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Mahlman, Nottingham, Slater

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PHOTOCONDUCTIVITY OF PbS

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1. Introduction

For a number of years, a program has been underway at the Electronics Corporation of America (formerly Photoswitch, Incorporated), under the auspices of the U. S. Air Force, to study the photoconductivity of PbS films. The work has been directed by W. B. Nottingham (Photoswitch and M. I. T.), Director of Research. The theoretical work has been formulated by J. C. Slater (M. I. T., consultant at Photoswitch). Experimental work has been directed by G. W. Mahlman, assisted by other physicists. This work is reported briefly in the present contribution.

The aim of the work has been to gain the maximum understanding possible of the actual operation of PbS photoconductive films, and at the same time to contribute to our theoretical understanding of the photoconductive process. Most workers in the field have felt that it was necessary to study single crystals to gain knowledge of the mechanism of photoconductivity. We have used a different approach, to draw as many conclusions as possible from chemically prepared cells similar to those in practical use. Though there is great variation from cell to cell, still there is enough uniformity so that we believe that our conclusions are valid and useful.

2. Experimental Work

Measurements have been principally of four kinds: the dark conductivity of cells as a function of temperature, down to liquid nitrogen temperatures; the conductivity under different levels of irradiance, as a function of temperature, or at given temperature as a function of irradiance; the time constant, as it depends on temperature and irradiance; and the spectral response. We shall first summarize the experimental results, then present a theoretical discussion of the major features of the cells' behavior.

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In Fig. 1 we show the conductivity, as a function of 1/T, plotted logarithmically, for a great variety of cells. The numbers attached to various cells indicate code numbers for the cells. The percentages indicate the amount of oxidation which they had received. We note that very low oxidation, or very high oxidation, lead to high conductivity at the low temperatures, but intermediate oxidations (around the value indicated by 20% to 40%) generally give high-resistance cells, which as a rule are also high-sensitivity cells. In Fig. 1, we also show for comparison a number of cells quoted by Hintenburger[1/] marked H_a, H_b, H_c; of these, H_a has low oxidation, H_b medium oxidation, H_c high oxidation. We see that H_b, which was a fairly sensitive cell, lies in the general range of some of the Photoswitch cells, though it does not have as high resistance as some. We also show several curves marked P-A, for bulk PbS, as reported by Putley and Arthur.[2/] By plotting all the cells on the same graph, it is clear that a pattern emerges: they seem to be lying closer and closer to a straight line (called Slater Line on the graph), which also is approximately tangent to the Putley-Arthur curves. The equation of this line is $\sigma = 1456 \times 10^{-1730/T}$, where σ is the conductivity in (ohm cm)$^{-1}$, and T is the absolute temperature. We shall come back to our interpretation of this line later.

In Fig. 2 we show a set of curves giving the conductivity as a function of 1/T, for a variety of irradiances, for a single cell. We see that strong enough irradiances were used to increase the conductivity by many orders of magnitude, at the lower temperatures. When the same results are exhibited in a different way, by plotting the conductivity as a function of irradiance, at a given temperature, it is found that sometimes the variation is sublinear, sometimes superlinear, without any apparent reason. A cell which showed a superlinear response at low temperatures, slightly sublinear at higher temperatures, is shown on a log-log plot in Fig. 3. To get the dark conductivity, it has been necessary at the lower temperatures to exclude room-temperature radiation, which makes a large change in conductivity under these conditions.

The time constant has been measured in two different ways. It was found early in the work that it depended very markedly on irradiance, as well as on temperature. Hence a measurement at one irradiance was by no means adequate to describe it. The first method used to measure it was to expose the cell to a fixed irradiance, which could take on different values, and to superpose on this a square-wave modulated light which, whenever possible, changed the conductivity by no more than 5%. The conductivity does not follow the square-wave signal exactly. Instead, for this small modulation, it decays approximately exponentially, and the time

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[1/] H. Hintenburger, Zeits. f. Physik 119, 1 (1942).

[2/] E. H. Putley and J. B. Arthur, Proc. Phys. Soc. B64, 616 (1951).

