Capacitance and Conductance Effects in Photoconducting Alkali Halide Crystals

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Measurements of the ac and dc response of illuminated F-centered potassium bromide single crystals have been carried out. The dependence of crystal capacitance and conductance on frequency, light intensity, electrode character and separation, F-center concentration, applied voltage, temperature, and optical bleaching time have been investigated. Most of the measurements were made on crystals containing both U and F centers, but a few were also made on additively colored and plain untreated crystals for comparison.

It was found that F centers in U-centered crystals bleached much slower under strong illumination than did those in additively F-centered crystals. The frequency response of the crystals depended significantly upon whether the electrodes were blocking or rectifying, but in both cases it was characterized by a single relaxation time given by the quotient of a series capacitance C_0 and G_∞, the normal conductance of the crystal. C_0 was found to be independent of all variable parameters except dark storage and bleaching time and is thought to arise from a charge-free layer located at one or both electrodes. Space-charge capacitance effects were apparently largely hidden by C_0 but did probably produce a small voltage-dependent nonlinearity observed at low frequencies with high applied voltages. G_∞, and thus the conduction-band electron concentration, depended linearly on light intensity over a wide range but underwent a transition from linear dependence on F-center concentration to independence thereof at high concentrations. Partly bleached crystals in total darkness exhibited appreciable conductivity, probably electronic in character. Most of the results on U-centered crystals can be tentatively explained in terms of electron trapping by negative-ion vacancies, F centers, interstitial hydrogen atoms, and hydrogen atoms in negative-ion vacancies.

I. INTRODUCTION

POLARIZATION effects arising from the buildup near electrodes of space charge under the influence of an electric field may be expected to appear in any material containing charge carriers which cannot pass freely from material to electrodes and/or from electrodes into the material. Such effects are therefore widespread and have, indeed, been observed in all materials except metals.

Polarization in liquid ionic conductors, including both strong electrolytes[1–3] and dielectric liquids containing impurities,[4] has been extensively investigated in the past for dc applied fields and, to a lesser extent, for ac fields. This work has led to the picture of a polarization, or double layer, capacitance localized near the electrodes and in series with the normal ionic conductivity of the material. The equivalent circuit is considerably more complicated when electrode reactions occur[5] or when two or more ions of different but comparable mobility are present. Space-charge effects attributed to ionic motion in solids have also been observed at high temperatures for glass[6] and various single crystals such as quartz[7] and at room temperature for selenium rectifiers.[8]

Electronic or hole conduction in semiconductors arising from either thermal or optical excitation may also give rise to polarization effects. Thus, Kolomoĭtsev[9] has recently observed polarization effects in calcite ascribed to electrons thermally ionized from impurities, and Kallman, Kramer, and Perlmutter[10] have reported polarization effects arising from optically released electrons in luminescent powders. Earlier work of Joffé[7] and others showed that electronic polarization effects were also apparently of importance in single crystals of F-centered alkali halides exposed to light in the F-absorption band.

In ionic conductors, space-charge polarization arises from the inability of the metallic electrodes to supply ions to the material or to accept ions. Such electrodes are termed blocking or polarized for the ionic carriers considered. There are two other possibilities which often appear in electronic conductors. If charge carriers can pass freely from material to electrode or from electrode into the material but cannot travel freely in both of these directions, the contact is said to be rectifying. In the ohmic case, carriers can move across the contact freely in either direction. Smith and Rose[11] have recently shown how either rectifying or ohmic contacts can be produced between n-type cadmium sulfide single crystals and indium or gallium electrodes. Earlier, Bube[12] found that the potential barriers rendering silver paste contacts rectifying on zinc sulfide single crystals could be largely removed by heating several minutes at 650°C.

There has been very little experimental work on polarization effects for ac applied fields in spite of the

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[1] D. C. Grahame, J. Am. Chem. Soc. **68**, 301 (1946).
[2] H. Chang and G. Jaffé, J. Chem. Phys. **20**, 1071 (1952). References to older literature are given in this paper.
[3] G. Jaffé and J. A. Rider, J. Chem. Phys. **20**, 1077 (1952).
[4] G. Jaffé and C. Z. LeMay, J. Chem. Phys. **21**, 920 (1953).
[5] D. C. Grahame, J. Electrochem. Soc. **99**, 370C (1952).
[6] D. M. Robinson, Physics **2**, 52 (1932).
[7] A. F. Joffé, *The Physics of Crystals* (McGraw-Hill Book Company, Inc., New York, 1928).
[8] G. Jaffé, Phys. Rev. **85**, 354 (1952).
[9] F. I. Kolomoĭtsev, Doklady Akad. Nauk SSSR **75**, 185 (1950).
[10] Kallman, Kramer, and Perlmutter, Phys. Rev. **89**, 700 (1953).
[11] R. W. Smith and A. Rose, Phys. Rev. **92**, 857 (1953).
[12] R. H. Bube, Phys. Rev. **83**, 393 (1951).

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fact that they allow capacitative and conductive effects to be separated uniquely. The present investigation was undertaken to explore some of the possibilities of this measuring technique applied to photoconducting alkali-halide crystals, and to use the results to gain a better understanding of photoconduction, space charge, and trapping processes within such crystals. A few of the experimental results have been reported previously.[13] It should be emphasized that the capacitative effects arising from free electrons described in the present paper are completely different from the low-frequency dispersion results obtained by Breckenridge[14] on specially treated alkali-halide crystals. Breckenridge's results arise from bound ionic-vacancy pairs which can reverse their direction of polarity in an electric field. The most characteristic feature of the present results, on the other hand, is that with the crystals in the dark one measures at low frequencies only the normal geometric capacitance of the crystal arising from the polarization of bound charges. When the crystal is illuminated with F-band light, however, the apparent capacitance at low frequencies increases by a factor of as much as 100 times. This "photocapacitative" effect is thus obviously closely connected with the free electrons produced by the absorption of light and is an entirely different phenomenon than that investigated by Breckenridge.

II. DISCUSSION OF SPACE-CHARGE THEORY

Before discussing the experimental results in detail, it will be useful to compare briefly some of the space-charge theories which may possibly apply to the experimental situation. Space-charge formation occurs whenever charge carriers cannot pass freely across the junction between the charge-containing material and one or both of its electrodes. In the present case, electrons can leave a photoconducting alkali halide crystal at a metallic anode in intimate contact with the crystal but cannot re-enter at a metallic cathode.[15] The crystal thus acts like two rectifiers connected back-to-back. In addition, we shall need to consider the behavior of these crystals with blocking electrodes such that electrons can neither leave nor enter at electrodes of either polarity.[16]

When a dc voltage is applied across a photoconducting alkali halide crystal, electrons will move toward the anode where they will either be discharged or, if blocked, will establish a negative space charge. At the same time, a positive space charge of ionized F centers, or negative-ion vacancies, will form near the cathode. The total static capacitance C_0 of the crystal will be the series combination of the two capacitances represented by the space charge at the electrodes. When space charge forms at both electrodes, the total capacitance will thus be half of that obtained with a single space-charge layer. As the applied voltage is increased, the concentration p of negative ion vacancies at the cathode will increase until the original F-center concentration N_F, assumed initially uniform throughout the crystal, is reached. An applied voltage of only the order of 0.5 volt is required to produce this condition for $N_F=5\times10^{15}$ cm^{-3}, and c_0, the initial free electron concentration, of 10^{10} cm^{-3}. Since larger voltages cannot increase p beyond N_F, all they can accomplish is to increase the width of the cathode exhaustion layer composed of negative-ion vacancies of concentration N_F.

When an ac voltage of sufficiently low frequency is applied, a space-charge distribution essentially equal to that which would be caused by a dc voltage equal to the peak ac voltage will be produced at the peak of each half cycle. If an exhaustion layer is established, it will move from one electrode to the other through the medium of F-center ionization and electron:negative-ion-vacancy recombination. The maximum ac capacitance at sufficiently low frequencies will therefore be of the same order of magnitude as that produced by a corresponding dc voltage although voltage-dependent nonlinearity may cause extensive harmonic generation. It should be pointed out that at sufficiently high frequencies, on the other hand, no appreciable space charge will have time to build up during a half cycle, and the admittance of the crystal will be entirely determined by its geometrical capacitance $C_g=\epsilon/4\pi L$, and its photoconductance $G_\infty=\mu ec_0/L$.[17] Here ϵ is the dielectric constant of the material in the absence of free charges; L, the separation of electrodes; and μ the microscopic electron mobility.

Unfortunately, there are available no exact ac or dc theories of space-charge formation which cover the voltage range from zero up to hundreds of volts. For the purposes of comparison with experiment, we can, however, make use of the predictions of several theories which cover different parts of the voltage range. For applied dc voltages less than about $2kT/e$ or 50 mv at room temperature, the author's linearized ac theory may be applicable.[18] When the space-charge capacitance C_0 is at least several times larger than C_g, which is usually the case, it predicts a frequency- and voltage-independent series capacitance of

$$C_0=\epsilon/4\pi L_{D(\mathrm{rms})}, \tag{1}$$

$$L_{D(\mathrm{rms})}=[\epsilon kT/2\pi e^2c_0]^{\frac{1}{2}}, \tag{2}$$

and a charging time constant of $\tau=C_0/G_\infty$. In Eq. (2), $L_{D(\mathrm{rms})}$ is the rms Debye length.

For larger voltages, an exact, nonlinear dc theory may be employed.[19] It is first necessary to distinguish

[13] J. R. Macdonald, Phys. Rev. **85**, 381 (1952); **90**, 364 (1953).
[14] R. G. Breckenridge, *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), p. 219. See also Y. Haven, J. Chem. Phys. **21**, 171 (1953).
[15] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1948), second edition, p. 169.
[16] Sample preparation and dimensions are discussed in Appendix I; experimental details in Appendix II.
[17] Theoretical expressions for capacitance and conductance will apply throughout to unit electrode area.
[18] J. R. Macdonald, Phys. Rev. **92**, 4 (1953).
[19] J. R. Macdonald, J. Chem. Phys. **22**, 1317 (1954).

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TABLE I.

Theory	Monomolecular C_0	Monomolecular τ	Bimolecular C_0	Bimolecular τ	F-center capture C_0	F-center capture τ
Linearized	$[IN_F/N_T]^{\frac{1}{2}}$	$L[N_T/IN_F]^{\frac{1}{2}}$	$[IN_F]^{\frac{1}{2}}$	$L[IN_F]^{-\frac{1}{2}}$	$I^{\frac{1}{2}}$	$LI^{-\frac{1}{2}}$
Exhaustion layer	$[N_F/(\phi+V_{dc})]^{\frac{1}{2}}$	$\frac{L}{I}\left[\frac{N_T^2}{N_F(\phi+V_{dc})}\right]^{\frac{1}{2}}$	$[N_F/(\phi+V_{dc})]^{\frac{1}{2}}$	$L[I(\phi+V_{dc})]^{-\frac{1}{2}}$	$[N_F/(\phi+V_{dc})]^{\frac{1}{2}}$	$\frac{L}{I}[N_F/(\phi+V_{dc})]^{\frac{1}{2}}$
Constant capacitance	...	LN_T/IN_F	...	$L[IN_F]^{-\frac{1}{2}}$	...	L/I

between static and differential capacitance. Static capacitance is defined by Q_{dc}/V_{dc} and differential capacitance by dQ_{dc}/dV_{dc}. Measurements with dc yield the static capacitance C_0, as do measurements with sufficiently low frequency ac alone, at least approximately. On the other hand, when a dc bias is applied and capacitance is measured with a much smaller ac voltage, the differential capacitance is obtained. Whenever there is dependence of capacitance on voltage, the differential and static capacitances differ, except at zero voltage where their limiting values are equal. The nonlinear theory predicts an expression similar to (1) but with the added voltage-dependent terms $\cosh\alpha V_{dc}$ for the differential capacitance and $\sinh\alpha V_{dc}/\alpha V_{dc}$ for the static capacitance. The constant α is $e/2kT$ for only one space-charge layer, $e/4kT$ for a layer at each electrode. The charge density at the cathode is given by $p=c_0\exp(2\alpha V_{dc})$. As we have seen above, this quantity cannot exceed N_F; this restriction thus limits the voltage range of applicability of the theory.

When an exhaustion layer has formed at the cathode, the usual exhaustion layer formula for its differential series capacitance is[20]

$$C_0=\epsilon/4\pi L_e, \tag{3}$$

$$L_e=[\epsilon(\phi+V_{dc})/2\pi eN_F]^{\frac{1}{2}}, \tag{4}$$

where ϕ is the difference between the work function of the metallic electrode and the electron affinity of the crystal.[15] The corresponding expression for the static capacitance arising from V_{dc} is

$$C_0=\frac{1}{V_{dc}}\left(\frac{\epsilon N_F e}{2\pi}\right)^{\frac{1}{2}}[(\phi+V_{dc})^{\frac{1}{2}}-(\phi)^{\frac{1}{2}}]. \tag{5}$$

This expression will not differ appreciably from that of Eqs. (3) and (4) until V_{dc} is considerably greater than ϕ. The expressions (1) through (5) show that if $\phi=0$ the static capacitance will start independent of V_{dc} as this quantity increases from zero, undergo a transition to an essentially exponential rise with V_{dc}, reach a maximum, then finally fall off proportional to $V_{dc}^{-\frac{1}{2}}$. If ϕ is not zero but is sufficiently large to cause an exhaustion layer to be formed, the capacitance will remain constant until V_{dc} is comparable to ϕ, then will decrease.

