Feidel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, (John Wiley & Sons, Inc., New York, 1951).

¹¹ A. G. Chynoweth and W. G. Schneider, J. Chem. Phys. **22**, 1021 (1954).

¹² H. Kallmann and M. Pope, Nature **185**, 153 (1960).

mobile negative charges must move through the sample, resulting in a *slow polarizing*.

Similarly, one can speak of a fast (R^-) and slow (R^+) discharge of polarization in anthracene, and it is clear that if a sample is fast polarized, then a release with radiation through the same electrode will be slow and vice versa.

5. Buildup of Polarization: ZnCdS Phosphors

For ZnCdS powders, the rise curves are very similar in shape to anthracene, but the difference between fast and slow polarizing is not as pronounced. Even with ultraviolet radiation, which is strongly absorbed in this material, this difference is rather small because the fluorescent radiation is strongly reabsorbed throughout the entire sample. Hence the production of free charges cannot be so readily restricted to a narrow region of the sample as in anthracene. One finds, however, that in ZnCdS phosphors a P^- polarizing is faster than P^+ , in agreement with the negative charge carriers being more mobile.

The rate of polarization buildup can be used as a very sensitive measure of charge mobility for the more mobile carrier, and lifetime for the less mobile carrier in a photoconductor. For example, starting with a quenched sample, one can use "flash" excitation and measure by observing the width and decay of the current pulse, the time required for the free charge to travel across the sample⁷ or be trapped.

6. Dependence of Polarization Buildup on Polarizing Light Intensity

According to the model developed for barrier polarization, σ_{\max} for a given V_0 should be independent of the polarizing light intensity. This is because σ_{\max} is essentially determined by γ and (d_1+d_3) , both of which quantities are sensibly independent of the light intensity. Only the rate at which the charge separation occurs should depend upon this intensity.

This is found to be true experimentally. Not only are

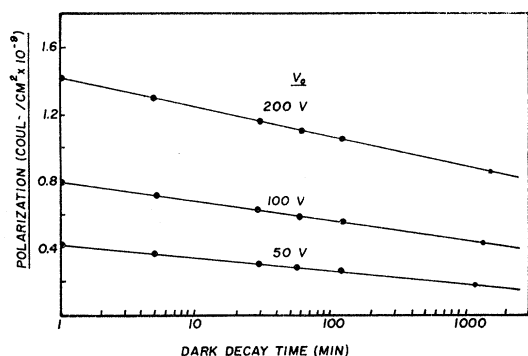


FIG. 6. Dark decay curves of barrier polarization in ZnCdS. In all cases, visible excitation is used during the polarizing. All measurements are made by the radiation release method so that the sample must be repolarized after each measurement.

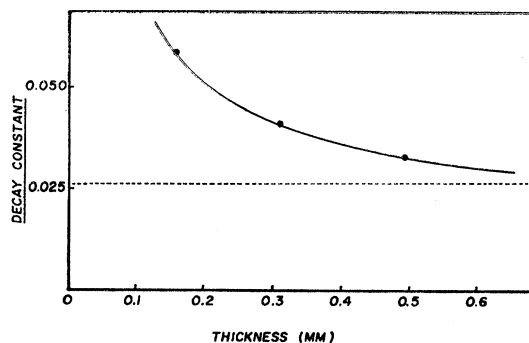


FIG. 7. The variation in the dark decay constant C_0 with sample thickness for ZnCdS samples.

the ultimate equilibrium values of polarization the same, but when the buildup curves are normalized, the general shape of the curves is the same. Similar results have been obtained with anthracene samples. These results point out the fact that for barrier type polarization, the main process is the reduction of the E_2 field to a near zero value while the external field is applied.

7. Dark Decay of Polarization

The dark decay of polarization is brought about by thermal release of trapped charges. Not only do the polarization charges Q^+ and Q^- decay in time, but free charges are also created in the d_2 region. All of these freed charges move in a direction so as to diminish the existing polarization.

Dark decay curves are shown in Fig. 6 for ZnCdS, where each point on the curves is obtained by a radiation release of the polarized sample. Since the thermal release and the displacement of free charges by an external field are much slower processes in anthracene than in ZnCdS, one would expect that the dark decay of polarization in the organic material is much slower than in ZnCdS. This is borne out by experiment.

A detailed analysis of the dark decay of the ZnCdS phosphors has been made. The dark decay can be well described by

$$d\sigma/dt = -C_0\sigma_0/(t+\alpha), \quad (15)$$

whose integrated form is

$$\sigma(t) = \sigma_0 \{ 1 + C_0 \ln[(t_0 + \alpha)/(t + \alpha)] \}. \quad (16)$$

Here, C_0 is a constant of the material and σ_0 is the polarization at time $t=t_0$, the time scale referring to the dark period following the removal of E_0 .

C_0 is found to be essentially constant for samples of comparable thickness even under widely differing excitation intensities and polarizing voltages. This constancy in C_0 for different polarizing intensities and V_0 points out that the same type of charge distribution has been produced under these various conditions.

Experiments do show, however, that thicker samples decay more slowly, so that the value of C_0 decreases with thickness as shown in Fig. 7. Whereas the amount

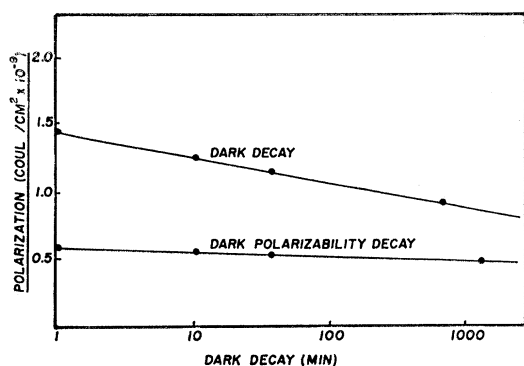


FIG. 8. A comparison of the decay of dark polarizability and dark decay in a ZnCdS sample. For dark polarizability the time scale refers to the elapsed time between field-free excitation and field application.

of polarization is almost independent of sample thickness for a given polarizing voltage, the decay rate is not. Polarization buildup approaches its equilibrium value as the internal field E_2 reaches a near zero value, with E_0 applied. The decay, however, is determined by the strength of the internal field $E_2' = -\gamma E_0$ and this field will be decreased with increasing d_0 . Thus thicker samples have a slower decay.

8. Dark Decay and Dark Polarizability: ZnCdS

The ZnCdS powders behave quite differently from anthracene in one important respect. The application of an external field alone can produce considerable polarization in ZnCdS materials depending on the pre-excitation of the sample. This will always be possible when residual charges remain in excited states for any length of time after removal of the exciting radiation. In anthracene, the number of free charges drops rapidly to a near zero value whereas in the ZnCdS materials they are observed for extremely long periods of time, as evidenced by conductivity measurements.

The ability to produce a polarization by field alone is termed dark polarizability. Figure 8 shows that the ZnCdS material has a pronounced dark polarizability. Here, the time scale for dark polarizability refers to the period between initial, field-free excitation, and subsequent field application. For this same time scale, the normal dark decay of a light-induced polarizing is also plotted. The decay of dark polarizability is much slower than the dark decay of normal barrier-type polarization.

These results may seem surprising at first glance, since both processes involve a decrease in the number of excited charges in the sample. Dark decay of polarization is determined by the number of charges freed per unit time from traps and displaced by the internal field. Dark polarizability depends upon the number of free charges available per unit time which again can only come from the release of trapped electrons. Thus one would expect that both processes have the same

source of free charges. Furthermore, since $\gamma \approx 1$ for barrier type polarization, the same magnitude of the field strength prevails in both systems. Nevertheless there is a large difference in the decay rates for these two processes which can be understood as follows.