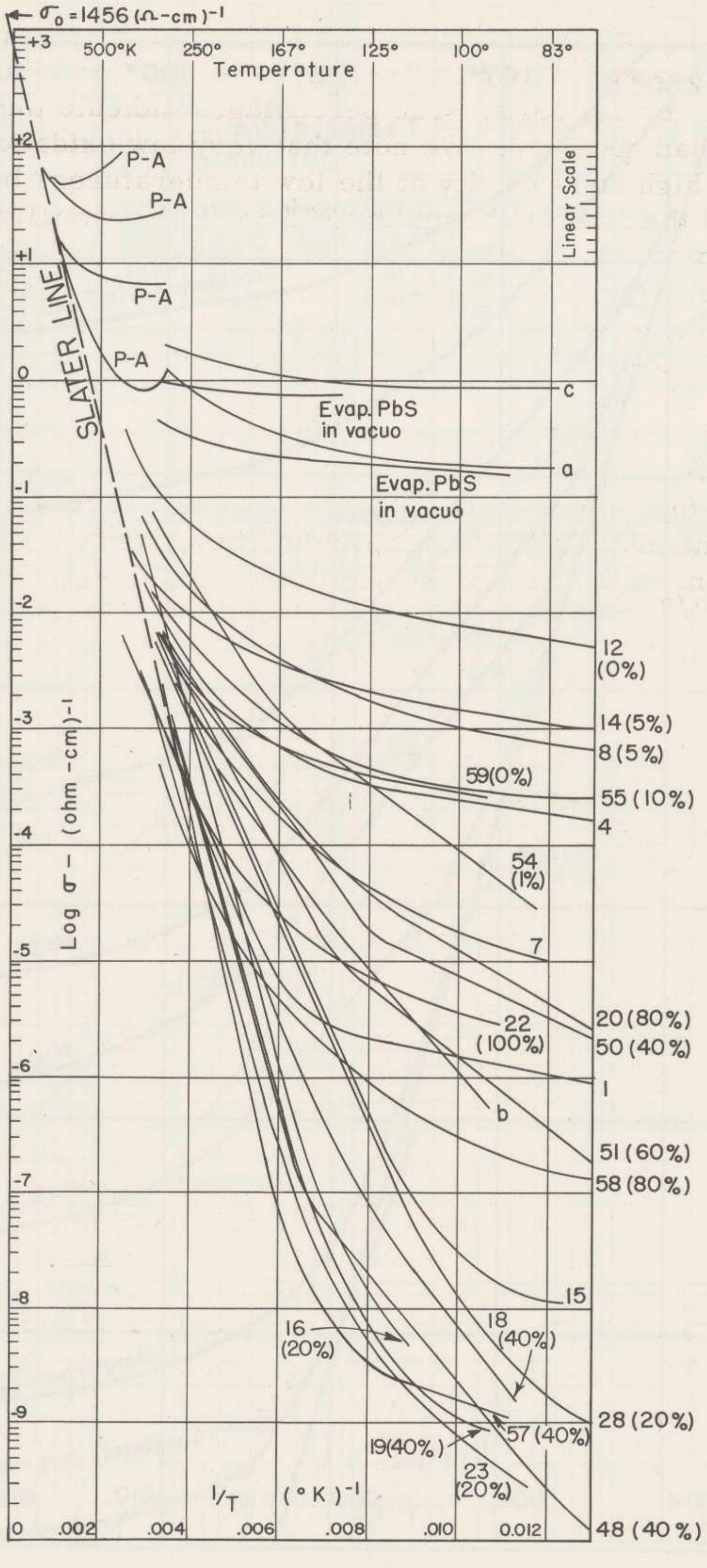

FIGURE 1 DARK CONDUCTIVITY AS A FUNCTION OF TEMPERATURE FOR A VARIETY OF PbS MATERIAL

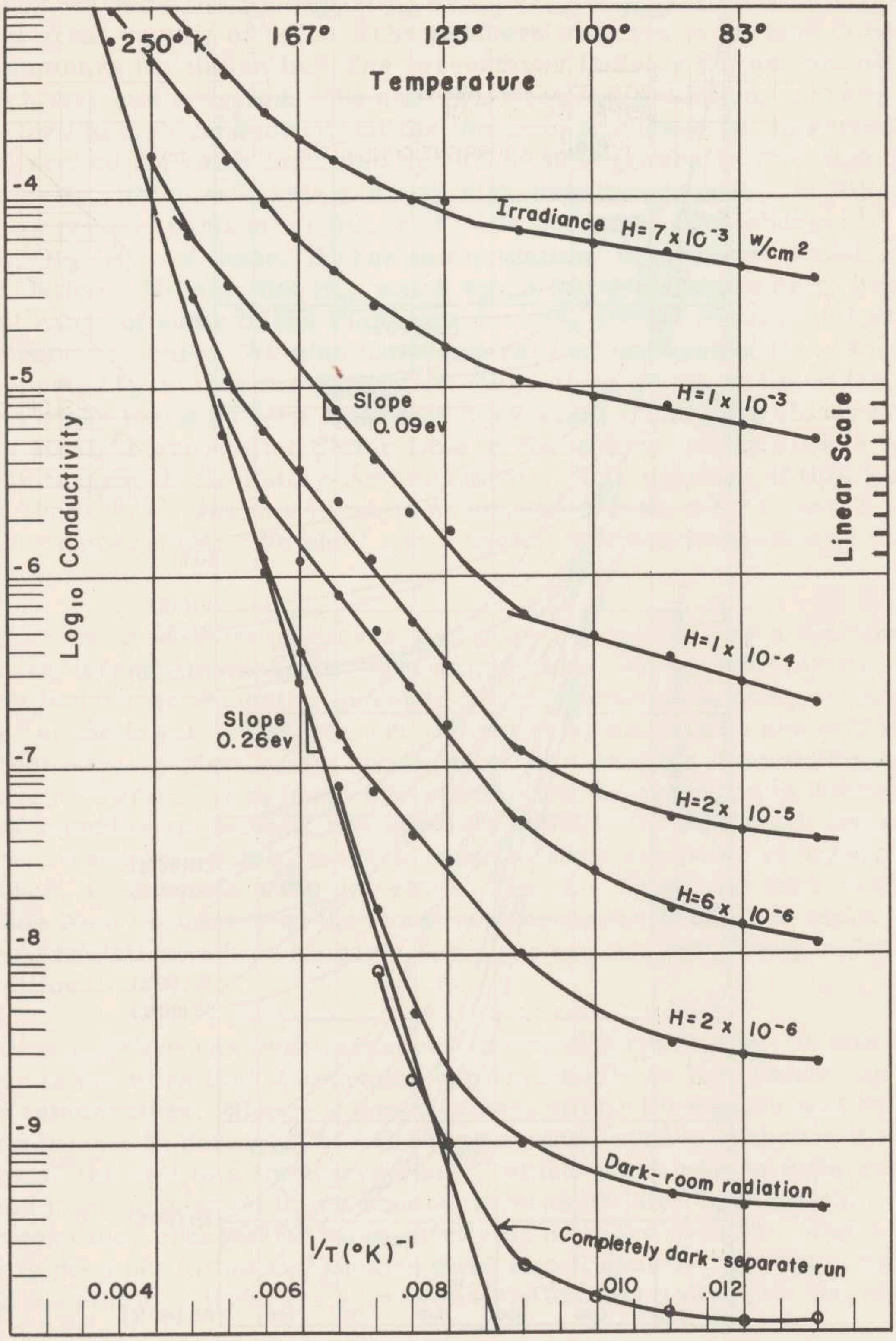

FIGURE 2 CONDUCTIVITY-TEMPERATURE CURVES AT VARIOUS IRRADIANCES FOR CELL R116X

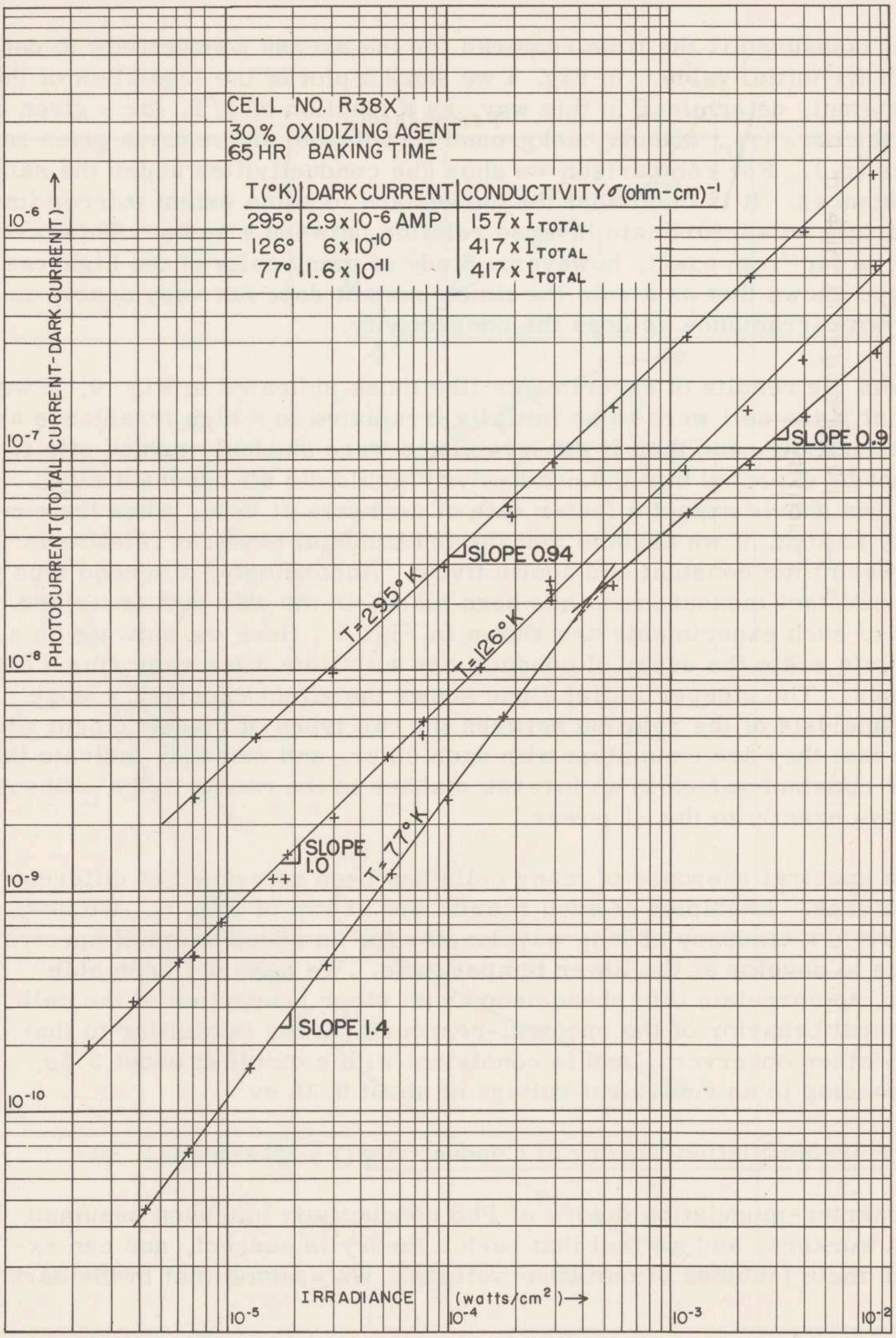

FIGURE 3 PHOTOCURRENT AS A FUNCTION OF IRRADIANCE FOR THREE DIFFERENT FILM TEMPERATURES

constant measured is the time required for the excess conductivity to decay to $1/\varepsilon$ of its initial value. In Fig. 4 we show a plot of the logarithm of the time constant, determined in this way, as a function of $1/T$, for a given cell, both in the dark (τ_D, without background irradiance) and under a given irradiance (τ_L). For comparison we show the conductivities under the same circumstances. It is clear that the curves are to some extent mirror images; they indicate an approximate inverse relation between τ and σ. This inverse relation is far from exact, however. Study of many cells of the high-resistance type shows that as a rule the time constant does not vary nearly as rapidly with irradiance as does the conductivity.