[20] H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948), p. 76.

Now, for future comparison with experiment, it is of interest to tabulate the dependence of C_0, and τ (defined as usual as C_0/G_∞) on N_F, L, and I, where I is the intensity of F-band illumination. For this purpose, it is necessary to distinguish between the various types of electron:electron-trap recombination which may possibly occur. The rate at which F centers are ionized by light in the F band is proportional to N_FI. The recombination rate is proportional to the product of c_0 and (a) c_0, in the bimolecular case of capture by ionized F centers whose electrons are in the conduction band; (b) N_F, in the case of capture by F centers themselves to form F' centers so long as c_0 and the concentration of F' centers are both much less than N_F; (c) N_T, the concentration of traps not arising from F centers or negative-ion vacancies, in the monomolecular case of all recombination with foreign traps. On setting ionization and recombination rates equal, one obtains the dependence of c_0 on I, N_F, and N_T and can form Table I. We have also included the dependence of τ obtained when C_0 is independent of all preceding quantities, including frequency.

Next, we shall use some typical experimental results to eliminate some of the above theories from further consideration. From the data of Fig. 3, we obtain for a strongly illuminated KBr crystal with $N_F\simeq 5\times10^{15}$ cm^{-3}, $C_0=31.2$ $\mu\mu$f/cm^2 and $G_\infty=1.25\times10^{-7}$ mhos/cm^2. Using the room-temperature value of 12.5 cm^2/volt-sec for the Hall mobility of photoelectrons in similar crystals obtained by Macdonald and Robinson[21] and neglecting any small difference between Hall and microscopic mobilities, one obtains $c_0=1.25\times10^{10}$ cm^{-3} from the above value of G_∞. This value of c_0 corresponds to an rms Debye length of 3.31×10^{-3} cm and a space-charge capacitance of 131 $\mu\mu$f/cm^2, more than four times larger than the observed value of C_0. A value of $\epsilon=4.9$ was used in this calculation.[22] Lack of agreement between measured and calculated values of C_0 is not surprising, since the above data were obtained with an ac voltage of the order of 5 volts rms. The nonlinear as well as the linearized theory should thus be inapplicable here.

A stringent test of the exhaustion layer theory is

[21] J. R. Macdonald and J. E. Robinson, Phys. Rev. **95**, 44 (1954).

[22] A. von Hippel, Tables of Dielectric Materials, Vol. 4, Technical Report No. 57, Laboratory for Insulation Research, M.I.T., January, 1953.

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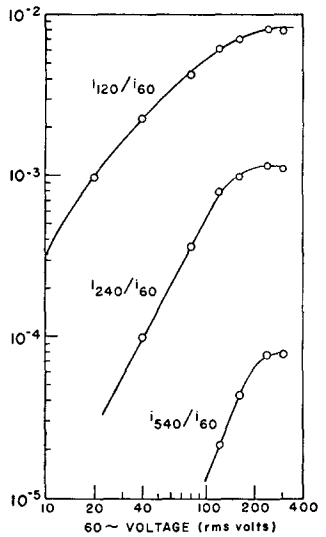

FIG. 1. Harmonic generation by photoconducting KBr Crystal U-1.

afforded by the calculation of ϕ from Eq. (3) or (5) with V_{dc} taken equal to zero. From the measured value of C_0 and the above value of N_F, we obtain $\phi \simeq 1.8\times10^5$ volts. Since this value is many orders of magnitude too large, it is clear that exhaustion layer formation cannot account for the results. Finally, if we arbitrarily write C_0 as $\epsilon/4\pi L_x$, where L_x is a charge-free region between either electrode and the bulk of the crystal, we obtain $L_x=1.39\times10^{-2}$ cm assuming that the charge-free region has the normal dielectric constant of the material. If equal charge-free regions abut each electrode, then $L_x=7.0\times10^{-3}$ cm.

A charge-free region producing a constant capacitance such as that discussed above and in Table I might possibly arise from the influence of surface states on the internal charge distribution.[23] More probably, it could arise in the present crystals from an absence of F centers or negative-ion vacancies in a region of thickness L_x (or $L_x/2$) at each surface of the crystal. How such a region could arise and experimental evidence for its existence will be discussed later.

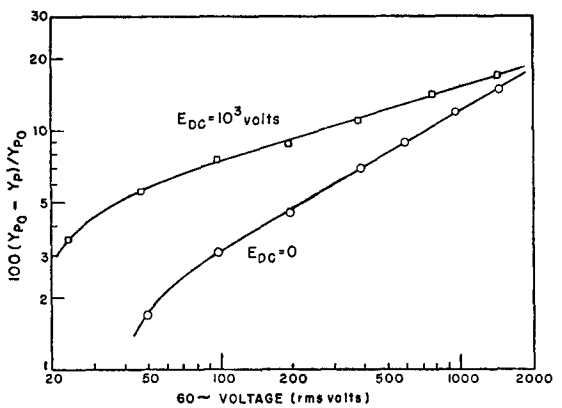

FIG. 2. Dependence of percentage relative change in admittance of photoconducting crystal U-1 on 60-cps voltage.

[23] J. Bardeen, Phys. Rev. 71, 717 (1947).

III. EXPERIMENTAL RESULTS

(a) Voltage-Dependent Nonlinearity

Most space-charge theories predict some voltage-dependent nonlinearity of space-charge capacitance, especially with high voltages applied. An attempt was made to observe any such nonlinearity with an illuminated crystal and only a surprisingly small amount observed. It was found that no appreciable ac voltage dependence of capacitance could be measured with a sensitive capacitance bridge in the range of 0.5 to 15 volts rms. Measurements were carried out at sufficiently low frequencies that the admittance of the crystal was almost entirely capacitative so that C_0, the low-frequency limiting value of the capacitance, was obtained.

Next, the series method for harmonic and total admittance measurements was employed.[24] Crystal U-1 containing an F-center concentration of about 5×10^{15} cm^{-3} was used. It had evaporated aluminum electrodes (rectifying) and was strongly illuminated with white light. At the measuring frequency of 60 cps, the admittance was still almost entirely capacitative. Figure 1 shows the voltage dependence of several harmonics, normalized with respect to the fundamental. All harmonics up to the 14th could be detected, but no harmonic generation by a high-grade mica capacitor of the same capacitance as the illuminated crystal was observed with the same apparatus. At 300 volts rms and above, where the harmonics seem to saturate relative to the fundamental, the total harmonic generation is still less than two percent of the fundamental.

Figure 2 shows how the percentage change in relative admittance varies with applied ac voltage up to 2000 volts rms for zero dc bias and for 10^3 volts bias. The capacitative decrease which may be inferred from Fig. 2 is very small and its dependence on voltage much less rapid than $V_{ac}^{-\frac{1}{2}}$, in keeping with the small amount of harmonic generation observed. These results are therefore inconsistent with simple exhaustion-layer formation. If, however, most of the applied voltage drop occurred across a voltage- and frequency-independent capacitance in series with one or both electrodes, the total capacitance would be largely determined by this constant capacitance. Larger nonlinear capacitative effects of the exponential or exhaustion-layer type occurring within the crystal would hardly affect the total capacitance but might quite possibly lead to the small nonlinearity observed.

(b) Frequency Dependence

We shall initially assume that a photoconductive crystal can be represented electrically by a frequency-independent capacitance C_0 localized near one or both

[24] See Appendix II.

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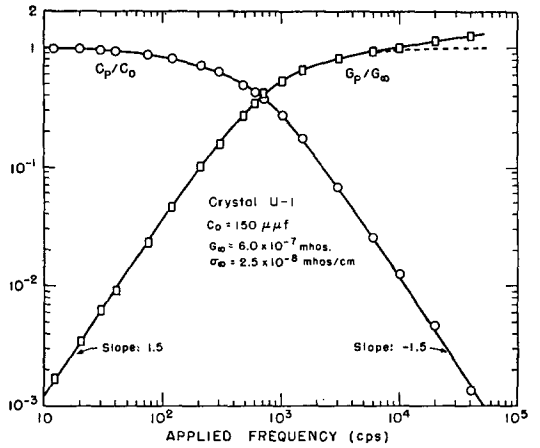

FIG. 3. Dependence of normalized parallel capacitance and conductance on frequency.

electrodes and in series with the bulk conductivity G_∞. This series combination is then in parallel with C_g, the geometrical capacitance of the crystal (measured, e.g., with the crystal in darkness or at a very high frequency). For ac, the frequency-independent series quantities C_0 and G_∞ can be replaced by their parallel equivalents C_P and G_P, whose frequency dependence will be of the form

$$C_P/C_0=[1+(\omega\tau)^2]^{-1}, \tag{6}$$

$$G_P/G_\infty=(\omega\tau)^2[1+(\omega\tau)^2]^{-1}, \tag{7}$$

where $\tau=C_0/G_\infty$. These are simply Debye dispersion formulas. A bridge measurement of parallel capacitance and conductance will therefore yield G_P and the sum of C_P and C_g. Thus, C_P may be obtained very easily from such a measurement.

Figure 3 shows the dependence of C_P/C_0 and G_P/G_∞ on frequency for crystal U-1 strongly illuminated and held at room temperature. It is found that τ, as calculated from the frequency at which $C_P/C_0=G_P/G_\infty$, is equal to that calculated from C_0/G_∞ to within five percent. There is thus no doubt that the G_P and C_P curves arise from the same dispersion mechanism. On the other hand, they differ from Debye curves in that the limiting slopes are $\pm\frac{3}{2}$ instead of ± 2.[25] It is probable, as we shall see later, that this deviation from the above simple theory arises from the fact that the electrodes used were only rectifying so electrons could discharge at the anode.

The dependence of C_P and G_P on the wavelength of the incident light was investigated for a number of newly F-centered samples using interference filters and various combinations of gelatin filters. It was found that only light in the F-absorption band produced capacitance and conductance additional to that of a specimen in the dark. Since M and R bands and colloidal aggregates[26] probably form in these crystals after considerable F-band illumination or long-term dark storage, white light illumination, such as that used in most of the present work, will release electrons from these centers, if they are present, as well as from F centers.

The same data shown in Fig. 3 are replotted in a different fashion in Fig. 4 and lead to the larger circular curve. This figure is essentially the circle diagram common in electrical circuit analysis, but we have chosen to plot G_P/ω *vs* C_P rather than the more usual but equivalent G_P *vs* ωC. In the form given in Fig. 4, the ordinate is proportional to the apparent dielectric loss ϵ'' and the abscissa to the dielectric constant. We shall not use these terms in this paper, however, because the dielectric constant and loss of a material are usually considered as intensive quantities, the same at each point in the material. In the present situation, the dispersion contribution to the capacitance and conductance of the specimen is localized in layers near the electrodes and is therefore by no means intensive. It may be noted that Debye-type frequency dependence, involving a single relaxation time, should yield a semicircle with

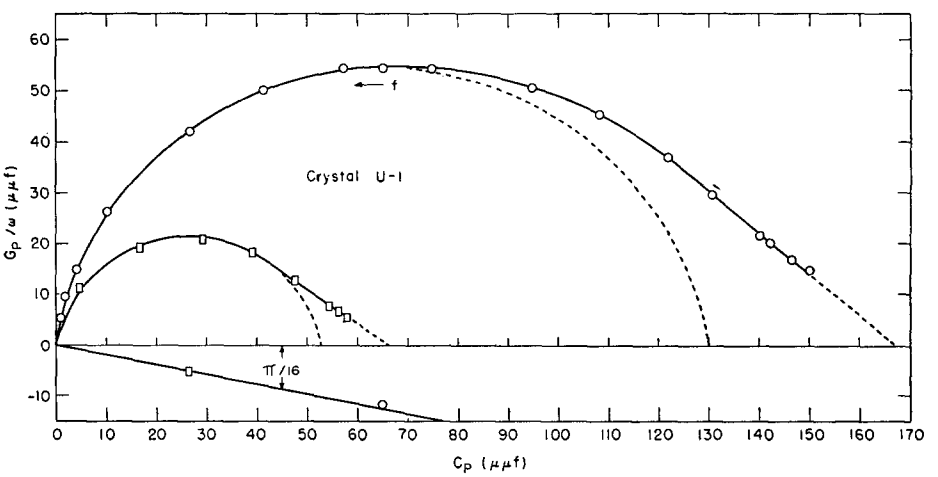

FIG. 4. Circle diagram plot of G_P/ω *vs* C_P for Crystal U-1. Small curve measured six months after large curve.

[25] The small increase of the G_P/G_∞ curve above its limiting value, shown dotted, may be explained as arising from the series resistance of the evaporated electrodes of this crystal as will be discussed later.

[26] F. Seitz, Revs. Modern Phys. **18**, 384 (1946); **26**, 7 (1954).