During the decay of dark polarizability, the sample is field free, whereas the internal field E_2' persists throughout the dark decay of polarization. It is known from ac conductivity measurements with a superimposed dc field that the application of a dc field diminishes the trap occupation (i.e., dc quenching).¹³ Further, during the dark decay of polarization, one actually measures the decay of a certain nonhomogeneous charge distribution. Each charge which is released from a trap into the conduction band is displaced by the polarization field and this contributes to the decrease of polarization. Recombination of an electron with a positive charge is not necessary for such a decrease. In the case of dark polarizability, the situation is quite different since no field is present during the decay period. Thus only a recombination of an electron with a positive charge would bring about such a decrease. But an electron released from a trap into the conduction band normally is trapped again, rarely contributing to the de-excitation of the sample. Therefore the dark polarizability is diminished only very slightly in time since it is determined by the degree of excitation decay of the sample. The very pronounced difference between the dark decay of polarization and that of dark polarizability is an independent proof that strong retrapping must occur in these phosphors.

9. Radiation Release of Polarization

Any radiation which produces free charges in the photoconductor also discharges polarization.

For anthracene Fig. 9a shows the R^+ and R^- releases of P^+ polarization and their corresponding internal field strengths measured by the voltage required to stop the discharge. The marked difference in the R^+ and R^- release rates for anthracene are completely analogous to the fast and slow polarizings previously discussed. An important point here is that σ_{\max} reaches the same ultimate value whether the sample be released R^+ or R^- . Indeed, partial releases can be made, first R^+ , then R^- , etc., and one finds that the release current is always in the same direction and that σ_{\max} has the same ultimate value as for a unidirectional release. Such experiments prove conclusively that the samples are discharged predominantly in the d_2 region. In barrier polarization it is impossible to produce a discharge current in d_1 or d_3 that exceeds that in d_2 . These results support the concept of a barrier polarization in which the polarization charges are accumulated near the electrodes. Figure 9b shows release curves for releasing radiation of different wavelengths. The marked difference between R^+ and R^- only occurs with a radiation

¹³ H. Kallmann and P. Mark, Phys. Rev. **105**, 1445 (1957).

which is nonuniformly absorbed. With more uniformly absorbed radiation this difference disappears since the more mobile carriers are uniformly distributed over the sample. Further evidence that the discharge occurs primarily in the d_2 region is seen from these results. Even after the prolonged discharge with uniformly absorbed light, σ_{\max} is reached when the discharge is continued with nonuniformly absorbed light transmitted through the negative electrode (dotted curves in Fig. 9b).

The shape of the release curve in ZnCdS gives the following approximate differential law for the depletion of polarization:

$$d\sigma/dt = -\sigma(0)\beta/(t+\beta)^2 = -\sigma(t)/(t+\beta), \quad (17)$$

where $\sigma(0)$ is the polarization at the onset of the release. β is related to the intensity of the releasing radiation and is found to be of the form

$$\beta = AI^{-n}; \quad (18)$$

where I is the excitation intensity and n lies between 1 and 2, indicating a strong dependence of the releasing rate on the intensity.

10. Discussion of the Polarization Depletion Laws

If \mathfrak{N} free charges of mobility μ are present in the sample per unit volume, and if $E_2'(t)$ is the instantaneous

field strength in d_2 , then one can readily show that the depolarization current is given by

$$d\sigma/dt = -e\mathfrak{N}\mu E_2'(t) = -e\mathfrak{N}\mu[\sigma(t)/k][d_1+d_3/d_0], \quad (19)$$

assuming that \mathfrak{N} and E_2' are constant throughout d_2 and that the displacement of charges is proportional to the field strength. During a dark decay, \mathfrak{N} decreases with time, while for radiation discharges, \mathfrak{N} is constant. In the former case, photoconductivity investigations show that the decay density of free charges is given approximately by the expression^{14,15}

$$\mathfrak{N} = C_1/(t+\alpha), \quad (20)$$

so that relation (19) can be written as

$$(d\sigma/dt)_{\text{dark}} = -C_2\sigma(t)/(t+\alpha), \quad (21)$$

where the constants C_1 , μ , and $(d_1+d_3)/d_0$ are contained in C_2 . By a similar argument, (19) becomes for radiation release

$$(d\sigma/dt)_{\text{release}} = -C_3\sigma(t). \quad (22)$$

Neither the dark decay law (21) nor the radiation release law (22) are observed. The measured dark decay rate is faster than the theoretically determined rate. In the experimentally derived relationship $\sigma(t)$ is replaced by σ_0 . In the radiation release, a factor $1/(t+\beta)$ is found experimentally which can only be associated with \mathfrak{N} so that $1/\beta = \mathfrak{N}_0$. Here, the inclusion of a time factor gives a radiation release law that is slower than that predicted by theory.

One cannot give unambiguous explanations for these behaviors but the following remarks are pertinent. First, the assumption that the charge displacement is proportional to the field strength is probably not completely valid since the charges have to cross several grain boundaries. Also, it is known from conductivity measurements with dc fields that the decrease in current is a stronger function than one directly proportional to the field strength. The experimental formula (17) can also be written as

$$(d\sigma/dt)_{\text{release}} = -[\sigma(t)]^2/[\sigma(0)/\beta], \quad (23)$$

in which the $[\sigma(t)]^2$ factor expresses this stronger dependence upon the field strength. One would expect that a similar formula holds for the dark decay as a function of time. If one assumes accordingly that

$$(d\sigma/dt)_{\text{dark}} = -C_4\mathfrak{N}[\sigma(t)]^2, \quad (24)$$

then the dark decay results show that \mathfrak{N} must decay considerably slower than $1/(t+\beta)$. This may indicate that because of the internal field, the shallow traps are not as highly occupied as in the field-free case. Indeed, it has been shown in conductivity measurements¹³

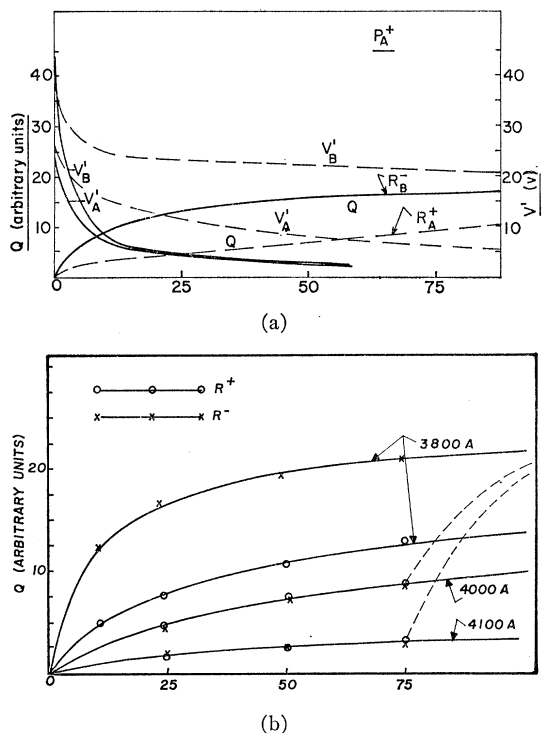


FIG. 9. The R^+ and R^- releases of P^+ polarization in anthracene. Release time measured in seconds. (a) for 3600 Å including internal fields; (b) release for various wavelengths.

¹⁴ J. T. Randall and M. K. F. Wilkins, Proc. Roy. Soc. (London) **A134**, 365 (1945).

¹⁵ R. Herman, "The Dynamics of Excited Electrons in Crystal-line Photoconductive Phosphors," Ph.D. thesis, New York University (1957).