From the results of experiments like those indicated in Fig. 4, it was clear that if the cell were to be initially irradiated to a high irradiance and high conductivity, and then if the irradiance were suddenly turned off, it would not be expected that the conductivity would die off exponentially. Rather, we should expect a faster rate of decrease at first, when the conductivity is high, if we assume that the fundamental physical relation is one between time constant and conductivity. Accordingly, a second type of time constant measurement has been made, in the way just described. Results of such experiments are shown in Fig. 5. Here we indicate on a logarithmic scale the decay of conductivity with time after removing a high irradiance. The steeper initial slope shows the effect expected. More careful analysis of the relation between the two types of measurement seems to show that they are consistent with each other, and that they indicate that the time constant varies in an inverse manner to the conductivity, although not always exactly to the -1 power.

The spectral response of many cells has been measured at different temperatures. Examples of such results are shown in Fig. 6. We see that there is a tendency at long wavelengths for an added hump of spectral response to develop at the lower temperature. We have not been able however, to correlate this phenomenon with other properties of the cell. The general behavior of the spectral-response curves is similar to that found by other observers, and is consistent with a cutoff at about 3.5μ, corresponding to an equivalent voltage of about 0.35 ev.

3. Barrier-Modulation Theory of Conductivity

A barrier-modulation theory of PbS conductivity has been assumed by most workers, and we feel that such a theory is correct, and can explain the main features of our observations. We assume that in the dark