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center on the abscissa in a plot of this type. The smaller curve in Fig. 4 also refers to crystal U-1 but was taken for the same light intensity about six months after the larger curve. During the intervening time, the crystal was bleached quite strongly with F light and given several gamma-ray exposures to bring the F-center concentration back to approximately its original value. It is evident that bleaching and redosing have reduced C_0 considerably.

These curves are similar in form to Cole-Cole plots[27] in that they yield circular arcs over part of their lengths. The centers of these arcs are shown in the figure and fall approximately on the same line. In spite of the similarity to Cole-Cole plots, the curves are, in fact, very different. The difference arises chiefly from the frequency dependence of the capacitance and conductance curves. If this dependence is computed from Fig. 4 treating it as a Cole-Cole plot, which implies a certain distribution of relaxation times, the dependence is very different from the experimental results shown in Fig. 3. Therefore, these data do not arise from a material having a distribution of relaxation times of the form demanded by the Cole-Cole equations. It is also worth noting that the curves of Fig. 3 cannot be fitted well by the Fuoss-Kirkwood theory[28] which involves a different relaxation time distribution function than that of the Cole-Cole theory.

Figure 5 shows the frequency dependence of C_P and G_P obtained for additively F-centered crystal AF-1 containing about 1.5×10^{16} F centers per cm^3. This measurement was made with the same light intensity as that employed for the U-centered crystal of Fig. 3. The areas of the two crystals were approximately the same, and the respective values of C_0 are obviously of at least the same order of magnitude. On the other hand, the conductivity σ_∞ is about 70 times smaller for the additively colored than for the U-centered crystal, in spite of the former's having had about three times as

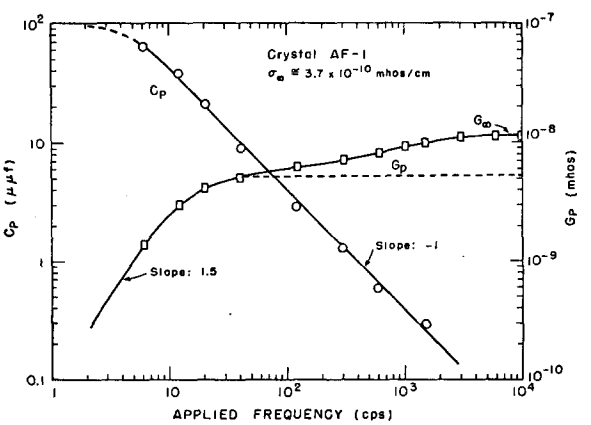

FIG. 5. Dependence of parallel capacitance and conductance on frequency for additively F-centered Crystal AF-1.

[27] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941)
[28] J. R. Macdonald, J. Chem. Phys. **20**, 1107 (1952).

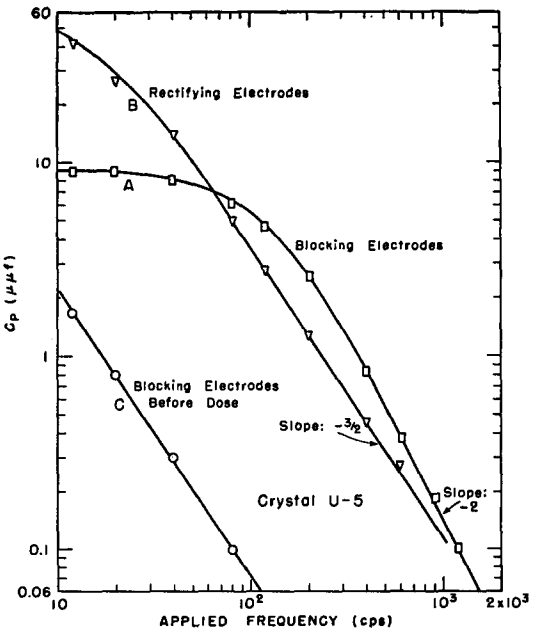

FIG. 6. Comparison of frequency dependence of parallel capacitance of a Type II specimen with blocking electrodes to that with rectifying electrodes.

many F centers. This result clearly indicates that there is a much higher conduction-band electron density for the U-centered crystal than for the additively-colored one. The shape of the curves for the additively-colored crystal is somewhat different from those presented in Fig. 3. Although the G_P curve may involve a $\frac{3}{2}$ slope at low frequencies in agreement with the result of Fig. 3, the C_P limiting slope is approximately -1 instead of $-\frac{3}{2}$. Because of their rapid bleaching under strong illumination and their low conductivity, which leads to large values of τ, we shall not consider capacitative results for additively-colored crystals further in this paper. Qualitatively, the same effects are obviously present in additively-colored as in U-centered crystals, although there may be quantitative differences in behavior.

The previous results have pertained to Type I crystals[16] with aluminum electrodes evaporated directly on the crystal surface. The frequency dependence of such crystals type involves limiting slopes of $\pm\frac{3}{2}$ instead of ±2. In order to determine if this difference arose from the rectifying electrodes employed, a number of Type II crystals were made up in such a way that for a given crystal the electrode conditions could be changed from rectifying to blocking. First, frequency dependence measurements were carried out for such crystals with silver paint electrodes directly on the ends of the crystals. Exactly the same results were obtained as with the aluminum-electrode Type I crystals previously considered, indicating that it is immaterial whether light enters the crystal through an electrode or between two electrodes. Since no appreciable difference in the rectifying character of aluminum or silver con-

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tacts was observed, it seems possible that such character may be at least partly controlled by gas adsorbed on or near the crystal surface or by surface states.[23]

Figure 6 shows the dependence of C_P on frequency for a single crystal with rectifying and with blocking electrodes. The bottom curve C was taken before the crystal had been exposed to gamma radiation, whereas the top two curves were obtained after sufficient exposure to produce about 5×10^{15} F centers per cm^3. Curve B for rectifying electrodes is of the same form as previously discussed and clearly shows the $-\frac{3}{2}$ slope at high frequencies. On the other hand, Curve A for blocking electrodes is considerably different. The only difference in the crystal for Curves A and B was that for B silver electrodes were directly on the crystal while for A they were separated from it by a thin sheet of mica. The line drawn in Curve A is a theoretical Debye curve fitted to the experimental points. The agreement is excellent and indicates that Debye-type frequency dependence is indeed obtained for blocking electrodes and that therefore a frequency-independent series capacitance C_0 is involved. The difference in limiting slopes of A and B is thus obviously due to the difference in the electrodes.

The difference in the low-frequency limiting values of C_P arises, however, partly from the mica sheets between crystal and metal electrode not being sufficiently thin that their capacitative reactance was negligible compared to that of the crystal itself. Thus, with blocking electrodes, the observed capacitance at low frequencies was smaller than that of the crystal itself, since the crystal capacitance and that of the mica sheets were in series. This effect cannot account for a reduction in the value of C_0 by more than a factor of two at most. The observed ratio between the values obtained with blocking and with rectifying electrodes is, however, greater than six as indicated by Fig. 6. It thus appears that the character of the electrode-crystal contact may affect C_0 directly.

Curve C in Fig. 6 shows that there are considerable photocapacitative effects present for a U-centered crystal even before gamma-ray dosage. These effects probably arise from a residual concentration of F centers of the order of 10^{13} to 10^{14} cm^{-3} not removed during the U-centering process. Since the crystal had blocking electrodes when Curve C was obtained, the limiting slope might have been expected to be -2; it is, however, about -1.4. This discrepancy was often noted for very low concentrations of F centers and/or very low light intensities. It probably arises from a number of causes. It is possible that the reduced slopes apparent with low carrier concentrations arise from the presence of another dispersion mechanism present in addition to the motional dispersion which we have been considering. Lawson, Miller, Schiff, and Stephens[29] have developed a dispersion theory in which dispersion arises from a finite ionization time for the ionization of charge carriers from neutral centers. This theory yields a limiting slope for parallel capacitance of -1 and for parallel conductance of 2. The theory is not directly adaptable in its present form to the present experimental situation, but it is possible that long average ionization time becomes of importance here for very low F-center concentrations or low light intensities and reduces the limiting C_P slopes. For either very low light intensities or very low F-center concentrations, the probability of excitation of any given F center will be very small, and its average ionization time will be long. It is interesting to note that residual capacitance greater than C_g could often be measured in the dark for crystals with F-center concentrations of the order of 10^{16} cm^{-3} and such measurements yielded limiting slopes again of the order of -1. Unfortunately, the influence of thermal ionization of electrons from any shallow traps which may be present becomes of greater importance as the light intensity is reduced. The combination of the two types of ionization make it impractical at present to apply the combination of motional and finite-ionization-time dispersions to the present experimental case in a quantitative fashion.

Figure 7 presents the results of frequency dependence measurements of G_P corresponding to the measurements of C_P shown in Fig. 6. The measurements of these two graphs were made at the same time, on the same crystal, and with the same light intensity. Curve A is again for blocking electrodes and the experimental points are well fitted by a Debye curve of the same time constant as that required to fit the corresponding C_P curve of Fig. 6. Curve B of Fig. 7 for rectifying electrodes shows that there is no appreciable dependence of

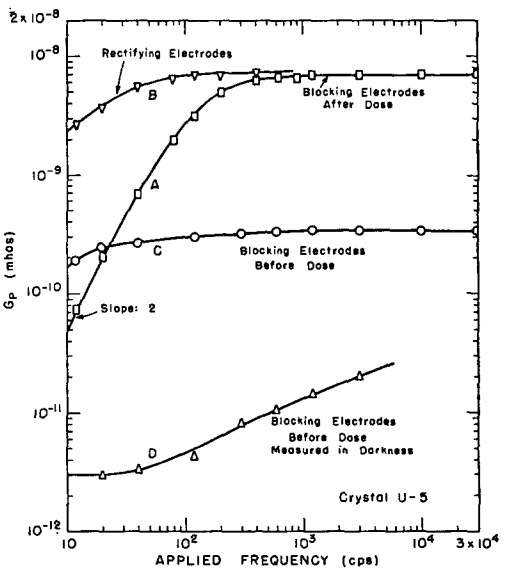

FIG. 7. Comparison of frequency dependence of parallel conductance of Crystal U-5 with blocking electrodes to that with rectifying electrodes.

[29] Lawson, Miller, Schiff, and Stephens, National Defense Research Council Report WDRC-14-153, July 1, 1943 (unpublished). See also reference 20, p. 103.

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G_∞ on electrode character. The time constant of Curve B is considerably longer than that of Curve A, however, and this result is in quantitative agreement with the relation $\tau = C_0/G_\infty$ and the evidence of Fig. 6 that C_0 is six or seven times greater for this crystal with rectifying than with blocking electrodes. The time constant of Curve C taken before gamma-ray dosage is even longer than that of Curve B but for a different reason from that accounting for the increase observed between Curves A and B. The value of C_0 for Curves A and C is substantially identical but G_∞ is some 20 times less for C than for A, as one might expect from the smaller concentration of F centers present in the former case. Within experimental error, this same factor of 20 is the ratio of the time constants of Curves C and A. Finally, Curve D was taken on the same crystal in the dark before dosage. The cause of the observed rise of Curve D at high frequencies with a slope of approximately $\frac{1}{2}$ is unknown.

Figure 8 presents results similar to those of Fig. 6 but for another crystal. This crystal was of approximately the same dimensions as that of Fig. 6 but it had a cleavage plane transversely across its entire cross section nearly midway between the electrodes. If charge carriers cannot cross this cleavage plane, the crystal should behave as two crystals in series, with the cleavage plane acting as a blocking electrode. If, on the other hand, carriers can discharge slowly across the midplane, as the frequency is decreased a frequency should be found below which the influence of this cleavage plane should be negligible. Below this frequency, C_0 would be that for the entire crystal, whereas at high frequencies the pertinent C_0 which would determine τ would be approximately half as large, reducing τ by a factor of two since G_∞ would be unchanged by the cleavage plane. Curve A shows that the latter hypothesis is apparently in better agreement with experiment. The solid line of Curve A is a Debye curve fitted to the high-frequency experimental points. At low frequencies, the dotted line shows how these points progressively deviate from the theoretical Debye curve. The result of a dc measurement of capacitance gave a value of 13 $\mu\mu$f, which is probably then the value towards which the dotted line is tending. The limiting value C_0 for the Debye curve is 6.7 $\mu\mu$f, however, and this is approximately half of the low frequency or dc value of 13 $\mu\mu$f. Figure 15 also shows the frequency dependence for this crystal with two rectifying electrodes and with one rectifying, one blocking electrode. As expected, the latter curve C falls between the rectifying-rectifying and blocking-blocking curves over most of its range and its limiting slope is between $-\frac{3}{2}$ and -2. Note that here the difference between the blocking and rectifying values of C_0 is smaller than that apparent in Fig. 6 and may be almost entirely ascribed to the effect of the mica layers used to produce blocking electrodes.