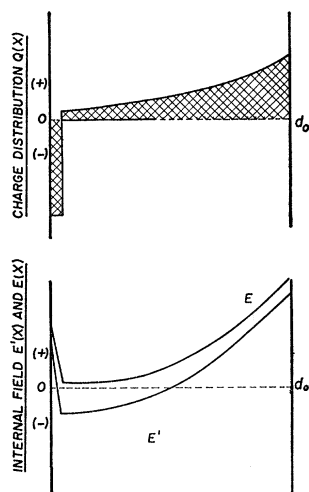


FIG. 10. The distribution of charges and the internal fields in bulk polarization for a ZnCdS phosphor. The inequality of $E'(x)$ and $E(x)$ at the electrodes signifies that the polarized sample is non-neutral.

that the turning off of the dc field reduces the conductivity because electrons are swept out of relatively shallow traps. This effect may be responsible for the slow decrease in n .

11. General Remarks on Barrier Polarization

Sections C1-C10. have presented the main features of barrier polarization in terms of a two-layer model. Although the formation of barrier polarization is closely connected to the resistivity of barrier layers at the electrodes (see Table I), these resistances have not been explicitly discussed. Samples of powdered material usually have these barriers introduced during the preparation and barrier polarization always develops except for the inhomogeneous excitation conditions of Case 3 in Table I. It is shown in the next section that even for this type of excitation, barrier polarization develops eventually when the resistance of the barrier is very large.

The main argument that this polarization can be described as barrier polarization lies in the observation that discharge currents occur predominantly in the d_2 region, that the field strengths in these regions are of the same order of magnitude as in the external field strength, and that the thickness dependence of polarization is related to V_0 and not E_0 .

D. BULK POLARIZATION

1. Introduction

When the resistance layers at the electrodes of the sample are not equal in magnitude, and when the density of the more mobile carriers during polarizing is greatest at the barrier of least resistance, then a discharge current can be produced subsequently which initially predominates in d_1 or d_3 rather than d_2 . Such a current gives a reverse release or reverse discharge because the carriers move in a direction reverse to that of a normal discharge in the d_2 region. It can only occur

if the point where E' is zero is not directly adjacent to the electrode as in the case of barrier polarization. This means that d_1 or d_3 is so extended that the charge motion can be made to predominate in one of these regions. Because of the extension of such a charge distribution, it is suitably described as *bulk polarization*.

Table I, Item 3, has given the general polarizing conditions which must exist to produce this bulk polarization. These are discussed in detail in the following sections.

2. General Description

When the resistance of the sample is comparable to the barrier resistances, bulk polarization is possible. The basic difference between this and barrier polarization is that the point where E' becomes zero can now be a function of the sample excitation and external field polarity.

If the sample is excited only close to one of the electrodes and if the less mobile carriers are drawn into the sample, its bulk acts as a large resistance for these carriers; then the carriers are trapped in the bulk of the sample. This is especially so if their reduced mobility is due to frequent trapping. If besides this high resistance of the bulk, large resistive barriers at the electrodes exist, bulk polarization will develop at the beginning of polarizing, but the polarization will go over into barrier polarization eventually, when enough less mobile carriers accumulate at the electrode barrier. How much bulk polarization is observed depends upon the ratio of the resistance of the bulk to that of the barrier (see Fig. 10).

The general model of bulk polarization is given in Fig. 10. In this figure, for which the negative carriers are assumed to have the highest mobility, positive charges are distributed over the whole bulk of the sample, E' goes through zero somewhere in the middle, and reverse release is possible in the d_3 region provided the releasing radiation is restricted to this depth. Figure 10 shows that E_1' is no longer equal to E_3' as a consequence of the nonneutrality of the sample. This nonneutrality arises from resistivity differences throughout the sample. The charges of higher mobility will also give rise to a charge accumulation directly at the surface of maximum excitation, the magnitude of which depends on the ease with which these charges can move out of the sample. The sample becomes charged with the sign of the less mobile carriers if the barrier at the left is smaller than the total resistance of the sample including the barrier at the right. If the more mobile charges would not move out of the sample at all, no dc current would flow at the equilibrium of polarization buildup.

Bulk polarization can also occur when the more mobile carriers are driven into the unexcited portion of the sample (Case 5 of Table I). This only happens when the resistance layers at the electrode are small for the

mobile carriers. At the moment of excitation removal, the supply of mobile carriers from the illuminated electrode ceases and the mobile carriers are partially removed from the sample. Consequently an excess of less mobile charges remains in a trapped distribution over the bulk of the sample.

The following description of bulk polarization is an extension of the two-layer model developed previously. Let the number of positive charges trapped in an elemental strip dx at x , be given by $p(x)dx$ and the number of negative charges be given by $n(x)dx$. With

$$\int_0^{d_0} E'(x)dx = 0, \quad (25)$$

the field $E'(x)$ at any point x due to this distribution is given by

$$E'(x) = E_p'(x) + E_n'(x), \quad (26)$$

$$E_p'(x) = \int_0^{d_0} \frac{x}{kd_0} \cdot p(x)dx - \int_x^{d_0} \frac{p(x)}{k} dx, \quad (27)$$

and

$$E_n'(x) = -\int_0^{d_0} \frac{x}{kd_0} n(x)dx + \int_x^{d_0} \frac{n(x)}{k} dx. \quad (28)$$

Equations (27) and (28) can be rewritten as

$$E_p'(x) = \frac{M^+}{kd_0} - \int_x^{d_0} \frac{p(x)}{k} dx, \quad (29)$$

$$E_n'(x) = -\frac{M^-}{kd_0} + \int_x^{d_0} \frac{n(x)}{k} dx, \quad (30)$$

where M^+ and M^- are the electrical moments of the respective charge distributions. The total field at any point x is simply

$$E'(x) = \frac{M^+ - M^-}{kd_0} + \int_x^{d_0} \frac{n(x)}{k} dx - \int_x^{d_0} \frac{p(x)}{k} dx. \quad (31)$$

Equation 31 is completely general; however, the functional forms of $p(x)$ and $n(x)$ are as yet unspecified. A determination of these charge distributions from which one can obtain information on the mechanisms for carrier generation and transport is one of the goals of the study of PIP effects. Some progress along these lines already has been made.

It is instructive to examine the charge distribution of Fig. 10 in terms of this discussion. Assume that the positive charges are given by $p(x)$ for every x , while the negative charges are restricted to one strip dx^- at x^- which is small compared to d_0 . For these negative charges, one can write, as in the two-layer model,

$$E_{n_1}' = [n(x^-)/k][(d_0 - x^-)/d_0]dx^-; \quad (x < x^-) \quad (32)$$

$$E_{n_2}' = [-n(x^-)/k][x^-/d_0]dx^-; \quad (x > x^-). \quad (33)$$

That is, the field due to the negative charges is constant but has a discontinuity at the point x^- .

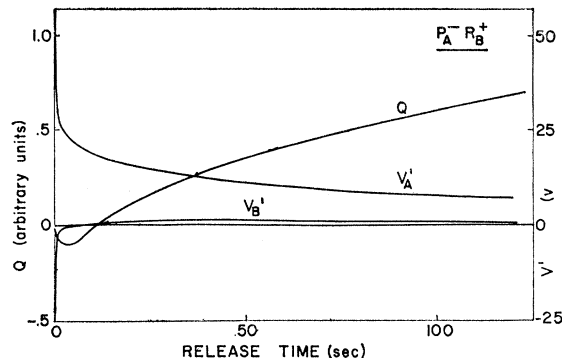


FIG. 11. The slow discharge of slow polarization in anthracene and the simultaneous decay of the internal fields.