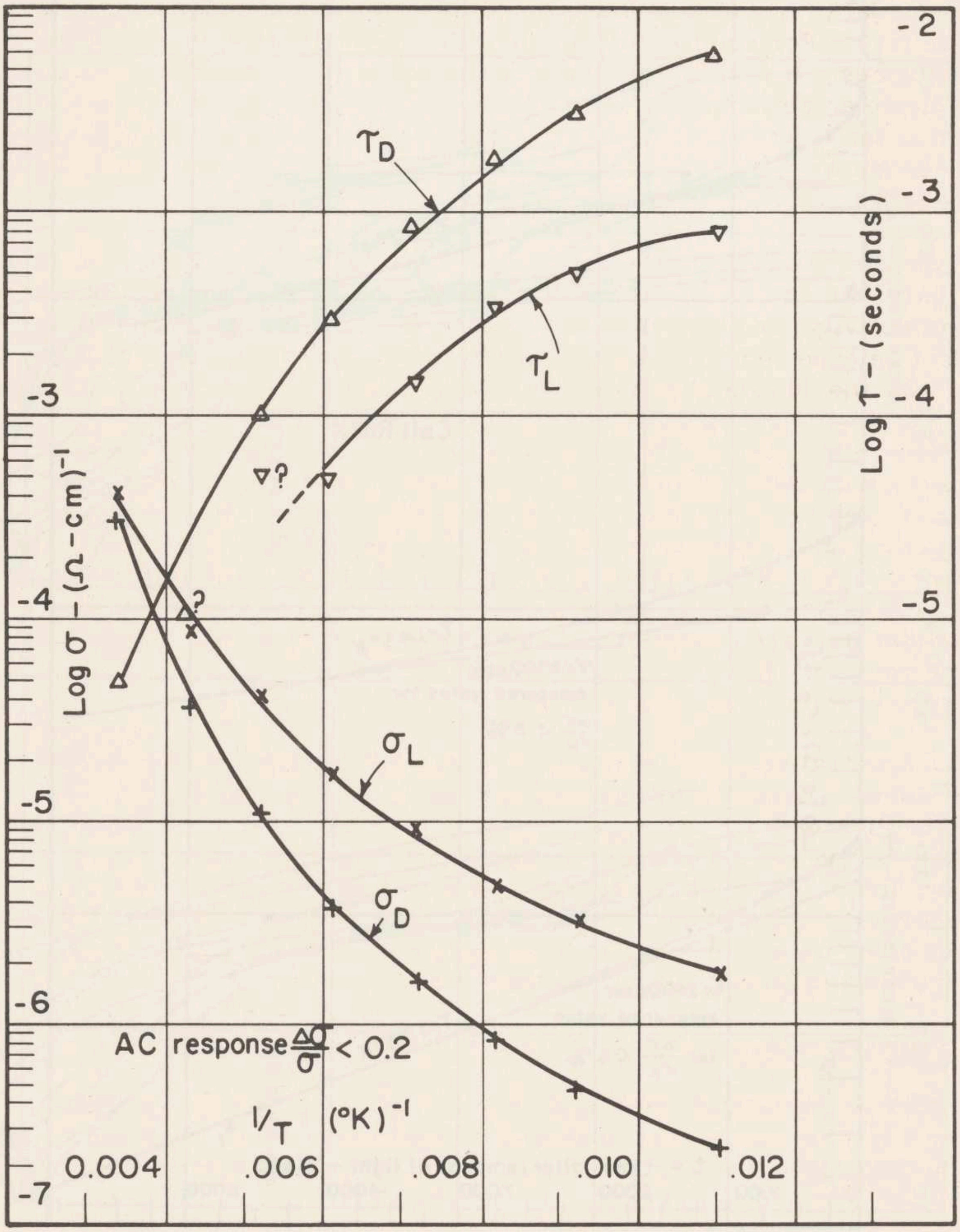

FIGURE 4 VARIATION OF TIME CONSTANTS WITH TEMPERATURES AND FILM CONDUCTIVITY

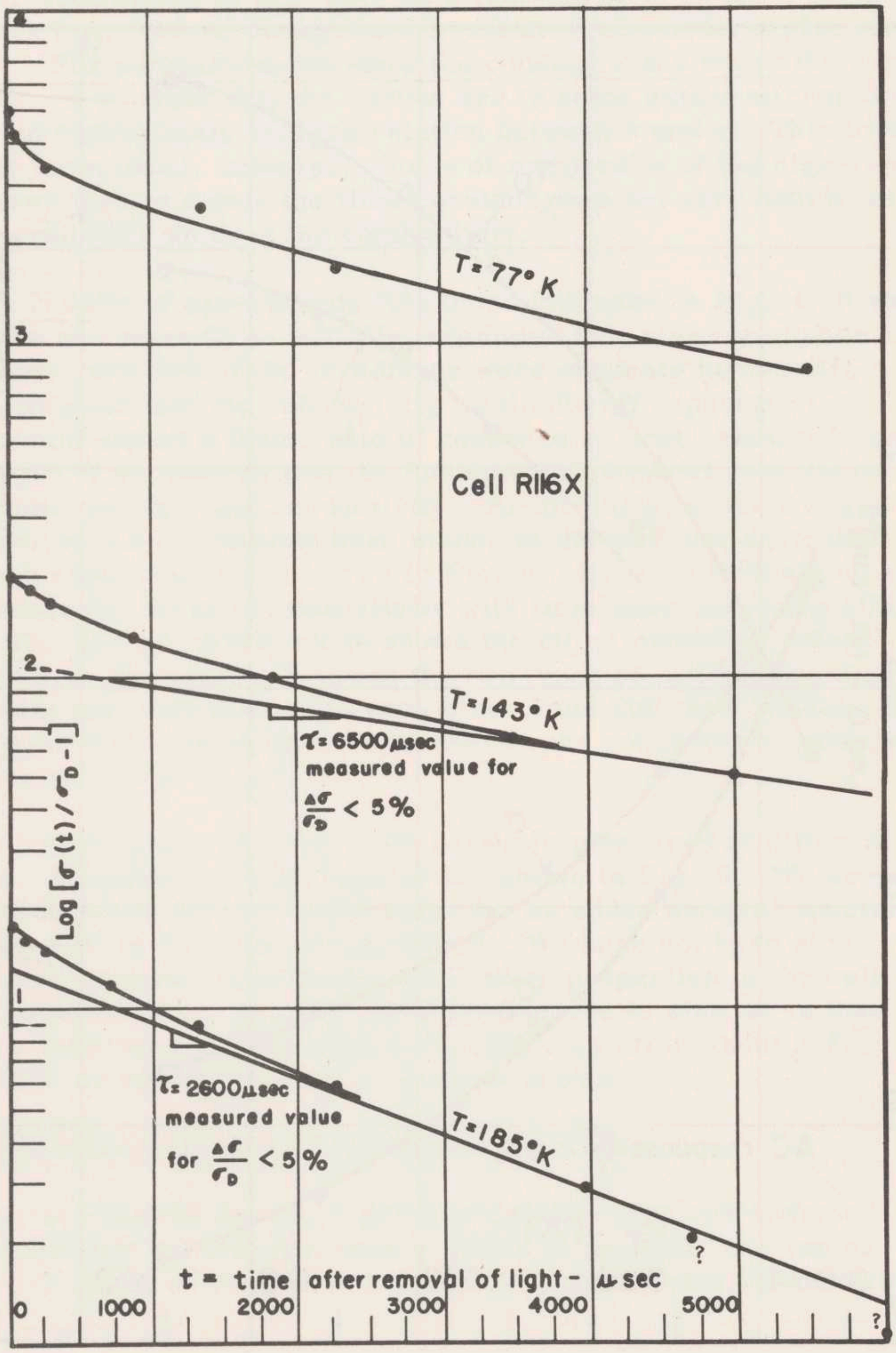

FIGURE 5 DECAY OF CONDUCTIVITY WITH TIME
FOR HIGH LEVELS OF ILLUMINATION

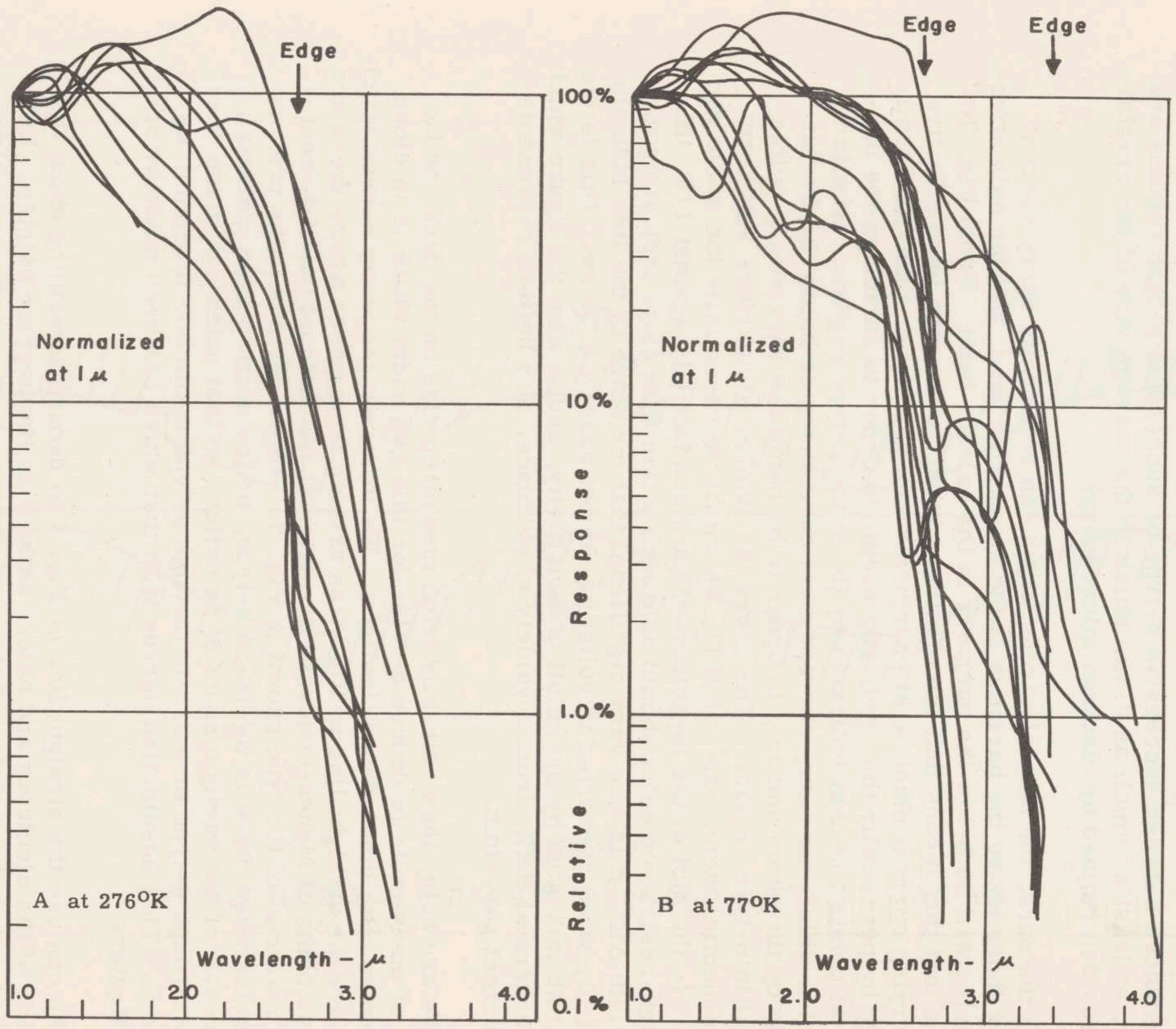

FIGURE 6 SPECTRAL RESPONSE OF PbS CELLS

the energy bands are distorted, as shown in Fig. 7. This could arise, as James[1] and others have suggested, from random fluctuations of impurities, resulting in alternating n- and p-type regions, or one type of region could be found on the surfaces of the crystallites, another type in the interior; the theory does not depend on the detailed assumption. We assume that the distances between successive n-type or successive p-type regions are small, at least as small as 0.1μ, which is the average size of the crystallites (as determined by electron microscopy).