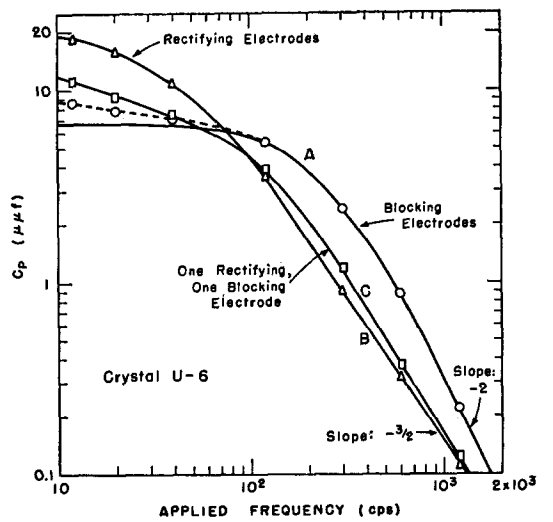

FIG. 8. Comparison of frequency dependence of parallel capacitance of Crystal U-6 containing a transverse cleavage plane for two blocking electrodes, two rectifying electrodes, and one blocking, one rectifying electrode.

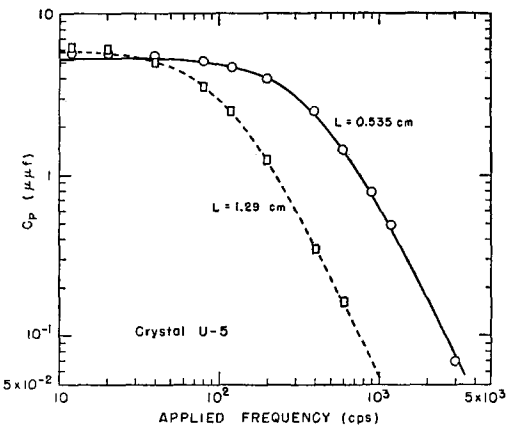

FIG. 9. Dependence of parallel capacitance on frequency for two values of electrode separation. The lines are Debye curves.

The Debye-type frequency dependence observed with blocking electrodes is a necessary but insufficient condition that the observed effects arise from a localized, frequency-independent capacitance. For example, such frequency dependence might also arise from the polarization of electrons localized in very shallow traps as postulated by Garlick[30] to explain a small photocapacitative effect in illuminated powder phosphors. However, because of the electrode influence on frequency dependence, Garlick's hypothesis cannot explain the present results.

Figures 9 and 10 show the frequency dependence of parallel capacitance and conductance of crystal U-5 with blocking electrodes for two different values of L, the electrode separation. The same electrodes were employed for both values of L. The lines in these graphs

[30] G. F. J. Garlick, *Luminescent Materials* (Clarendon Press, Oxford, 1949), p. 123.

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are theoretical Debye curves and fit the experimental points well. The time constants for the C_P and G_P curves corresponding to a given L are, of course, the same. Since the Debye curves are completely specified by the series quantities C_0 and G_∞, we need consider only the experimental dependence of these quantities upon L.

Figure 9 shows that a reduction in L by a factor of 2.41 makes less than a five percent difference in the value of C_0. If the observed values of C_0 arose from an intensive process in the crystal, C_0 would be inversely proportional to L and would be biggest for smallest L. The small observed variation is, however, in the opposite direction and since it is so small, the photocapacitative effect must arise from processes localized near the electrodes and may be considered to involve a frequency-independent series capacitance. It should be noted here that if the capacitance of the mica spacers used to produce blocking electrodes were much smaller than that of the crystal itself, the former capacitance would dominate the measured capacitance and one would expect little dependence of measured capacitance on electrode separation. In the above measurement, however, the series mica capacitance was of the order of two to three times as large as the crystal capacitance so that the latter dominated the series combination.

The high-frequency conductance should be inversely proportional to L. In the present case, the value of G_∞ corresponding to the smaller length should therefore be larger than the value corresponding to the larger length by a factor of 2.41. The observed ratio is, however, 3.2. This result implies that the electrical length of the crystal after shortening is smaller than the mechanical length by about 1.9 mm. Somewhat similar behavior is obtained for space-charge effects in electrolytes.[3] Time was not available unfortunately for a more complete investigation of the dependence of G_∞ on L for these crystals. The difference L_x between the electrical and mechanical length of the crystal is in agreement with the idea that a charge-free region at one or both of the electrodes is responsible for C_0. The value 1.9 mm for this layer leads to a value of C_0 about five times smaller than the observed value. It is probable, however, that a more accurate determination of L_x from measurements of G_∞ with a wide range of electrode separations would yield better agreement with that derived from the experimental C_0.

If there is no charge in the region L_x, there can be no F centers or negative-ion vacancies there. If we assume a region $L_x/2$ thick at each electrode, then during each half cycle the cathode region will be electrically neutral while the anode region will contain an approximately normal concentration of electrons c_0 for rectifying electrodes or perhaps an excess of electrons for blocking electrodes. At sufficiently high frequencies, however, electrons will not have time during a half-cycle to move into the L_x region. Thus, it appears plausible that $L_x/2$ may determine C_0 and L_x determine G_∞. If this

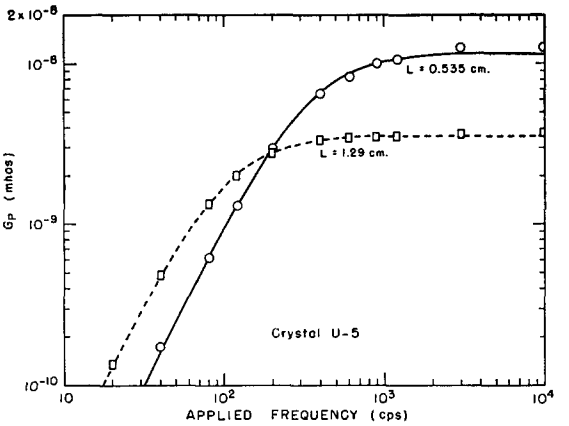

FIG. 10. Dependence of parallel conductance on frequency for two values of electrode separation. The lines are Debye curves.

is the case, the above discrepancy is reduced by a factor of two.

A charge-free region near the surface may occur by the diffusion to the surface of negative-ion vacancies in a layer of thickness L_x (or $L_x/2$). If the crystal initially contained a uniform distribution of negative-ion vacancies stabilized as either U or F centers, any nonzero ionization rate of these centers would produce negative-ion vacancies which could slowly diffuse to the surface and disappear. Thus, one might expect that long dark-storage of U- or F-centered crystals could increase L_x. In addition, continued optical ionization of an F-centered crystal would tend to destroy F centers and negative-ion vacancies initially near the surface. In agreement with this hypothesis, U-centered crystals stored in the dark for a year or more were found to produce no F centers under subsequent gamma-ray irradiation in a region as large as 1 mm in from each surface. The line of demarcation in the crystal where the F centers began was visible with the eye and was surprisingly sharp. In addition, the reduction in C_0 (and increase in L_x) shown by the two curves of Fig. 4, which was caused by considerable F-center bleaching and redosing, further confirms the above hypothesis.

Although all the results of the present work combine to indicate that there is a charge-free layer at one or both electrodes, the above explanation of its genesis does not, apparently, agree completely with all the data. In spite of the fact that many of the crystals used in this work were U centered a year or more before F centering, their surfaces were usually cleaved off before using them for measurements. Further, additively-colored crystals which showed the same photocapacitative effects were measured within a week or two of their coloration. In the length-dependence study, if there were a charge-free region initially at each electrode, the reduction of the electrode separation by a factor of more than two should have eliminated one of these regions and caused a much larger change in C_0 than observed. It is therefore evident that further work

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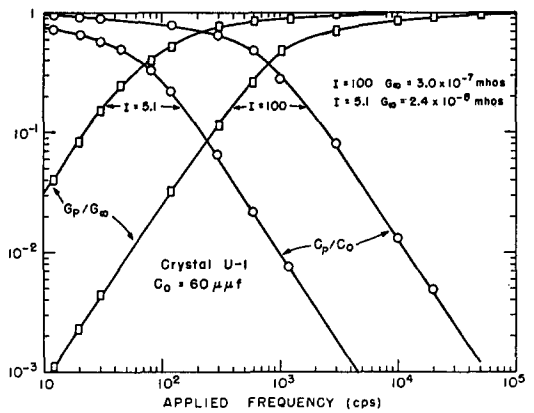

FIG. 11. Dependence of normalized parallel capacitance and conductance on frequency for two fixed light intensities.

will be required to yield a better understanding of the production and character of the charge-free layer.

(c) Light Dependence

The light dependence of C_0 and τ predicted by various space-charge theories for different types of recombination is summarized in Table I. It will be noted that the last two rows predict, for monomolecular or F-center type recombination, a light-independent C_0 and a τ proportional to I^{-1}. These results are in approximate agreement with experiment. Both ac and dc measurements extending over almost four decades of light intensity showed no dependence of C_0 on I. Since the exhaustion layer theory has been shown to be inapplicable, we are again forced to the conclusion that C_0 arises from a charge-free layer near the electrodes.

If we consider the expressions for C_P/C_0 and G_P/G_∞ given by Eqs. (6) and (7) in the light of these results, we see that these quantities should be functions of the ratio $(f/I)^2$, since τ is proportional to I^{-1}. On the other hand, for crystals with rectifying rather than blocking contacts, we should instead expect, as shown by the results of Fig. 3, that C_P/C_0 and G_P/G_∞ would be

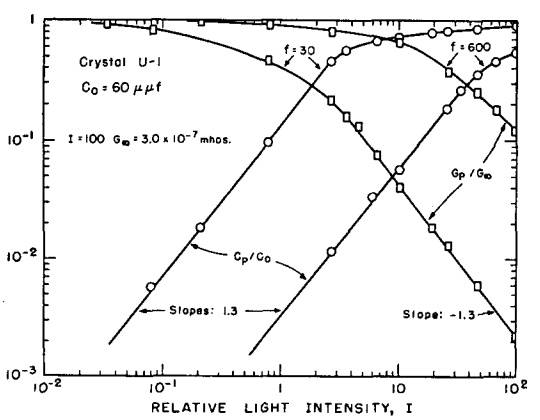

FIG. 12. Dependence of normalized parallel capacitance and conductance on light intensity for two fixed frequencies.

functions of $(f/I)^{\frac{1}{3}}$ instead of $(f/I)^2$. These expectations are largely realized.

Figure 11 shows the normalized frequency dependence of C_P and G_P for two different relative light intensities. The usual limiting slopes of $\pm\frac{3}{2}$ are present: C_0 is independent of light intensity, G_∞ is approximately proportional thereto, and the curves for the two different light intensities differ principally in a frequency translation arising from the difference in τ occasioned by the light-intensity dependence of G_∞. For comparison with Fig. 11, we have plotted in Fig. 12 the dependence of C_P/C_0 and G_P/G_∞ on light intensity for two constant frequencies of approximately the same ratio as the two light intensities of Fig. 11. The values of C_0 and G_∞ are the same for Figs. 11 and 12.[31] The curves of Fig. 12 are approximately mirror images of those of Fig. 11. Thus, the dependence on I^{-1} is nearly the same as that on f as indicated by the above considerations. Instead, however, of being functions of $(f/I)^{\frac{1}{3}}$, these curves are more nearly functions of $f^{\frac{3}{2}}/I^{1.3}$ as is shown by the limiting slopes of Fig. 12. The reason for this small discrepancy is unknown.

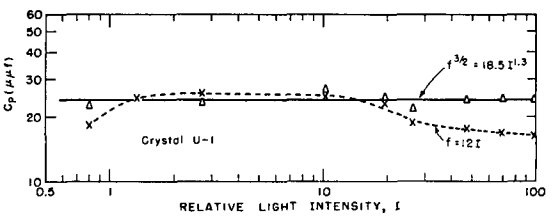

FIG. 13. Dependence of parallel capacitance on light intensity for $f/I = 12$ and $f^{\frac{3}{2}} = 18.5 I^{1.3}$.

The dependence of C_P and G_P on $f^{\frac{3}{2}}/I^{1.3}$ is shown more graphically in Figs. 13 and 14. If f and I are varied together so that $f^{\frac{3}{2}}/I^{1.3}$ remains constant, there should be no change in C_P. Figure 13 shows that this is indeed the case over a wide range of light intensities and frequencies. Also shown on this graph are the results of keeping (f/I) constant while varying I. The variation of C_P is obvious in this case, proving that the exponents of f and I are indeed somewhat different. Figure 14 shows how G_P depends on light intensity for two constant values of f/I. The variation in G_P is linear over most of the range of light intensities and thus proves the linear dependence of G_∞ on light intensity. The deviations from linearity at high light intensities are not so much due to a failure of the linear relation between G_∞ and I as due to variation in G_P arising from keeping f/I rather than $f^{\frac{3}{2}}/I^{1.3}$ constant. This conclusion is confirmed by Fig. 15 which shows the results of a direct measurement of the dependence of G_P on I at a sufficiently high frequency that the terms involving $f^{\frac{3}{2}}/I^{1.3}$ completely cancel out and $G_P = G_\infty$.

[31] For convenience, the actual quantity plotted for normalized conductance in Fig. 12 was $(G_P/I)/(G_P/I)_{I=0}$. From Eq. (7), together with the linear dependence of G_∞ on I, this ratio may be shown to equal G_P/G_∞.