From (27) one has for the strength of the field at the electrodes due to the positive charge distribution,

$$E_p'(0) = M^+/kd_0 - Q^+/k; \quad E_p'(d_0) = M^+/kd_0, \quad (34)$$

where Q^+ is the total trapped positive polarization charge. Since the positive charges migrate towards the negative electrode in Fig. 10 (i.e., the point where $x^+ = d_0$), the field at $x=0$, upon removal of the polarizing field may be described by $-\gamma V_0/d_0$, and (27) now becomes

$$E_p'(x) = -\frac{\gamma V_0}{d_0} + \frac{Q^+}{k} - \int_{x_f}^{x_0} \frac{p(x)}{k} dx, \quad (35)$$

or

$$E_p'(x) = -\frac{\gamma V_0}{d_0} + \int_0^x \frac{p(x)}{k} dx. \quad (36)$$

The value of x which makes Eq. (36) equal to zero, that is x such that

$$\int_0^x \frac{p(x^+)}{k} dx^+ = \frac{\gamma V_0}{d_0}, \quad (37)$$

essentially determines the effectiveness of a reverse discharge. For $x \ll d_0$, reversal effects are large. Equation (33) shows that a negative charge layer close to $x=0$ does not contribute to the field at the reversal point to any large extent. This is because the factor x^- in Eq. (33), if x^- close to zero, will make $E_{n_2}' \approx 0$ regardless of the magnitude of $n(x^-)dx^-$. In other words, one would have to have a large excess of the more mobile carriers (in this case the negative ones) to strongly alter the field conditions where the reversal is possible. This will occur only under very special situations.

There exists another type of bulk polarization which can be produced by the application of ac fields in the absence of concomitant radiation.¹⁶ The sample is initially excited in the absence of a field so that its electron traps are filled to a certain extent, but the sample conductivity is low. Thereafter, the application

¹⁶ F. Chernow, Ph.D. thesis, New York University (to be published).

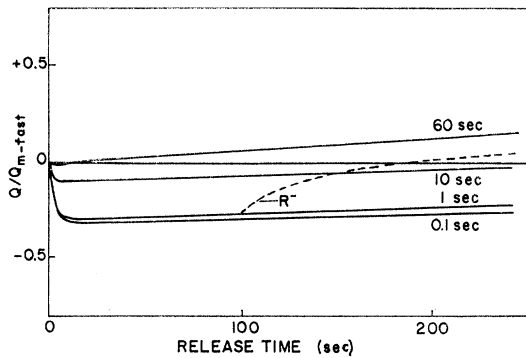


Fig. 12. The slow discharge of slow polarization in anthracene for different polarizing times.

of an ac field draws electrons from the traps into the electrodes and leaves the positive charges in the sample. This situation is observed in ZnCdS phosphors, giving a polarization charge distribution in which positive layers develop adjacent to each electrode. This type of polarization can also persist for considerable periods of time.

3. Bulk Polarization Effects: Polycrystalline Anthracene

Bulk polarization in anthracene is obtained with P^- polarizings. If an R^+ release is performed, a reversal of the release current is initially observed. On the other hand, the R^- release is fast since the positive charges move into the sample; R^- releases always measure the total polarization. Experimental results are shown in Figs. 11 and 12, wherein all of the characteristics of bulk polarization are displayed. In Fig. 11, besides the released charge, the corresponding field measurements are given. V^- describes the field under R^- release in the d_2 region, and V^+ the field under R^+ release which starts in the d_3 region. Figure 11 shows that at the beginning of the R^+ release, the charge motion is reversed. But several seconds after the onset of the discharge, the release current changes its sign and becomes normal. The same behavior is displayed by the field measured at the side of the sample originally positive. This field becomes zero at about the same time that the reverse charge reaches its maximum. In the case of Fig. 11, the sample was polarized for more than one minute. For still larger polarization periods, the reverse discharge at the beginning of the release would become smaller and eventually vanish.

Figure 12 compares reverse releases for various polarizing times. For short polarizing times, the R^+ release remains reversed and shows practically no indication of changing into normal release. For longer polarizing times, the reverse charge release is ultimately surpassed by the normal release, and the polarization tends to go over into barrier polarization. The magnitude of the reverse charge release is small in the case of long polarizing times (only about 5% of the R^- release) but much larger for short polarizing times (about 40%

of R^-). But in the latter case, R^- is also small, being not more than 1.0×10^{-9} coul/cm² compared to 1.0×10^{-8} coul/cm² for full polarization. In Fig. 12, for a short polarizing time, a subsequent R^- release is shown after 2 min of an R^+ release. This curve shows that in spite of the R^+ release, polarization still remains in the sample, but the total charge released during R^+ and subsequent R^- together are found to be smaller than that released by an initial R^- release. This can only mean that the negative charges exceeded the positive ones.

For short P^- polarizing periods, the slow moving negative charges are still near the negative electrode and d_3 is therefore quite large. A reverse release can be produced in this region until E_3' drops to zero. But even if E_3' is brought to zero there is still polarization in the sample. For prolonged polarizing times, the point where E' is zero (transition between E_2' and E_3') moves closer to the positive electrode and thus decreases d_3 . Under these circumstances, it is possible for the discharging radiation to produce free charges both in d_3 and d_2 so that a transition from reverse to normal release can occur. This comes about because the discharge, first predominating in d_3 , decreases with time, since this discharge tends to diminish fields, E_3' faster than E_2' . Then the discharge in d_2 takes over. For this polarization distribution, the total charge is not zero so that the field due to the positive charges is weaker initially than that brought about by the negative charges.

Since the reversal of charge release requires absorption in a relatively narrow layer, it was of interest to learn whether a highly absorbed radiation such as 2536 Å instead of the 3600 Å radiation would yield different results. For these experiments, the normal glass electrodes were replaced by transparent Vycor electrodes. But even with this more strongly absorbed radiation, no significant differences were found in the reversal characteristics. This is probably due to the fact that the range where the sample is strongly excited is not so much determined by the penetration depth of the incident radiation but rather by the diffusion of the excitons produced by this radiation. This diffusion

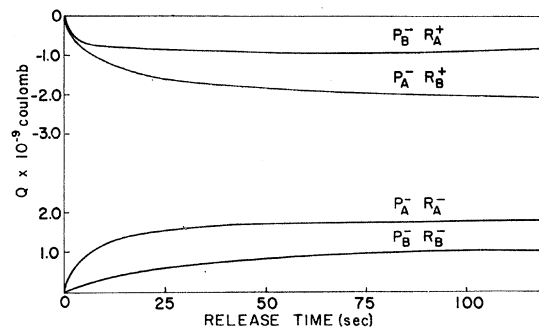


Fig. 13. The fast and slow discharge of slow polarization in polarized anthracene sandwiched between Vycor electrodes. These discharge curves were obtained in Vycor samples polarized for 10 sec.

length is of the order of 0.5 to 1.0 μ , which is the determining factor for sample excitation range. Re-absorption of the fluorescent light serves to further this excitation range to some extent.

There was one important behavioral difference observed, however, with Vycor samples. Apparently better electrode contacts could be achieved than with standard conducting ones. Reverse charge effects are much stronger as shown by Figs. 13 and 14 where similar experiments as in Fig. 12 are carried out for 10 and 300 sec polarizing time, but with Vycor electrodes. Here the normal fast-release R^- is also shown. For these electrodes, it is not much stronger than the reverse release R^+ ; there is only a weak tendency for the latter to go over into the normal release. Only after long polarizing was such a transition observed.