In the dark, the only electrons which can effectively carry current will be those above the barriers in the conduction band, and the only effective holes will be below the barriers in the valence band. From Fig. 7, we see that this means that the electrons in the conduction band effective in carrying current must be at energies which are higher than the Fermi energy by practically the whole gap width, in order to surmount the barriers at points like that indicated by (b) in the p-type regions. Similarly the holes which can carry current must have energies below the Fermi energy by the same amount, in order to be below the barriers at points like (a) in n-type regions. Therefore the number of carriers will have an exponential factor $\exp(-\Delta E/kT)$, where ΔE is essentially the whole gap width. In the plot of the logarithm of dark conductivity against $1/T$, then, the high-resistance cells should approach a line with slope indicating the gap width ΔE. It is now very significant that the slope of the line indicated in Fig. 1, when converted to volts, is almost exactly 0.35 ev. This is the gap width indicated by the cutoff of sensitivity, and is also the figure which the workers at RRE, from a variety of evidence, now believe represents the correct gap width.

We are able, then, directly from measurements on the dark conductivity of many cells to deduce a value for this gap width which is in close agreement with other determinations. We interpret the many curves which lie above the straight line in Fig. 1 as arising from cases where there are devious paths of higher-conductivity material which shunt the high-resistance material of the type shown in Fig. 7. These devious paths presumably arise when there is too much n-type, or too much p-type material, as a result of the wrong amount of oxidation, so that paths can arise entirely through n-type or entirely through p-type material, involving no barriers. This assumption agrees with that which has been made by other investigators.

We can use the straight line of Fig. 1 to deduce something about the mobility of the electrons and holes, as well as the barrier heights. Let us assume that the mobility of those electrons whose energies are high

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[1] H. M. James, Science 110, 254 (1949).

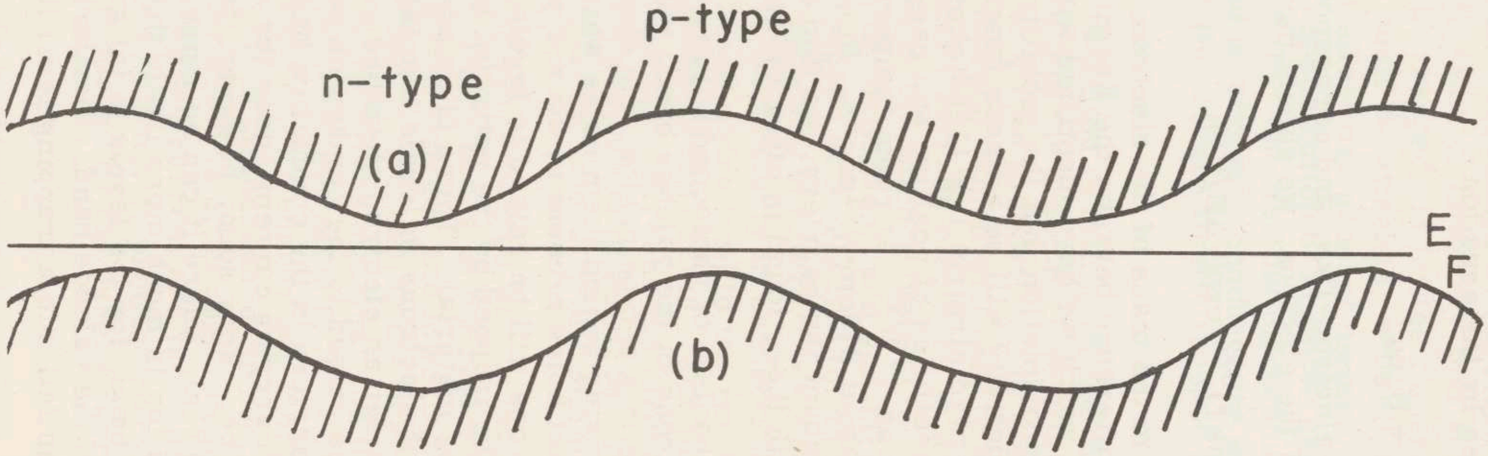

FIGURE 7

ENERGY BANDS IN A REGION OF p- AND n-TYPE BARRIERS enough to surmount the barriers is μ_e, and the mobilities of those holes with energy low enough to get below the barrier in the valence band to be μ_h. Let there be N_e such electrons per unit volume, N_h such holes. The conductivity would then be given by the equation

$$\sigma = N_h e\mu_h + N_e e\mu_e \qquad (1)$$

If the energy bands were free-electron-like, and corresponded to an effective mass equal to the mass of the electron, we should have

$$N_h = N_e = (2/h^3)\,(2\pi mkT)^{3/2}\,\exp(-\Delta E/kT), \qquad (2)$$

where h is Planck's constant, m the mass of the electron, k Boltzmann's constant, and ΔE the energy difference between the Fermi level and the top or bottom of the barriers, which we have identified with the whole gap width. If we assume as an approximation that the mobility varies as $T^{-3/2}$, then the logarithm of the conductivity will be a linear function of $1/T$. From the intercept of the observed straight line ($1456(\text{ohm-cm})^{-1}$) we can then compute the sum of the mobilities of positive and negative carriers, which will be assumed to vary as $T^{-3/2}$. At room temperature, we find that this sum of mobilities is about $370 \text{cm}^2 \text{v}^{-1} \text{sec}^{-1}$. In other words, for those particles which can surmount the barriers, we find a fairly high mobility, quite comparable with those found in other crystals.