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Note that the linear dependence of G_∞ on I is in agreement with the constant-capacitance assumption provided recombination is monomolecular or takes place by F-center type electron capture.

We have been previously concerned with the effect of fairly strong light intensities on these photoconducting crystals. Their electrical behavior in the dark is also of interest for comparison with results under illumination. Figure 16 shows the frequency dependence of conductivity for three Type I crystals measured in the dark. All these crystals had about the same electrode areas but their separations ranged from 1.46 to 5.42 mm. Curves A and B refer to the same crystal which was of untreated KBr. Curve A was taken when the crystal had evaporated aluminum electrodes, one of which was very thin and of relatively high resistivity. This curve shows a fairly constant value of conductivity

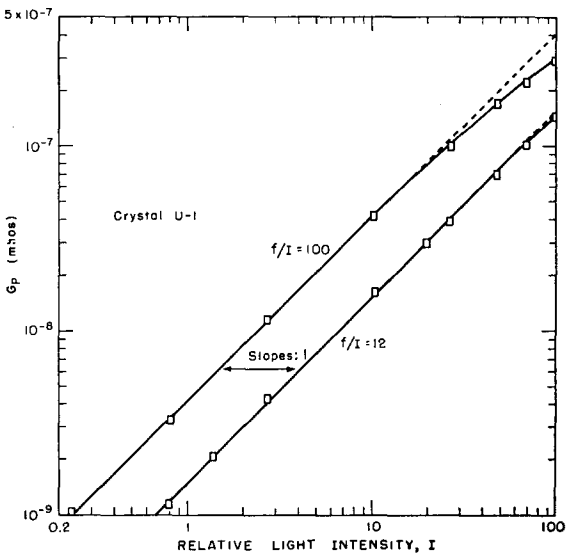

FIG. 14. Dependence of parallel conductance on light intensity for $f/I = 12$ and 100.

at low frequencies and a transition region which leads to a final ω^2 dependence on frequency. If this latter portion of the curve were considered as corresponding to a series rather than a parallel resistance, one would obtain a frequency-independent value of series resistance of the order of 10^3 ohms. This resistance value is in qualitative agreement with dc measurements of the resistance of the thin semitransparent aluminum electrode, and it thus seems clear that this portion of the conductivity curve arises from electrode resistance. In order to test this hypothesis, both aluminum electrodes were covered over with silver paint, reducing the electrode resistance to one ohm or less. Curve B was then obtained. Instead of removing the frequency dependence entirely as was expected, it was reduced to a ω-type dependence. The reason for this dependence is unknown, but it seems clear that electrode resistance is important in producing the ω^2 rise in Curve A.

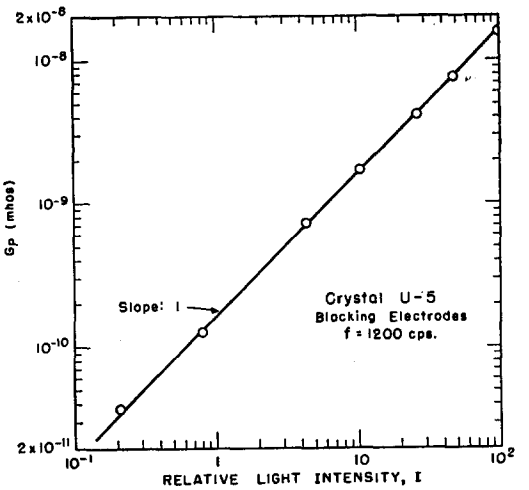

FIG. 15. Dependence of parallel conductance on light intensity for $f = 1200$ cps.

The low-frequency portions of Curves A and B are interesting. This more-or-less frequency-independent conductivity in a plain KBr crystal must arise from ionic motion, ionic vacancy motion, or from surface leakage. Since great care was exercised to eliminate the latter effect, it is likely that the measured conductivity arises from one or both of the other two conduction processes. However, it can be shown that the ionic mobility at room temperature is several orders of magnitude too small to yield the observed values. On the other hand, if we use Etzel and Maurer's results[32] for

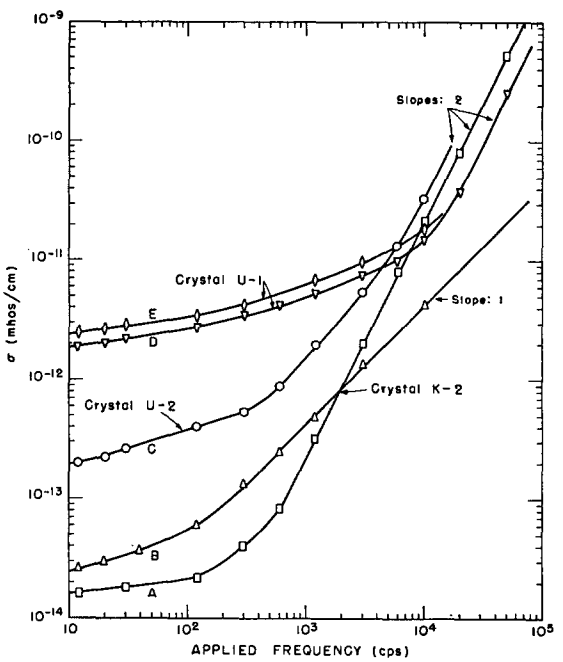

FIG. 16. Dark conductivity of 3 Type I crystals *vs* frequency. Crystal K-2 is plain untreated KBr; U-1 and U-2 are U-centered crystals. U-1 has been exposed to gamma radiation; U-2 has not.

[32] H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

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the concentration of positive-ion vacancies present in KCl,[33] 10^{17} cm^{-3}, and extrapolate their vacancy-mobility data to room temperature, a conductivity value only three times smaller than the limiting value of Curve *A* is obtained. Since we are here dealing with KBr rather than KCl, it is reasonable to conclude that the observed low-frequency conductivity arises from the motion of positive-ion vacancies. This view is strengthened by the fact that Curve *B* was measured during warmer weather than was Curve *A* and the laboratory temperature was somewhat higher. A temperature differential of only 5°C is required to explain the difference in the low-frequency conductivity values of the two curves on the basis of vacancy motion. Since the quasi-static current observed for these crystals an hour or more after a high dc field is applied is in approximate agreement with their low-frequency dark conductivity values, it may be postulated that this current also arises from vacancy motion. Neither the ac nor dc conductivities observed on plain KBr crystals showed any light dependence whatsoever. The dark conductivity of both plain KBr crystals and those containing *F* centers was ohmic, thus reducing the possibility that field-emission is responsible for the observed results.

Curve *C* was measured on a *U*-centered crystal which had never been exposed to radiation. As expected, it also shows the electrode-resistance characteristic at high frequencies. Since the conductivity is a factor of about ten times greater than that of crystal *K*-2, there are either 10 times more positive-ion vacancies in *U*-2 than in *K*-2 or the conduction arises from thermal ionization of electrons from shallow traps. Both *K*-2 and *U*-2 came from the same batch of crystals. It is easy to calculate from the known electron mobility[21] that the low-frequency conductivity of crystal *U*-2 could be produced by only about 10^5 conduction-band electrons per cm^3. At the completion of the *U*-centering process not all *F* centers have been destroyed; of the order of 10^{13} to 10^{14} cm^{-3} still usually remain in the crystal. It is possible that exposure to *F*-band light bleaches some of these remaining *F* centers and that most of the resulting electrons are captured by shallow traps rather than by negative-ion vacancies. If these traps are sufficiently shallow, it is possible that as many as 10^5 electrons per cm^3 could be maintained in the conduction band in the dark by thermal excitation alone. It can easily be shown[34] that the equilibrium concentration of conduction-band electrons produced from 10^{14} *F* centers per cm^3 by thermal ionization is negligibly small at room temperature.

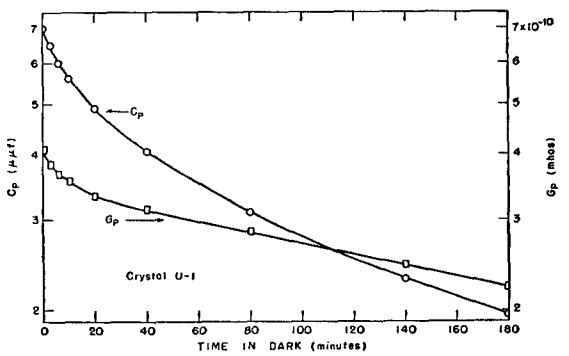

FIG. 17. Decay of parallel capacitance and conductance in the dark after 10-minute bleaching using heat filter No. 3961. Crystal *U*-1.

The argument that the main contribution to the dark conductivity of crystal *U*-2 arises from free electrons is strengthened by consideration of Curves *D* and *E* in Fig. 16. When Curve *D* was obtained, crystal *U*-1 had been exposed to about 10^3 roentgens of Co^{60} radiation, producing about 5×10^{15} *F* centers per cm^3. It had also been exposed to strong *F*-band light and a fraction of the *F* centers destroyed. We may suppose that its dark conductivity is another factor of 10 times larger than that of *U*-2 because of the possible production of more shallow traps by the gamma rays and their population by electrons from bleached *F* centers and other sources. Curve *E* was taken sometime later after the crystal had been re-exposed to gamma rays and partly bleached out once more, again increasing the dark conductivity. Table II summarizes conduction-band electron concentration for various conditions. It will be noted that all these Type I crystals with evaporated aluminum electrodes show the electrode-resistance rise in dark conductivity at high frequencies. We may now refer back to the conductance curves of Figs. 3 and 5 and explain the continued rise in G_P above the dotted saturation value as being due to electrode resistance.

In Fig. 17, some measurements of the secondary photoeffect in crystal *U*-1 are presented. This crystal, then containing about 5×10^{15} *F* centers per cm^3, was left in total darkness for several days. It was then strongly illuminated for 10 minutes; the light extinguished; and the decay of capacitance and conductance in the dark measured at 20 cps. A number of rough measurements have been carried out to establish that C_P and G_P reach their final values within a time of 10^{-2} second or less after an *F*-centered crystal is exposed to light. Usually, these quantities also drop essentially to zero within the same time interval after illumination is removed. In some instances, however, such as that shown in Fig. 17, C_P and G_P dropped in the dark to many times less than their illuminated values but still to values which were appreciably above final dark values. Each of the dark decay curves shown in Fig. 17 can be quite accurately represented as the sum of two exponentials. If we assume that the added capacitance and conductance represented by these curves is due to the presence of conduction-band

[33] This concentration is almost certainly due to the presence of an equal concentration of divalent impurity atoms present in the "pure" crystal; it is unrelated to the thermal equilibrium concentration of positive- and negative-ion vacancies.

[34] Reference 15, p. 143, Eq. (15).

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electrons in the crystal in the dark, these curves indicate how the concentration of electrons decays. The decay is monomolecular and, since the curves are made up of two exponentials, it seems likely that the electrons are trapped by two (or more) types of traps located at different depths below the conduction band. We may postulate that with the crystal illuminated and a fairly high concentration of electrons in the conduction band, a much larger number of shallow traps contain electrons than would be the case in the dark. When the light is extinguished, these traps give up their electrons by thermal ionization until a new equilibrium between electrons in traps and electrons in the conduction band is established. It is probably the effect of these thermally ionized electrons which we observe in Fig. 17, and the decay in electron concentration occurs as electrons leave shallow traps and become permanently trapped at deeper levels. We shall discuss the nature of some of these traps later.

The experimental values of the decay constants for the exponential decay of C_P and G_P are very nearly in the ratio 3:2 for the latter portion of the curves of Fig. 7 after the initial rapid decay has died out. This result is made very plausible by consideration of the Debye-curve expressions of Eqs. (6) and (7) with τ given by C_0/G_∞. In the present case G_∞ is so small that $G_P=G_\infty$ at 20 cps, and C_P becomes $C_0/(\omega\tau)^2=G_\infty^2/\omega^2C_0$. Thus, changes in G_∞ and in C_0 may cause changes in C_P. Let us suppose that the only physical change which occurs during the decay is the reduction in G_∞ produced by the trapping process discussed above. Thus C_0 remains constant during the decay; such stability is consistent with all other measurements of C_0. Then if G_∞ decays exponentially, C_P will also decay exponentially, but with twice the decay constant of G_∞. For this crystal with rectifying electrodes, the frequency-response curves show that $(\omega\tau)^{\frac{1}{2}}$ is involved rather than $(\omega\tau)^2$ as for Debye curves. When the above treatment is modified by the change of exponent from 2 to $\frac{3}{2}$, one finds that C_P is proportional to $G_\infty^{\frac{3}{2}}$; thus, the decay constants of C_P and G_P will be in the observed ratio of 3:2. This treatment also applies, at least approximately, to the initial rapid-decay portion of the curves. Therefore, the C_P curve yields further independent evidence that C_0 does not change when G_∞ does so.