Apparently in Vycor samples, because of the better contact, the accumulation of positive charges at the negative, excited electrode is small. The polarization

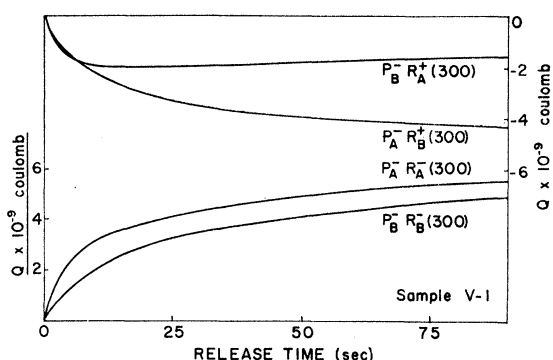


FIG. 14. The fast and slow discharge of slow polarization in polarized anthracene sandwiched between Vycor electrodes. These discharge curves were obtained in Vycor samples polarized for 300 sec.

consists primarily of negative charges trapped over the whole sample. This is emphasized in Figs. 15 and 16 where the sample is fast polarized P^+ . Normally no reversal of charges is observed since the less mobile charges tend to accumulate at the illuminated electrode. For these samples, however, even P^+R^+ gives a reversal, which slowly goes over into a normal release. Simultaneously, there is a strong reduction in the total polarization, as measured by an R^- release. Figure 16 shows this decrease quite noticeably, indicating that the sample is far from electrical neutrality and is negatively charged, just as in the case of P^- and R^+ release. This can be understood by assuming that most of the positive charge has moved out of the sample and that a considerable amount of negative charge stays in the sample over a distance which is not small compared to the absorption depth of the radiation or the respective diffusion length of the excitons. This type of reversal has been investigated in more detail by Moore and Silver.¹⁷

¹⁷ W. Moore and M. Silver, J. Chem. Phys. **33**, 1671 (1960).

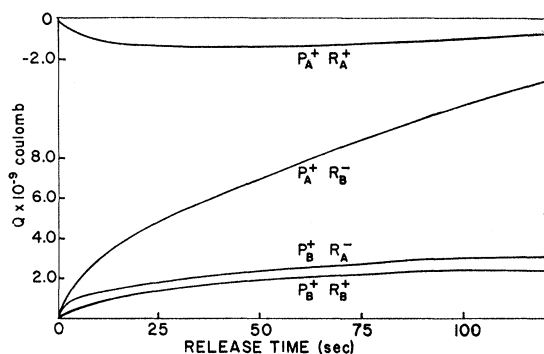


FIG. 15. The fast and slow discharge of fast polarization in polarized anthracene sandwiched between Vycor electrodes.

The importance of removal of positive charges from the sample is also borne out by the following experiment. If one polarizes an anthracene sample in which insulators are inserted between the photoconductor and the electrodes, polarization is still observed although smaller than without insulators. But charge reverse releases cannot be produced under any method of polarizing or release. One must conclude, therefore, that the accumulation of positive and negative charges at the insulator faces brings about such a strong barrier polarization that it surpasses all significant effects of bulk polarization. Further experiments have been carried out making one electrode removable which introduces a rather high resistance layer at this electrode. As a consequence of this, a P^- polarizing through this electrode does not produce reversal effects. In this case, the mobile position charges cannot escape as easily from the sample and their accumulation at the barrier reduces the electric field in d_3 to such an extent that reversals cannot be produced in this region. Equations (33) through (37), but with the negative and positive charges interchanged, show that the narrow layer of mobile charges must exceed the number

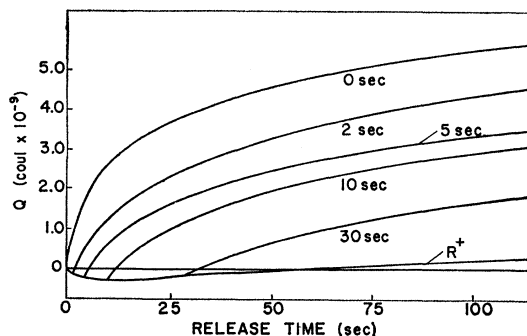


FIG. 16. The slow discharge of fast polarization in polarized anthracene samples sandwiched between Vycor electrodes. The reversal is shown by the R^+ curve. After a specified time the sample was fast discharged. The specified reverse discharge time is given on the fast discharge curves. The decrease in polarization is demonstrated by the result that the 2-, 5-, 10-, and 30-sec curves do not rise to as high a value as the 0-sec curve.

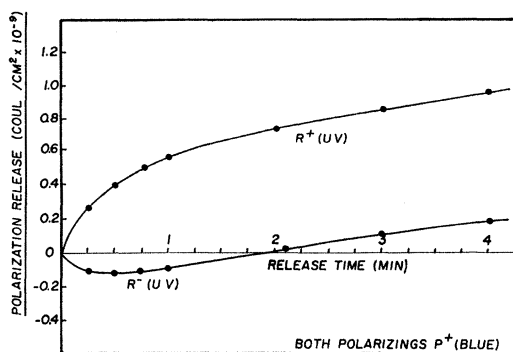


FIG. 17. The R^+ and R^- releases of a P^+ polarizing in ZnCdS. The sample was polarized with blue light and released with ultraviolet excitation.

of less mobile charges considerably, in order to make the reverse discharges disappear even for short polarizing periods. In the case cited above apparently some negative charges have been removed from the sample but only very little positive because of the high resistance at the negative electrode.

In this way the examination of polarization can provide some rather detailed information about the resistance near the various electrodes.

4. Bulk Polarization Experiments: ZnCdS Materials

In the inorganic ZnCdS phosphors, the positive charges have the smaller apparent mobility and are more readily trapped so that charge reversals occur with P^+R^- experiments rather than P^-R^+ as for anthracene. The region of maximum sample excitation must be at the positive electrode during polarization in order to draw out the more mobile negative charges. Table V bears out this point. Figure 17 compares the respective ultraviolet releases R^+ and R^- for P^+ polarizing with blue light. Here the R^-

TABLE V. Dependence of reversals in ZnCdS on polarizing polarity and excitation.

Polarizing condition	$R^-(uv)$ maximum reversal (coul/cm ²)
$P^-(uv)^a$	zero
$P^+(uv)$	zero
$P^-(blue)^b$	zero
$P^+(blue)$	0.15×10^{-9}
$P^-(green)^c$	zero
$P^+(green)$	0.58×10^{-9}
$P^-(red)^d$	zero
$P^+(red)$	0.20×10^{-9}

^a uv 3200-3900 Å.

^b Blue 3500-4800 Å.

^c Green 4600-5900 Å.

^d Red 6400 Å—far infrared.

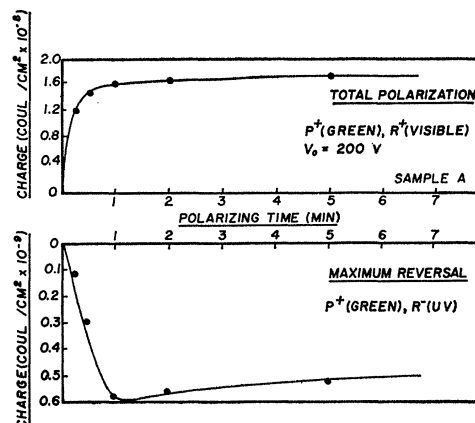


FIG. 18. Variation in total polarization and reversal maximum as a function of the polarizing time in ZnCdS.

release results in a reversal. As in the case of anthracene the competition of currents in d_3 and d_2 ultimately swings the reverse release into the normal direction. The R^+ release always yields a normal discharge indicating that the negative charges producing the discharge of polarization do not move across the d_1 region appreciably, but across d_2 as in barrier polarization release.

Figure 18 compares the buildup in total polarization and maximum charge reversal as a function of the polarizing time. As in Fig. 16, total polarization is always measured by an R^+ release (as opposed to R^- releases in anthracene). This figure shows that the maximum reverse charge goes through a maximum and diminishes. The initial increase is associated with the buildup in total polarization whereas the decrease is assumed to come from a slow shifting of the $E'=0$ point closer to the negative electrode. The decrease in reversal as a function of polarizing time is a much slower process in ZnCdS than in anthracene, as seen by comparing Fig. 18 with Fig. 12.