(d) Temperature Dependence

The majority of the work reported in this paper has been carried out at room temperature. Measurements of the frequency dependence of C_P and G_P for one crystal at 25°C and at 125°C showed, however, that C_0 was independent of temperature in this range as expected and that G_∞ increased by a factor of 2.2 on raising the temperature to 125°C. The increase in G_∞ indicates that the product μc_0 increased by the same factor. Unlike the mobility of ionic vacancies, which increases with increasing temperature, electronic mobility in polar crystals decreases with temperature. Thus, the average concentration of electrons in the conduction band, c_0, must have increased by a factor greater than 2.2. As Glaser and Lehfeldt[35] have shown, this increase cannot, at these temperatures, arise from an increase in the quantum yield associated with the optical ionization of F centers. The most reasonable explanation of the increase is that there is present a large number of shallow traps some of which contain electrons originally from F centers. If the electron concentration in these traps is determined by thermal equilibrium between conduction-band electrons and electrons in the shallow traps, an increase in temperature will increase the conduction-band concentration.

TABLE II. Conduction-band electron concentration for various conditions. The light source was a 500-watt slide projector whose output was focused on the crystal.

c_0 (cm^{-3})	No dose $N_F \approx 10^{12}-10^{14}$ cm^{-3}	Saturation dose $N_F \gtrsim 5\times10^{15}$ cm^{-3}
Crystal dark	10^5 to 10^7	10^6 to 10^8
Crystal illuminated	10^7 to 10^9	10^{10}

Since the conduction-band concentration increases linearly with light intensity, we must assume that the concentration of empty shallow traps is much greater, for any light intensity employed, than the concentration of shallow traps containing electrons. If we temporarily neglect the decrease in μ with increasing temperature, we can compute a very rough average thermal activation energy of the shallow traps of 0.04 ev.[36] The temperature dependence of μ will make the actual activation energy larger than 0.04 ev but will probably not increase this figure by a factor of more than two or three. This small a trap activation energy indicates that the shallow traps, when empty, are almost certainly electrically neutral. Note that the above calculation of activation energy is based on a trap concentration independent of temperature, which is probably not the case here [see Part (f) of this section.] The possible nature of these traps will be discussed later. Temperature dependence of the optical bleaching of F centers will be discussed later in connection with Fig. 19.

(e) Gamma-Ray Dose Dependence

When a U-centered crystal is exposed to penetrating gamma-rays, the quanta absorbed in the crystal produce a conversion of U centers to F centers. The number of F centers produced by a given dose of radiation will be proportional to dose so long as this number is small compared to the number of U centers available for conversion. There were between 5×10^{17} and 10^{18} U centers per cm^3 in the crystals used in the present investigation; therefore, one would expect to find a

[35] G. Glaser and W. Lehfeldt, Nachr. Ges. Wiss. Göttingen **2**, 91 (1936).

[36] Reference 15, p. 159, Eq. (12).

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linear relationship between dose and F-center concentration up to concentrations of 10^{16} cm^{-3} or greater. Optical measurements of the absorption coefficient at the peak of the F band, in conjunction with the factor of Hilsch and Pohl[37] relating absorption coefficient to F-center concentration, showed that this expectation was justified. It was found that $(N_F-N_0)=5.8\times10^{12}r$ cm^{-3} up to almost 10^4 roentgens, where r is the dose of Co^{60} gamma radiation in roentgens and N_0 is the initial concentration of F centers before dosing. The coefficient in this equation varied by a few percent from crystal to crystal.

The theories of Table I predict various dependencies of C_0 and G_∞ (or c_0) on N_F. It was actually found from both ac and dc measurements that there was little or no dependence of C_0 on N_F over a range of at least 10^3 in N_F. This result is thus in agreement with the charge-free layer hypothesis. For monomolecular or F-center capture type recombination, the last row of Table I shows that c_0 should be proportional to N_F (or r) or be independent of N_F, respectively. In Fig. 18 the high-frequency conductivity of two different crystals is plotted *versus* r and neither dependence is obtained. Because of the presence of the residual concentration of F centers in these crystals before any dose, we have actually used as ordinate in this figure the conductivity at a dose r, $\sigma(r)$ minus that at zero dose, $\sigma(0)$. The initial values of $\sigma(0)$ are shown on the graph by the two horizontal dotted lines. To avoid appreciable bleaching of F centers during a measurement of $\sigma(r)$, relatively low light intensity was used.

Figure 18 shows that the experimental points can be well fitted by a relation of the form $[\sigma(r)-\sigma(0)]=[\sigma(\infty)-\sigma(0)][\beta r/(1+\beta r)]$ up to 10^3 roentgens. Further, $\sigma(\infty)$ is almost reached by a dose of 10^3r. For very low doses less than $10r$, the increase in σ produced by gamma-ray absorption is proportional to N_F as expected for monomolecular recombination; however, for the range between 10^3 and 10^4 roentgens where N_F is still increasing linearly with dose, σ does not increase appreciably. The concentration c_0 is determined, for any light intensity, by the equations of detailed balance governing the flow of electrons from F centers to shallow and deep traps. The most reasonable explanation for the above dependence of c_0 on r (and on N_F) is that additional traps such as F centers themselves are produced proportional to r in the range of r here considered. This hypothesis, and its consequences, will be discussed in more detail later.

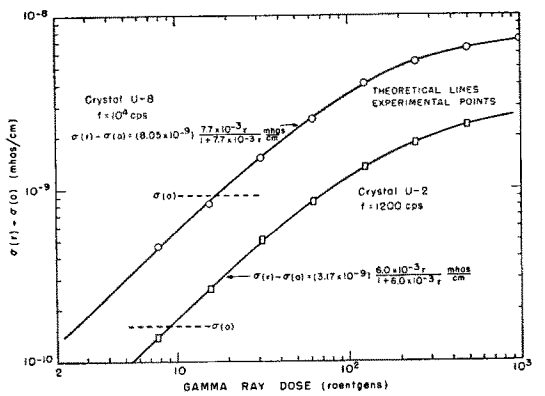

FIG. 18. Dependence of high-frequency conductivity on Co^{60} gamma-ray dose. $\sigma(0)$ is the conductivity observed before dosing.

[37] R. Hilsch and R. W. Pohl, Z. Physik **64**, 606 (1930).

(f) Optical Bleaching Results

If all electrons ionized to the conduction band from F centers were eventually trapped by single negative-ion vacancies, there would be no bleaching of F centers. On the other hand, if all such electrons were trapped elsewhere than at negative-ion vacancies, there would be a monomolecular, exponential decay of F-center concentration with time of the form $N_F=N_0\exp(-k_1t)$, where k_1 is the probability per unit time of F-center ionization. For photoionization, k_1 is proportional to the F-band light intensity.

Figure 19 shows the results of optical measurements of the bleaching of an F-centered crystal under strong illumination at two different temperatures. After four hours of bleaching, the temperature was abruptly increased from 25°C to 125°C. At 125°C the bleaching is definitely exponential since the points fall on a good straight line on the semilogarithmic graph. The decay constant for this portion of the curve is 1.28 hr^{-1}. At room temperature, the decay is somewhat more complex but can be quite accurately represented by the sum of two exponentials of different decay constants. For the longer-lived component, the value of the decay constant is 1.78×10^{-2} hr^{-1}. This increase in temperature thus increases the decay constant by a factor of 72.

It is worth noting that the initial rapid decay observed at room temperature can be produced once more when it has disappeared after several hours of bleaching by leaving the crystal in darkness for 10 or more hours. No change in N_F is produced by such dark storage, however. The rapid decay apparently arises from the slow formation in the dark of trapping centers which have a considerably larger capture cross section for electrons than the traps which lead to ordinary bleaching.

If we neglect the rapid initial decay present at room temperature, it is still probable that the succeeding decay is only approximately of a monomolecular type. Since F centers in U-centered crystals bleach considerably slower on exposure to F light than do F centers in additively-colored crystals even though there is a higher conduction-band electron concentration in the former, it seems likely that more re-formation of F centers occurs in U-centered than in additively-colored crystals. If the flow of electrons back to negative-ion vacancies is much smaller than the flow from F centers to the conduction band, however, the observed decay

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of F-center concentration will still be at least approximately exponential, as observed.

The temperature increase from 25 to 125°C apparently increases k_1 by a factor of 72. A similar increase in k_1 produced by an increase in light intensity by a factor of 72 would cause an increase in c_0 by this same factor. The results of Part (d) of this section show, however, that the same temperature increase enlarges c_0 by no more than a factor of about four. It is, therefore, obvious that the temperature increase differs from the light-intensity increase in enlarging the concentration of traps other than negative-ion vacancies and thereby reducing the flow of conduction electrons back to negative-ion vacancies. This contention is borne out by the observation that a 72-fold increase in light intensity at room temperatures produces a very much smaller increase in bleaching rate than the temperature increase which increases the decay constant by 72 times. Evidently the receiving end of the process is the determining factor.

In addition to observing optically the build-up on exposure to gamma radiation of the F band and the decay of the U band using a U-centered crystal less than 1 mm thick, optical bleaching at room temperature was carried out on the same crystal after a total gamma-ray exposure of 1.5×10^5 roentgens. At this exposure, the U band was greatly reduced and more than 10^{17} F centers per cm^3 had been formed. There were no absorption bands observable in the range from 200 to 800 mμ other than the U and F bands. Bleaching was carried out with a 750-watt tungsten bulb in the slide projector without a heat filter so that some heating occurred. Glass lenses served to keep any U-band light from reaching the crystal. As F-band bleaching progressed, the U band was re-formed.[38] On the basis of equal oscillator strengths, fewer U centers were re-formed than F centers destroyed, although the reverse process indicated that an F center was produced for each U center destroyed by gamma radiation. In fact, additional absorption in the long-wavelength tail of the F band became apparent after considerable bleaching. Such absorption probably arises from M and R centers or colloidal metal aggregates.[26] Since the spectrum of the bleaching light employed extended to the wavelengths of this absorption, further bleaching eventually reduced this long-wavelength absorption as well as the F band. These results indicate that the efficiency of the F-to-U conversion is less than 80 percent a few degrees above room temperature, and that M or R centers, or both, may be formed. The absorption coefficients for the various bands were in good agreement with the hypothesis that those F centers which, on bleaching, did not re-form U centers formed M or R centers instead. The F-to-U conversion during bleaching probably occurs in the following sequence. Since it is reasonable to expect a small attachment force to exist between a negative-ion vacancy and a hydrogen atom, a negative-ion vacancy produced from an F center by photoionization first captures a hydrogen atom, then a conduction-band electron is captured by the vacancy-atom complex, and thus a U center is re-formed. The first part of the process should require a much greater time than the latter part and should be quite temperature-dependent. Alternatively, it may be possible that an interstitial hydrogen atom might capture an electron to form a hydrogen negative ion. This ion might then wander until captured by a halogen negative-ion vacancy to re-form a U center.

At room temperature even in the dark, there is considerable probability that a hydrogen-atom:negative-ion-vacancy complex will eventually capture a conduction-band electron and re-form a U center. This process probably accounts for the growth of the U band during dark storage observed by Alger[38] in a U-centered crystal containing F centers after partial F-center bleaching. At very low temperatures, this probability will be negligible because of the virtual absence of free electrons in the dark. If a number of such complexes have been formed at room temperature and the crystal is then cooled with liquid nitrogen or helium, another mechanism may be envisioned whereby U centers can be re-formed. This mechanism involves the absorption of a light quantum by the valence-band electron of a negative ion situated close to a given complex. If radiation of about 1030 mμ is absorbed by KBr, just sufficient energy will be given a valence electron to raise it to a U-center energy state, and a U center and a hole will be formed. This absorption band is likely to be exceedingly weak because of the limited concentration of complexes which can be formed at room tem-

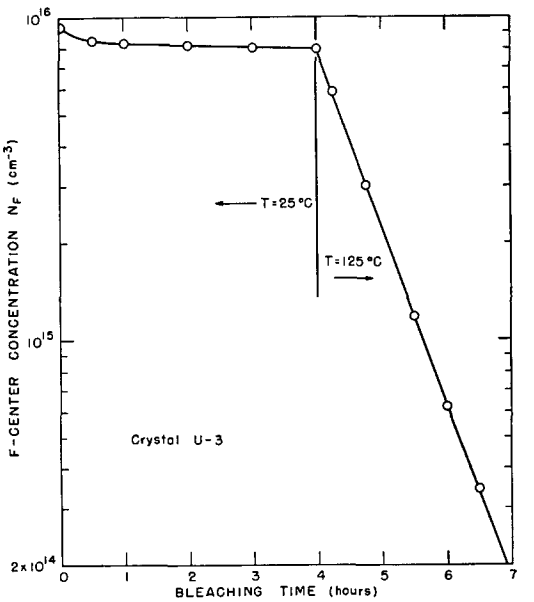

FIG. 19. Optical bleaching of F centers at two temperatures.

[38] In agreement with unpublished observations of R. S. Alger (private communication).

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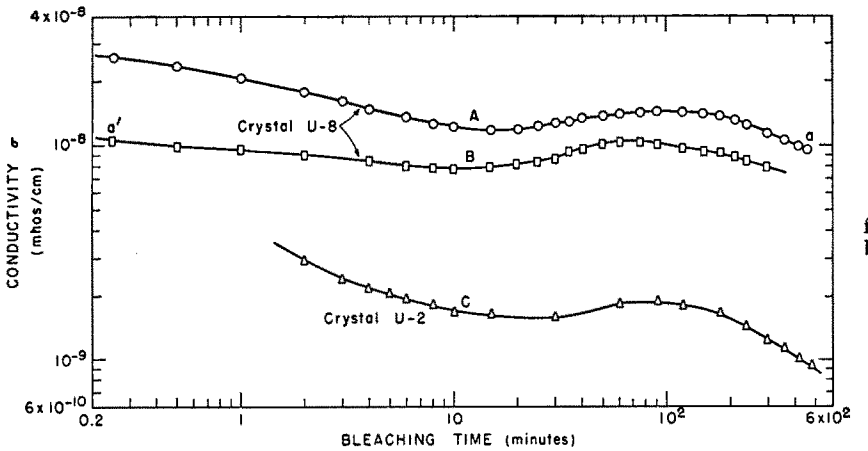

FIG. 20. Dependence of high-frequency conductivity on optical bleaching time.

perature even in the dark, and it may be below the range of detection with present techniques.

Finally, Fig. 20 presents measurements of the conductivity at 10^4 cps of two F-centered crystals *vs* bleaching time using the 500-watt bulb, slide projector, and heat filter 3962. These curves are, therefore, a measure of the variation of conduction-band electron concentration with bleaching time. The curve shape is surprising in that it shows both a minimum and a maximum, and these points occur at approximately the same times for all three curves. Curve A is the initial bleaching curve for crystal U-8. After a day of bleaching, the crystal was left in the dark overnight and bleaching resumed the next day. Curve B shows the results obtained during the second day. Note that c_0 is slightly increased after a night in the dark, possibly indicating the presence of fewer traps at time a' than at time a.

The bottom curve C was measured under the same conditions as the top curves for a crystal which was first exposed to gamma radiation until about 5×10^{15} cm^{-3} F centers were produced, then bleached until most of these centers were destroyed, and finally re-exposed to radiation to produce about the same F-center concentration. In spite of this complicated history and the probable formation of some M and R centers during the first bleaching, the curve shape is of the same character as that of the upper two curves. Note that the vertical separation between the curves for crystals U-8 and U-2 is about doubled over that for the same crystals in Fig. 18. The relative decrease in c_0 for U-8 is almost certainly due to the formation of additional electron traps in this crystal by bleaching and re-dosing.

(g) Direct Current Measurements

Direct current measurements of capacitative effects connected with electron motion must be carried out in a time short compared to that necessary for appreciable positive-ion vacancy polarization to be established. All such measurements on a wide variety of crystals confirmed the lack of dependence of C_0 on light intensity, temperature, applied voltage up to 1000 volts dc, and F-center concentration. Measurements on crystals with rectifying electrodes consistently gave larger values of C_0 than when blocking electrodes were employed; in addition, it is worth noting that no dependence of C_0 on polarity was observed for a crystal with one blocking, one rectifying electrode.

Figure 21 shows the dependence of charging current on time for an F-centered crystal with relatively low illumination, about 10^{-3} of the maximum used in this work. One thousand volts was applied to this crystal at $t=0$. The initial drop, extending over the first minute or two is probably due to polarization set up by electronic motion, since variation in light intensity changed the current during this time. The drop apparent after 10 minutes may be due to vacancy motion; light caused little change in current for this region of the curve.

Discharge currents have also been measured for a few crystals. One crystal containing about 10^{16} cm^{-3} F centers and no more than 10^{18} cm^{-3} U centers which was charged with 500 volts applied for 20 hours in low ambient room light showed a particularly interesting dark discharge curve. The discharge current started near zero, reached a maximum of more than 10^{-6} amperes in 20 minutes, and thereafter decayed approximately as t^{-1} for several weeks with a decay rate very sensitive to temperature. Such behavior is quite analogous to that of electrets. An integration of the discharge-current curve yielded a total charge of about 10^{-1} coulomb! Since the geometrical capacitance of the crystal was less than one $\mu\mu$f, the effective dc dielectric constant was therefore of the order of 10^7. The above charge storage in a space-charge layer would require a normal concentration of mobile charges of almost 10^{22} cm^{-3}. This large a concentration is difficult to explain. This crystal was not well moisture-proofed and had been kept in a moist atmosphere for four months prior to measurement. Further, heating at 125°C for 30 minutes destroyed its ability to store such large charges. It is therefore likely that the effects observed arose from a reversible electrode reaction at

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the interface between crystal and silver electrode analogous to that of a storage battery. All other crystals showed more normal charge storage consistent with a concentration of about 10^{17} cm^{-3} positive-ion vacancies.

A number of experiments were carried out in which a crystal was charged while strongly illuminated, the light extinguished, and the crystal then discharged in total darkness. In order to obtain the total charge stored in the crystal, discharge into the polystyrene sink capacitor for more than an hour was usually required. No difficulties from vacancy motion were thought to arise in such measurements because the charging time could be made sufficiently short that negligible vacancy polarization could occur. This experiment showed that if the discharge time were made sufficiently long, the same value of C_0 would be obtained for dark discharge as for discharge with the crystal illuminated. Such dark discharge is very slow since it must occur through the motion of the very few conduction-band electrons present in the dark.

When a dc voltage is applied to a well insulated, illuminated crystal containing F centers, electrons will leave the crystal at a rectifying anode and cannot reenter except by leakage or breakdown after the charging voltage is removed. During the time the electrons leak back in, the crystal is positively charged and should attract negative charges. Macroscopic indication of such behavior was observed with several crystals by charging an illuminated crystal with 10^3 volts, removing the applied voltage, and then using the crystal to attract small bits of paper. Such attraction lasted for as long as an hour. Since the sign of the crystal charge was not determined in these experiments, it is not conclusively established that the observed behavior arose from missing electrons; it is possible that positive-ion vacancy polarization was also of importance here.

IV. DISCUSSION OF RESULTS

Space is unavailable for a complete discussion of the present results, nor is such a discussion warranted by the limited data presented herein. We shall, however, summarize certain tentative conclusions suggested by the data. First, it seems clear that the capacitative effects observed are only indirectly, if at all, connected with space-charge formation. They most probably arise from a charge-free layer containing no F centers located between one or both electrodes and the bulk of the crystal. Such layers may arise from diffusion of negative-ion vacancies to the surface of the crystal. Although it was found that there was a significant difference in frequency dependence of parallel capacitance and conductance depending on whether electrodes were blocking or rectifying, for most purposes the electrical properties of a photoconducting crystal can be represented by a frequency-independent capacitance C_0 in series with the normal conductance G_∞ of the crystal appropriate to the light level employed. Even though

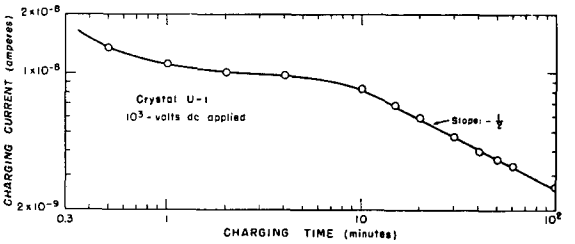

FIG. 21. Decay with time of dc charging current of an illuminated crystal.

the capacitance C_0 does not arise from space-charge formation, the small voltage-dependent nonlinearity observed almost certainly does. Space-charge capacitative effects were probably not observed because the space-charge capacitance was in series with the much smaller charge-free layer capacitance C_0.

The observed linear dependence of G_∞ on light intensity can arise either from monomolecular recombination of electrons with traps whose concentration N_T is independent of F-center concentration N_F or from recombination with traps whose concentration is proportional to N_F, such as F-centers themselves. In the first case, G_∞ should be proportional to N_F; in the second, independent of it. As shown by Fig. 18, monomolecular recombination seems to be dominant at low values of N_F; however, for F-center concentrations greater than about 5×10^{14} cm^{-3}, the type of recombination goes through a transition region until the second type is dominant for $N_F=5\times10^{15}$ cm^{-3} or greater. Since the linear dependence on light held up to the highest intensities available, it is clear that for both types of recombination, the empty trap concentration must always be considerably greater than that of filled traps.

In the U-centered crystals with which we are here concerned, there will be a high concentration of U centers before any gamma-ray dosing and a low concentration of F centers. In addition, there will be some hydrogen atoms at interstitial positions in the lattice left from the original U-centering process. The initial, monomolecular traps mentioned above must be relatively independent of F-center concentration below $N_F\simeq5\times10^{14}$ cm^{-3} and might possibly be either U centers themselves or interstitial hydrogen atoms. It is unlikely, however, that U centers play such a role because their concentration is essentially independent of N_F until N_F reaches 5×10^{16} cm^{-3} or more. It is therefore likely that the initial shallow traps are interstitial hydrogen atoms which can capture an electron to form hydrogen negative ions. As N_F increases from its low initial value, the conversion of U centers to F centers will produce new interstitial hydrogen atoms proportional to N_F. When the concentration of hydrogen atoms thus produced becomes comparable to those initially present, recombination will cease being monomolecular and G_∞ will tend towards independence

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of N_F. Since electron binding in hydrogen-atom traps will be small, a large fraction of them may be expected to be empty on the average because of thermal ionization. They may thus play the role of the shallow traps envisioned in Section III-c to explain dark conduction and dark conductivity decay and in Section III-d to explain temperature dependence results.

Although hydrogen-atom traps can apparently explain many of the experimental results in U-centered crystals, it must be mentioned that F'-center formation may also be of importance, especially when N_F is of the order of 10^{15} cm^{-3} or greater. At -100°C Pohl found that the mean range of electrons in additively colored KCl crystals was inversely proportional to N_F above N_F values of about 10^{15} cm^{-3} and attributed this result to F'-center formation.[39] At room temperature or above in KBr, F' centers will be considerably less stable, but it is still possible that some of our effects arise from F'-center formation or from a combination of trapping by F centers and interstitial hydrogen atoms.

The optical bleaching behavior of Fig. 19 requires the existence of at least two different types of traps. If there is present a large concentration of shallow traps with small recombination cross section and a much smaller concentration of traps of large cross section, then the initial rapid decay of Fig. 19 will arise from the latter. Since this rapid decay region can be regenerated by dark storage, during which we know the U band increases somewhat, it is reasonable to suppose that the traps responsible for this decay are U-center precursors. During dark storage, interstitial hydrogen atoms perhaps move about until they become attached to negative-ion vacancies or to negative- and positive-ion vacancy pairs. These U-center precursors will have a large electron recombination cross section, and those which were formed during dark storage but did not capture electrons to form U centers will rapidly do so when the conduction-band electron concentration is increased by illumination. As we have seen in Section III (f), although a temperature increase to 125°C does not increase c_0 very much, it does increase the bleaching rate greatly. The temperature rise must therefore much increase the formation rate of empty deep traps which can hold electrons more or less permanently at this temperature. Since the hydrogen-atom diffusion rate will increase strongly with temperature, it is probable that at 125°C the rapid monomolecular bleaching of F centers observed is again due to electron capture by U-center precursors formed at a greatly increased rate at this temperature in an illuminated crystal. The increase in the deep trap concentration will tend to reduce c_0; the relatively small increase observed probably arises from the over-riding effect of increased thermal ionization of the shallow traps.

Data are insufficient to make it worthwhile to attempt a detailed explanation of the conductivity decay curves of Fig. 20. It is probable that they can be largely explained in terms of trapping by the two above kinds of traps, although the maxima reached after about 100 minutes of bleaching are difficult to interpret. Although much of the previous data were explained in terms of only two principal types of traps, it is quite possible that trapping by M and R centers, colloidal metal aggregates, dislocations, etc., may also be of importance. Unfortunately, many of the explanations of the results presented in this work were reached after the experiments were completed. It is obvious that many further experiments could be carried out to check and extend the present results and explanations, and it is hoped that this study will stimulate others to do so.

[39] Reference 15, p. 126.

ACKNOWLEDGMENTS

I wish to thank Dr. P. Pringsheim, Dr. P. H. Yuster, and Dr. C. Delbecq of the Argonne National Laboratory and Professor F. Seitz and Professor R. J. Maurer of the University of Illinois for many valuable discussions. I welcome this opportunity to express my appreciation to the Argonne National Laboratory and especially to Dr. O. C. Simpson for a visiting appointment.

APPENDIX I. CRYSTAL PREPARATION

The alkali-halide crystals employed in this investigation were all potassium bromide obtained from the Harshaw Chemical Company. These crystals were treated in various ways. Several were additively F centered[15] by prolonged heating at 500°C in sodium vapor to produce approximately 1.5×10^{16} F centers per cm^3 homogeneously distributed within the crystals. The F-center concentration was determined from the optical absorption coefficient at the F-band maximum. As shown by Hilsch and Pohl,[37] the F-center concentration N_F is proportional to this coefficient.