ZnCdS and anthracene have different responses to radiation. Whereas in anthracene, wavelengths greater than 4000 Å are absorbed very little, the range of noticeable absorption in ZnCdS materials extends considerably beyond the absorption edge. One would

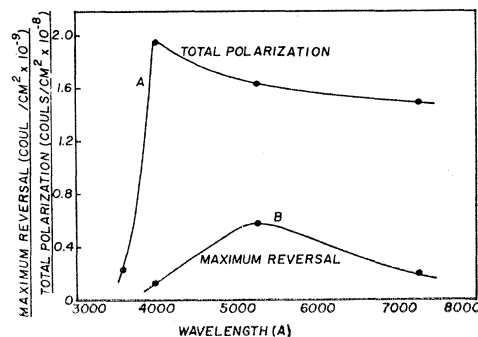


FIG. 19. Variation in the total polarization and reversal maximum as a function of the polarizing wavelength.

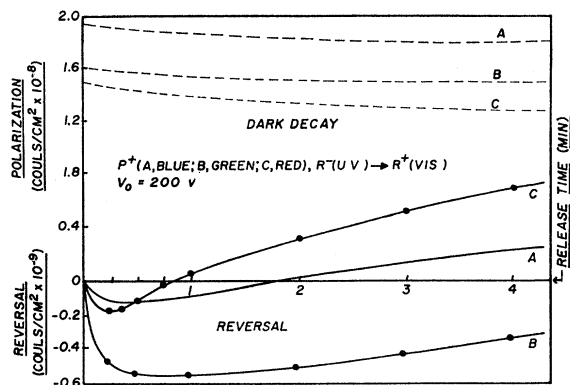


FIG. 20. The shape of the reverse release curve in ZnCdS under different polarizing wavelengths.

expect that the d_3 region and thus the reversal effect should become smaller as the radiation penetrates further into the sample from the positive side. The respective experiments are shown in Fig. 19, however the maximum reverse discharge does not occur at the shortest wavelength, but rather with green polarizing light. Such radiation also brings about the slowest transition from reverse discharge to normal discharge, as given in Fig. 20. As expected the reversals decrease for long wavelengths. The reason that the reverse releases are not strongest for blue polarizing probably has its origin in the superposition of two types of excitation; one that is produced by the external radiation and the other by fluorescent light which is more uniformly absorbed throughout the sample and which seems to be predominant for blue polarizing. The external radiation creates a negative layer close to the positive electrode with a somewhat larger positive layer nearby. Since the latter is still close to the electrode, the field E_3' (adjacent to the negative electrode) will be relatively small. Superimposed on this is the polarization distribution brought about by the fluorescent light which, for this phosphor, is in the yellow to red band of wavelengths. Because of the more uniform absorption of this light, the d_2 region due to

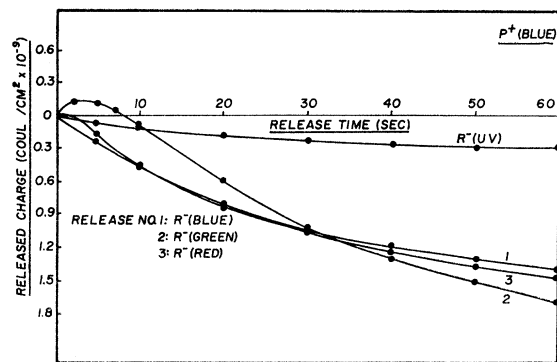


FIG. 21. Reverse releases in a ZnCdS sample having small surface barriers. The sample is polarized P^+ with blue light.

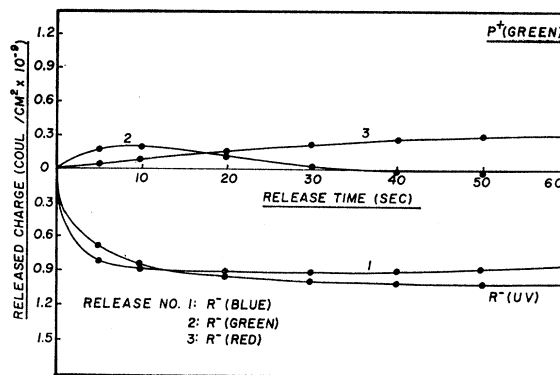


FIG. 22. Reverse releases in a ZnCdS sample having small surface barriers. The sample is polarized P^+ with green light.

this polarization alone is large with positive charges moving across the entire sample to the negative electrode. The charge separation produced by the external excitation is related to the wavelength as follows. With blue light, the density of excitation is very high; consequently, the recombination is high, and the lifetime of the carriers small. Thus the total separation is not very large. With a longer wavelength, the smaller recombination rate allows a larger total charge separation for the same amount of absorbed light. Thus for blue light the polarization due to the fluorescent light may be overpowering and consequently only small reversals are obtained.

With an increasing wavelength of the excitation, the polarization brought about by the fluorescent light becomes less important and thus the amount of reversal release increases until, with red light polarizing, almost uniform excitation of the sample is obtained and d_3 becomes smaller again, so that in a release there is a more rapid transition from reverse to normal charge motion.

Figures 21–23 show the cases of polarization release in samples prepared with small resistance layers at the electrodes. These samples are prepared by having the ZnCdS powder matrix fluid during the application of both glass electrodes. This results in a rather good con-

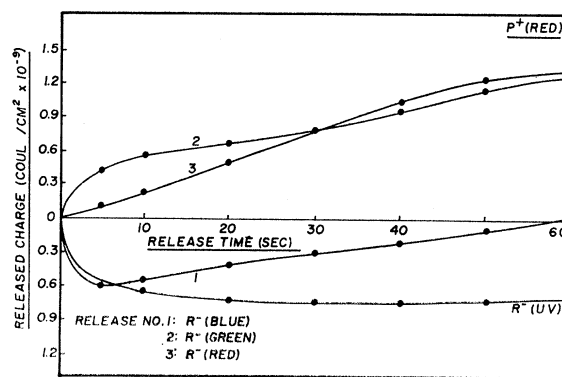


FIG. 23. Reverse releases in a ZnCdS sample having small surface barriers. The sample is polarized P^+ with red light.

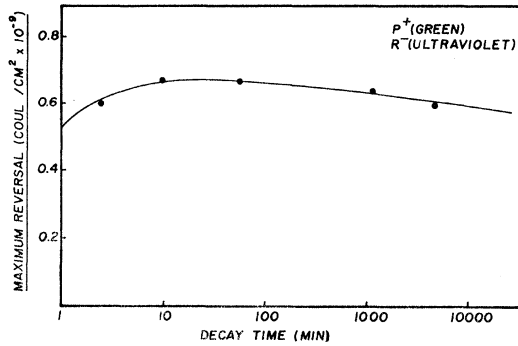


FIG. 24. The variation in the reversal maximum in ZnCdS as a function of the dark decay time.

tact to these electrodes, with correspondingly small resistance barriers. The figures describe the R^- releases with various wavelengths after P^+ polarizings with these same wavelengths. The general nature of the release curves can be explained by the assumption that there is practically no negative charge layer in the sample, but only a positive sheaf of charges roughly matching the penetration of the exciting radiation. In terms of the charge-layer model and the approximations used here, this means that a positive layer of charge is placed at approximately the "half-depth" of excitation. With blue light during polarizing, one observes a reverse release even with red light as discharging radiation, although this releasing radiation almost uniformly excites the sample. This shows that the d_3 region extends practically throughout the whole sample, so that the discharge does not transfer into the normal direction. The small normal release at the onset of green release is up to now unaccounted for. It would appear that the sample is almost bulk polarized and the normal discharge is due to a small dominance of the barrier polarization which quickly diminishes. With green light as the polarizing radiation, the positive charge layer moves deeper into the sample and the blue release brings about only reverse discharge, whereas that by green light displays practically no reversal and finally, release by red light gives only a normal release. These effects are still more pronounced with red light polarizing. Here, blue light already shows a strong return to normal release. Thus the d_3 region has shrunk to a small layer near the negative electrode.

These features of bulk polarization can also be visualized with the help of the resistance layer model [Eqs. (10)–(12)]. An inhomogeneously excited sample

TABLE VI. Change in total polarization (anthracene) (short polarizing time).

Q_m (10^{-8} coul)	Q_2 (10^{-8} coul)	Q_3 (10^{-8} coul)
0.32	-0.04	0.28
0.32	-0.08	0.26
0.32	-0.14	0.20

can be considered as being composed of two regions with different resistivities, the lower resistivity belonging to the region of strongest excitation. The influence of these resistance layers is most pronounced when the less mobile charges are driven away from the narrow region of strongest excitation into the high resistant bulk of the sample, as in a P^+ polarizing in ZnCdS. For a P^- polarizing, the difference in resistance between the two layers become less significant because the majority of the charge motion involves the more mobile charges. In the case of P^+ polarizing one has two regions of different resistivities, that of lower resistivity close to the negative electrode; consequently a positive charge layer must develop across the common boundary. This positive charge accumulation across such a boundary is what is observed in bulk polarization.

If surface barriers exist at the electrodes then the charge layer, developed between the two regions of different resistivity, will not be as easily detected. Indeed, the influence of surface barriers may become great enough to prevent the detection of any bulk

TABLE VII. Change in total polarization (anthracene) (long polarizing time).

Q_m (10^{-8} coul)	Q_2 (10^{-8} coul)	Q_3 (10^{-8} coul)
12	-0.3	9.5
12	-0.4	7.5
12	-0.5	6.8

polarization effects even though they are present. This is then the case of barrier polarization. The transition has been verified when lifting electrodes are applied so that particularly high resistive layers were created at the electrodes.

A comparison of the dark decay in the d_3 region with that in the d_2 region shows that the d_3 region is also one of high resistivity. This is proven by the relative insensitivity of the reversal maximum to decay time as shown in Fig. 24, indicating that E_3' diminishes more slowly than E_2' . This may mean that the normal decay of polarization consists of a certain component of decay of the negative layer through the d_1 region; otherwise, a decay restricted to the d_2 region would diminish the field in d_3 as well. But these results could also be interpreted to mean that the position where the field changes its sign has moved. This could occur, for example, if the negative layer has become more concentrated towards the positive electrode.

5. Charge Excess in Bulk Polarization

The problem of charge neutrality in a polarized sample has been frequently discussed throughout this paper. Here it is shown that bulk polarized samples definitely display an excess of the less mobile charges. One can determine in the following way whether the

total charge is zero. For charge neutrality, the total polarization should be the same, no matter through which electrode the polarization is discharged. This is because the depolarization must occur either by neutralization of the two charge layers across d_2 or by transporting the total charge across one of the electrodes. In both cases, the total released charge must be the same. Only if the charge of one sign is transported across d_1 and the other charge is transported across d_3 would the total release be different. If one charge layer is larger than the other, the amount of discharge depends upon the side through which the discharge is performed. For instance, when one has only one layer, say, of positive charges, then the amount of discharge will be larger if the discharge is performed through the electrode farthest from the charge layer. If the charge layer is centrally located, the amount of charge release depends upon whether radiation is used which is strongly absorbed or uniformly absorbed across the whole sample. In the latter case, the total discharge is zero since equal currents flow in both halves of the sample. Another way to check the neutrality is to discharge first through one side, removing a portion of the polarization, and then to discharge the remainder through the other side of the sample. One then sees if the total amount of charge that is released in this latter case is the same as for a unidirectional release.

The following observations concern anthracene samples. The sample is polarized P^- which produces bulk polarization. It is then fast released by R^- . This release neutralizes the positive charge layer near the electrode and thereafter the negative charges which are distributed over the whole sample. The total discharge obtained this way is designated Q_m . After repolarizing, the polarization is released by R^+ which is slow and produces reversals. Thereafter, without repolarizing, the sample is released again by R^- until the polarization is completely removed. The amount of polarization removed by R^+ is designated Q_2 while that by the succeeding R^- is Q_3 . The results of this experiment are

TABLE VIII. Change in total polarization (ZnCdS).

	P^+ (blue) coul/cm ²	P^+ (green) coul/cm ²	P^+ (red) coul/cm ²
1. Total polarization at time of maximum reverse release (no preceding release)	1.90×10^{-8}	1.57×10^{-8}	1.47×10^{-8}
2. Actual total polarization at this time after $R^-(uv)$ release	1.49×10^{-8}	1.14×10^{-8}	1.21×10^{-8}
3. Change in total polarization by $R^-(uv)$ release	0.41×10^{-8}	0.43×10^{-8}	0.26×10^{-8}
4. Maximum reversal	0.15×10^{-9}	0.58×10^{-9}	0.20×10^{-9}

TABLE IX. Polarization in single anthracene crystals.

Polarizing method	Release method	Polarization
P^+ (3600 A)	R^- (3600 A)	3.2×10^{-11} coul/cm ²
P^- (3600 A)	R^- (3600 A)	3.4×10^{-11} coul/cm ²
P^- (3600 A)	R^+ (3600 A)	3.2×10^{-10} coul/cm ² (reverse discharge)

given in Table VI for short polarizing times and in Table VII for long polarizing times.

For a neutral sample, one would expect

$$|Q_3| = |Q_m| + |Q_2|, \quad (38)$$

since practically no charge is released through d_1 during the R^- release. The tables clearly show that $|Q_m| + |Q_2|$ is in all cases much smaller than $|Q_3|$. Thus these samples are far from neutral, particularly for short polarizing times. For these short polarizing times, one finds that the following relation approximately holds,

$$|Q_m| = |Q_2| + |Q_3|. \quad (39)$$

This suggests that almost all of the charge in the sample is negative, in agreement with Fig. 14, where for short polarizing times the discharge does not go over into the normal direction. For longer polarizing times, the return of R^+ to normal release has been noted. This result is probably due to the fact that some positive charges have accumulated near the negative electrode.

Analogous results are obtained with ZnCdS samples, as shown in Table VIII. Here the phosphor is polarized P^+ using blue, green, and red light respectively. For each polarization, an $R^-(UV)$ release is performed up to a certain time and therefore an R^+ (visible) total release is made. These releases are compared to a total release made without the reverse release. One sees again a lack of sample neutrality. Here the difference between the total polarization measured by R^+ and that obtained by R^- and subsequent R^+ is not as large as in anthracene meaning that the deviation from neutrality is not as great in ZnCdS samples as in anthracene.

E. POLARIZATION IN SINGLE CRYSTALS

1. General Remarks

In the previous sections it has been shown that barrier layers adjacent to the electrodes are most important for bringing about strong polarizations. All the effects and experiments described were carried out on powdered or multiple-crystalline materials, where barrier layers at the electrodes are most naturally formed. Indeed special care has to be taken to reduce them, at least to a certain degree. The outstanding feature was that after removal of the excitation and the external field large electric fields exist at both electrodes but do not bring about an injection of electrons or

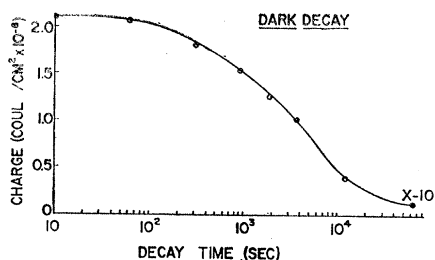


FIG. 25. Decay of polarization in a cadmium sulfide crystal with metal electrodes.

positive holes into the photoconductive material. This was true even for field strengths greater than 100 000 v/cm and can only mean that very large barriers exist which allow the passage of charge, only if large numbers of free charges are available. The situation with single crystals is quite different. Even with no special care, crystal contacts are so superior to those on powder materials that large fields cannot develop at the electrodes. Consequently the polarizations may be rather small under certain polarizing conditions, even though the contacts may be non-ohmic. Since anthracene single crystals and CdS crystals have different behaviors, each is treated separately.