In addition, a large number of crystals were U centered. A U center is thought to be a hydrogen negative ion trapped at the site of a missing halogen ion in the crystal lattice.[40] Thus, an F center, which is an electron trapped in a negative-ion vacancy, can be converted into a U center by the addition of a hydrogen atom. The F-absorption band maximum for potassium bromide at room temperature occurs in the visible at 620 mμ, whereas the wavelength of maximum absorption by U centers is located in the ultraviolet at about 228 mμ. Crystals were U centered by first being additively F centered with potassium vapor for 15 hours at 600°C. This treatment produces a maximum concentration of F centers approaching 10^{18} cm^{-3} and renders the crystals opaque. Without cooling, the potassium vapor is then trapped out and hydrogen admitted to the Pyrex reaction chamber. A slow flow of hydrogen is maintained for 40 to 50 hours and then the crystals are rapidly cooled to room temperature. Almost all of

[40] Reference 15, p. 147.

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the F centers are converted to U centers by this process and the crystals are transparent in the visible once more. The above procedure is essentially a single-stage process since the crystals are not cooled to room temperature after being additively F centered. A two-stage process where such cooling does occur has been described by Friedman and Glover.[41]

The photoconductivity with which we are concerned in the present paper arises principally from the optical excitation of electrons from F centers to the conduction band. It is thus desirable to have available a method of easily producing a given concentration of F centers homogeneously distributed in a crystal. The gamma-ray conversion of U centers to F centers furnishes us with such a method. When a U-centered crystal containing about 10^{18} U centers per cm^3 is exposed to penetrating gamma rays such as the radiation of Co^{60}, some U centers are converted to F centers. The dependence of F-center concentration on dosage is linear until the number of F centers produced approaches the number of U centers originally available, and this does not occur for our crystals until about 10^4 roentgens have been received. Since the absorption coefficient of the crystal for gamma rays of the 1-Mev energy range is very low, the F-center distribution formed in this way is essentially as uniform as the original U-center distribution.

In addition to allowing F-center concentrations to be conveniently controlled, the U- to F-center conversion yields another important advantage which makes U-centered crystals more suitable for the present work than additively-colored ones. This advantage is that F centers produced in U-centered crystals by the U to F conversion bleach out on exposure to F-band light much less rapidly than do F centers produced by additive coloring. Thermal bleaching of F centers is also exceedingly slow in U-centered crystals. This slower bleaching is probably connected with the presence of fewer deep electron traps in U-centered crystals than in additively colored ones. An added advantage of the presence of fewer traps in U-centered crystals is that for a given light intensity and given concentration of F centers the equilibrium concentration of electrons in the conduction band will be higher in the U-centered than in the additively-colored crystal; the former will thus be more photoconducting.

Two general types of specimens have been prepared from plain potassium bromide single crystals, from additively colored, and from U-centered crystals. These two types of specimens will be referred to as Types I and II. In the first type, a square crystal was cleaved to a thickness of between one and six mm. The area of the sheet was about 5 cm^2. On one side of this sheet a heavy mirror coating of aluminum was evaporated, and on the other side a thin aluminum coating of about 70 percent light transmission in the visible was evaporated. After evaporation, the edges of the crystal were carefully ground to remove any aluminum which might have shorted the coatings together. These metallic coatings served as electrodes with incident light passing into the crystal through the front electrode and being reflected at the back electrode. This arrangement helped to make the light intensity within the crystal more uniform. It was largely unnecessary, however, since the F-center concentrations used were always sufficiently low that there was little decrease in F-band light intensity for light passing through the crystal. In the other general type of specimen, the crystals were parallelopipeds as long as 2 cm with air-drying silver paint electrodes applied to square end faces of about 0.5 cm^2 area. For these samples, light passed transversely into the crystal between the electrodes. In all cases contacts were made to the metallic electrodes by attaching fine wires to them with silver paint.

Since metallic electrodes directly on the crystal gave rectifying contacts, a number of crystals of the second type were made up to have blocking electrodes. This was accomplished by gluing 0.01 to 0.05 mm thick clear mica sheets to the ends of the crystals with polystyrene coil dope. The mica projected well beyond the edges of the crystals. Then silver-paint electrodes were painted on the outside of the mica. The series capacitance/cm^2 of two such mica layers between crystal and metal is of the order of 40 to 200 $\mu\mu$f/cm^2.

The final stage in specimen preparation involved heating the samples for an hour at 120°C in the dark and then dipping them in molten ceresin wax. This procedure was necessary to eliminate surface conductivity in these hygroscopic crystals. The wax coating was very thin over the semitransparent aluminum electrode or, in some cases, was removed entirely from this electrode without deleterious effects. Finally, the samples were mounted on flat polystyrene holders attached to General Radio double banana polystyrene plugs. The electrode wires were then connected to the plugs, and the sample thus made a compact, rigid unit which could be directly plugged into a capacitance bridge. A summary of some of the pertinent characteristics of the principal samples used in the present work is presented in Table III.

TABLE III. Summary of sample treatment, type, dimensions, and measured dark capacitance.

Sample	Treatment	Type	Electrode area (cm^2)	Electrode separation (mm)	C_d (including fringing) ($\mu\mu$f)
U-1	U centered	I	4.81	2.02	11.3
U-2	U centered	I	4.81	5.42	3.9
U-3	U centered	...	...	...	...
U-5	U centered	II	0.443	12.9	0.4_0
U-6	U centered	II	0.540	14.4	0.4_0
U-8	U centered	II	2.00	10.0	1.3
AF-1	Additively F centered	I	4.83	1.57	14.5
K-2	Untreated	I	4.84	1.46	15.8

[41] H. Friedman and C. P. Glover, Nucleonics **10**, 24 (1952).

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APPENDIX II. EXPERIMENTAL DETAILS

The principal light source used to produce photoconductivity in F-centered crystals was a slide projector employing a tungsten filament bulb of either 500 or 750 watts. Such a source has a high light output at 620 mμ. The entire output of the slide projector was sometimes focused on the crystals by means of lenses of 12- or 20-cm focal length. To avoid heating during such exposure, glass heat filters[42] were usually employed. In order to investigate the effect of light intensity, it was desirable to have some means of controlling the intensity precisely. Only light in the F-absorption band is effective in producing photoconductivity in these crystals, but the F band is so wide that gelatin neutral-density filters could not be employed for this purpose because of their wide density variations over the F band. To overcome this difficulty, perforated metal sheet filters which were truly neutral were employed. Their transmittance was calibrated with both a Beckman Model B spectrophotometer and a Cary Recording spectrophotometer, Model 11. These same instruments were also employed for transmittance measurements on the alkali halide crystals used in the investigation. It may be pointed out that although the gelatin neutral-density filters could have been used in conjunction with an interference filter transmitting in the F band, the use of such an interference filter was found to reduce the maximum available light intensity below a desirable level.

Most of the measurements reported in this paper were of sample capacitance and conductance at frequencies between 6 and 5×10^4 cps. Such measurements were carried out by the substitution method using a General Radio Type 716-C capacitance bridge in conjunction with a Type 722-D variable air capacitor for initial balance. To eliminate the capacitance of the sample holder and leads, the initial balance was made using a dummy holder containing leads but no crystal. The ac source employed was a Hewlett-Packard Model 202-B oscillator. The ac voltage applied to the crystals seldom exceeded five volts. The output of the bridge was amplified by a battery-operated Tektronix preamplifier having a gain of 1000 and was displayed on a Dumont Type 304-A oscillograph. To reduce residual 60-cycle pickup from the unshielded sample, a parallel-T rejection filter tuned to this frequency was also employed. For accurate frequency setting, either a 60-cycle line-voltage signal or the output of an electrically-driven 1000-cycle tuning fork was connected to the horizontal oscillograph input and the appropriate Lissajous figure produced by varying the oscillator frequency. Individual measurements were made in a period of a few seconds and the light extinguished between measurements to avoid heating of the specimen. Whenever sufficiently high light intensities were employed that appreciable bleaching was apparent during the course of a series of measurements, the measurements were repeated in reverse order. Since bleaching was always small enough during a set of frequency response measurements that it could be considered linear with time, an average of ascending and descending results substantially removed the effects of such variation.

In order to measure any harmonics produced by nonlinearity of these crystals and to measure the total admittance for large applied ac voltages, 60-cycle line voltages as high as several thousand volts were passed through a three-section RC filter to reduce harmonic content and then applied to the crystals. The voltage developed across a resistance of 4×10^4 to 10^5 ohms in series with the crystal was amplified by a preamplifier of gain 100 or 1000 and the harmonic content of this voltage measured with a Hewlett-Packard wave analyzer. To avoid overloading the preamplifier, the 60-cycle component of the voltage applied to it was greatly reduced using the parallel-T 60-cycle rejection filter. The ratio of the voltage of any given harmonic across the series resistance to the fundamental 60-cycle component is then the ratio of harmonic and fundamental currents in the photoconducting crystal.

In addition to ac measurements, some measurements were also made of the dc capacitance of the specimens. Such measurements were carried out by charging the specimen with 1000 volts, then discharging it into a 30-second-period Leeds and Northrup ballistic galvanometer calibrated in terms of capacitance. An Aryton shunt slightly under-damping the galvanometer was used in such measurements. In some cases, the specimens required more than five seconds to discharge. To allow measurements of capacitance to be obtained for longer discharge times, the specimens were first discharged as long as necessary into a 0.1 μf polystyrene-dielectric capacitor. This capacitor had negligible charge absorption and leakage and would hold a charge for a week or more with little or no decay. After the specimens were completely discharged into the polystyrene capacitor, it in turn was discharged into the galvanometer and the total dc capacitance thus determined.

The ballistic galvanometer was sometimes used as a current-indicating instrument to observe charging or discharging currents and to determine leakage or residual sample resistance. This latter quantity was also measured more accurately by using the sample whose resistance was to be determined as a resistance in series with the polystyrene capacitor and the voltage source. After a given period of time, the charge which had leaked into this capacitor was measured by the galvanometer used ballistically, and, from this result the series resistance could be computed. In such measurements, it was necessary to apply the charging voltage for about an hour to allow initial polarization currents to decay to a quasi-equilibrium value before beginning charge integration in the polystyrene capacitor.

In all these dc measurements, involving as they did a

[42] Corning, numbers 3961 or 3962.

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1000-volt source of voltage and an extremely sensitive galvanometer, special care had to be exercised to reduce leakage currents in the apparatus to negligible values. The crystal specimen to be measured was plugged into contacts on a polystyrene strip mounted on porcelain stand-off insulators. These contacts were connected to the movable center contacts of a D.P.D.T. relay all of whose contacts had been remounted on polystyrene. In the unenergized condition, the crystal was connected to the 1000-volt supply voltage; in the energized condition it was connected to the galvanometer or to the polystyrene capacitor. Relay switching was necessary so that the sample could be completely enclosed within a light-tight box for measurements of capacitance *versus* light intensity while charging and discharging. In addition to being able to control the charging and discharging of the specimen from outside the box, the polarity of the voltage applied to the crystal could be similarly controlled by means of a D.P.D.T. impulse relay. This polarity was reversed after each charge-discharge cycle to reduce ionic and ionic-vacancy polarization effects as much as possible.

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A Theory of Thermal Diffusion in Liquids*

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A theory of thermal diffusion in liquids has been developed based on Denbigh's interpretation of the "net heat of transport" which arises in the thermodynamics of irreversible processes. The thermal diffusion ratio α is expressed in terms of the energies of vaporization of the pure components, the excess energy, entropy and volume of mixing, and the concentration dependence of ΔU_e. The efficiency with which the two species pack together is also introduced. The Hildebrand-Scatchard solution theory is applied to these results and α is expressed in terms of solubility parameters, molal volumes and packing efficiencies.

The equations are compared with previously published experimental results, and reasonably explainable packing efficiencies are obtained.

In the appendices the effects of nonrandomness of mixing are considered and the theory is extended to ternary mixtures.

IN a recent paper by Rutherford and Drickamer,[1] a theory of thermal diffusion in liquids was presented. This theory is based on a molecular interpretation of the "net heat of transport" due to Denbigh[2] and is an attempt to give a quantitative measure of the average intermolecular potentials defined in regular solution theory in terms of known thermodynamic properties of the pure liquids. The theory of Denbigh was extended by introducing a correction for differences in size and shape of the molecules. In reference 1 and succeeding papers[3–6] the theory is compared to experimentally determined thermal diffusion ratios for a wide variety of systems both at atmospheric pressure and under pressure to 10 000 atmospheres.

In this paper Denbigh's interpretation of the "net heat of transport" is reconsidered. Expressions for the energy quantities which appear in the theory are obtained in terms of partial molal "cohesive" energies of the components in the solution. In this manner a general expression for the thermal diffusion ratio α is obtained which involves only the heats of vaporization of the pure components, the excess energy, entropy and volume of mixing, and the slope of the excess energy-composition curve.

The Hildebrand-Scatchard[7,8] expressions for the heat of mixing and chemical potential are then introduced to give an expression for α in terms of properties of the pure components and the composition of the solution. This theory has a much firmer foundation than the previous one[1] since no assumptions concerning energy relationships in the solution are involved which have not been accepted as reasonable approximations in solution theory for 25 years. In the light of the revised theory, the data included in the above papers[1,3–6] have been reinterpreted.

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