2. Polarization in Single Anthracene Crystals

Measurements of persistent polarization were made with single anthracene crystals of a thickness of about 10 μ and an area of $\frac{1}{10}$ cm².¹⁸ The electrodes were water solutions which provided an excellent contact between the solution and the crystal. The measurements were performed with the apparatus described in Sec. B and the persistent polarization was determined with the radiation release method. The results, given in Table IX, show that the polarization is much smaller than with the multicrystalline material.

In the case of slow polarizing P^- and slow release R^+ , a noticeable increase in polarization was found due to negative charges trapped in the bulk of the crystal with their center, however, closer to the negative electrode through which the crystal was excited during polarizing. This is indicated by the observation that P^-R^- displayed a reverse discharge, i.e., a discharge in the d_3 region of Fig. 1, and that P^-R^- was considerably smaller than P^-R^+ .

The most interesting result is that negative charges are trapped in the bulk of the anthracene crystal and there are practically no positive charges. This is important in view of recent findings^{19,20} that the so-called photoconductivity of organic materials is not as much due to free charge carriers created in the bulk of the crystal, but rather to hole injection from the electrode. From these photoconductive measurements alone one

could not say whether negative charges are produced at all, since the measurements showed that a considerable portion of the so-called negative current was due to a hole emission at the opposite electrode. These PIP results show quite clearly that negative charges are also produced in such single crystals. From these measurements one cannot decide whether the negative charges formed in the crystal are also produced by injection from the negative electrode or are created by the radiation inside the crystal itself. But recent polarization observations of Moore and Silver¹⁷ indicate that both processes occur. These observations with anthracene crystals show how important polarization measurements can be for classifying the processes going on in the organic materials.

Finally some remarks are necessary on the smallness of polarization found in anthracene crystals. That almost no polarization is observed with a P^+ polarizing is certainly due to the fact that in such single crystals very little positive charges are trapped. Since barriers are not present all the positive charges injected into the crystal move very rapidly out of the crystal.

For the negative charges the situation is somewhat different. First the polarization obtained with P^-R^+ is not so much smaller than the reverse releases P^-R^- observed with multiple crystalline layers. Secondly one must consider that in such thin crystals positive hole emission may also occur in the dark if the field strength is large enough. Therefore persistent polarization in such thin crystal can only develop when the injection of holes is extremely small, otherwise the polarization would disappear. This hole emission may be a limiting factor for persistent polarization in such thin crystals.

3. Polarization in Single Crystals of CdS

Experiments carried out with single crystals of CdS have confirmed the ideas put forward in the introduction of this section. Two different arrangements were employed. First, experiments were carried out with thin CdS crystals with gold plated electrodes which supplied good contacts to the crystals.²¹ It was difficult to detect any persistent polarization at all with these crystals. Only when these crystals were subjected to

TABLE X. Polarization effects in CdS crystals.

Polarizing and release conditions	Polarization (coul/cm ²)
P^- (uv, 150 v); R^+ (vis)	10^{-10}
P^- (ir, 150 v); R^+ (vis)	10^{-10}
P^+ (uv, 150 v); R^+ (vis)	2.2×10^{-8}
P^+ (ir, 150 v); R^+ (vis)	1.8×10^{-8}

¹⁸ H. Kallmann and M. Pope, Rev. Sci. Instr. **29**, 993 (1958).

¹⁹ H. Kallmann and M. Pope, J. Chem. Phys. **32**, 300 (1960).

²⁰ H. Kallmann and M. Pope, Nature **186**, 31 (1960).

²¹ J. Kostelec, "Persistent Internal Polarization in Single Cadmium Sulphide Crystals," Master's thesis, New York University (1957).

infrared irradiation during polarizing was some persistent polarization obtained which exceeded the weak dark polarization. The polarization release always occurred in the d_2 region, and the resultant polarization was considerably weaker than that obtained with powder layers. A decay curve is reproduced in Fig. 25.

These experiments indicate that under most polarizing conditions all charges are easily swept out of the crystal, probably by electron injection and ejection at the electrodes. That infrared irradiation brought about some polarization may be due to the strong direct activator excitation produced by such radiation. In this way positively charged activators are produced which are not at once neutralized by the external supply of electrons.

To extend these single crystal investigations, a different type of arrangement was utilized in which artificial barriers were introduced at one electrode. Crystals were used without gold coated electrodes; one side was covered with a thin insulating Mylar sheet with a conducting layer on the face away from the crystal. Its other side was supplied with a normal electrode with reasonably good contact. With this arrangement the results are quite different than with the crystals which had evaporated electrodes on both sides. The crystals were illuminated during polarizing with UV or IR irradiation through the insulating layer and it was found that both types of radiation yielded practically the same degree of polarization. The results are given in Table X.

When the insulated side is negative practically no polarization of any persistence is observed just as in the case of the crystals with evaporated electrodes. However when the insulated side is positive, strong polarization is observed, sometimes even stronger than with the powdered materials, and the polarization is of relatively long persistence. Figure 26 gives a decay curve of the P^+ (insulating side) polarization obtained in this way.

The explanation is quite obvious. With the insulating side negative, electrons are driven out of the crystal through the noninsulated electrode. The crystal remains filled with positive trapped charges as long as the external field is applied. When it is removed an internal field immediately develops which draws electrons from the non-insulated electrodes into the interior which recombine with positive holes. This goes on until only a

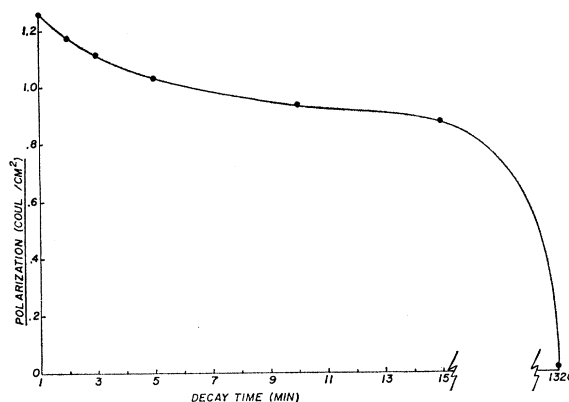


FIG. 26. Decay of polarization in a cadmium sulfide crystal with an insulating layer.

small number of positive holes are left in the interior and as a consequence only a small polarization persists.

However if the insulating side is charged negatively, electrons are accumulated in the insulating layer and trapped. In addition, the positive charges probably attract electrons from the noninsulating electrode and the crystal may acquire a net negative charge as long as the external field is applied. Some of these charges will be localized in traps. The moment that the external field is removed an internal field appears which tries to eject electrons through the noninsulating electrode, but since a large number of the electrons are trapped, they cannot be expelled from the sample and remain trapped in the crystal with a persistence, in some cases, of more than one day. The difference between this and the case of the noninsulated crystal is apparently twofold. Because of the rather homogeneous resistivity through the crystal, no appreciable charge accumulation occurs in the noninsulated crystal and any small amount which may develop is rapidly cancelled out by electron injection from one of the electrodes. The latter is also the case for the insulated crystal with the insulated layer negative. Here electron injection can occur after removal of the external field and consequently the polarization charge is very rapidly neutralized. This is experimentally observed.

These experiments with single crystals, although only in their first stage of investigation, again show the importance of barrier layers for bringing about polarization effects.