Next we consider the mechanism of photoconductivity. Infrared radiation can be absorbed by electrons in the valence band, raising them to the conduction band. If we are in a p-type region, the electrons will be raised from levels like (b), leaving behind them holes which will be trapped by the potential barriers against holes present in the n-type region. If we are in an n-type region, electrons will be raised to levels like (a), and the electrons themselves will be trapped by the potential barriers against electrons present in this p-type material. There is an additional mechanism leading to the trapping of electrons in levels like (a), and of holes in levels like (b). Let us consider an electron absorbed in p-type material, from a level like (b). It will be raised to the conduction band, with an energy high enough to surmount the barriers in the conduction band. It will start traveling through the crystal, carrying current under the action of any applied voltage which there may be. Very soon, however, it will fall into an electronic level like those in (a), where it can no longer conduct, and will be trapped. Such a transition is much more likely than a recombination with a hole in the valence band, for the levels in (a) are nearly empty, whereas there are few holes in the valence band. Similarly a hole released in the n-type material will soon fall into a trapping level like those shown in (b).

When we have spoken of electrons or holes being trapped, we have referred merely to the case where they were located in ordinary conduction levels, in regions surrounded by barriers which prevented them from escaping. It is highly likely, however, that very soon such electrons or holes would really be trapped, at lattice imperfections or other types of sites to which they could be attached, with slight decrease of energy. This possibility does not affect our general picture, however. In either case, there will be a net concentration of negative charge in the regions (a), and of positive charge in (b), whether the electrons and holes concerned are free to move around by ordinary conductivity within the restricted regions indicated by (a) and (b), or are tightly trapped by special sites in those regions.

As long as the radiation is falling on the material, more and more electrons will be fed into the trapping levels (a), and more and more holes into the levels (b), at a rate proportional to the illumination. There is a reverse process, however, which will lead to an eventual equilibrium. We can have recombination between electrons in levels like (a), and holes which happen to be present in the valence band in the same part of the crystal in the normal process of conduction; and similarly there can be recombination between holes trapped in levels like (b) and electrons which happen to be passing over the potential barriers. We shall discuss these recombination processes later, particularly in connection with the time constants, for it is these processes which lead to the rather long time constants observed with PbS photoconducting films. For the present, however, we may merely note that equilibrium between the direct and reverse processes will lead to a steady-state population of electrons in states (a), and holes in states (b), depending on the intensity of illumination.

These concentrations of charge will produce local fields within the crystal, raising the energy bands in the regions (a), where there is a concentration of negative charge, and lowering the bands in regions (b). This will have the effect of decreasing the energy separation between the top of the barriers in the p-type material and the bottom of the barriers in the n-type material from the value 0.70 ev indicated in Fig. 7 to a lower value, the net decrease of this energy gap increasing with the illumination. This in turn will result in an increased current, and this is the mechanism of barrier modulation which is often used to explain the PbS conductivity. The electrons carrying the current are those already present in the material, so that the change in conductivity produced by this mechanism can be greater than what would be produced by the excess carriers actually introduced by the illumination.

We are now ready to formulate this mechanism of photoconductivity in mathematical language, preparatory to comparing it with our observations on conductivity and time constant. Let N be the number of trapped carriers per unit volume, produced by the radiation. In the regions (a), these carriers will be electrons trapped in the conduction band, and in the regions (b) they will be holes trapped in the valence band. These carriers may be quite free, in the limited regions of space to which they are confined by the barriers, or more likely they may attach themselves to impurity atoms or lattice defects of one type or another, as we have mentioned earlier. In any case, they will contribute to the density of volume charge, negative in region (a), positive in region (b), which will have the effect of lowering the barrier height by purely electrostatic action. Later, to make things specific, we shall assume that the density N varies sinusoidally with position (simply to have a tractable mathematical formulation of the alternating n- and p-type regions with the charges of opposite sign trapped in them), and shall apply Poisson's equation to derive the related sinusoidal variation of potential, which is to be superposed on the sinusoidal potential already postulated in the unilluminated crystal, of such a sign as to lower the barriers. For the moment, we need only note that the barrier height will be lowered by an amount proportional to N; we shall write the barrier height ΔE as $\Delta E_o - aN$, where ΔE_o is the value met in the unilluminated crystal, which may be as great as 0.35 ev, but may be smaller if the barriers are not as well developed. As we have stated, the constant a will later be derived by Poisson's equation.

Our aim now will be to ask how N varies with time, under the action of illumination, and of the natural processes of recombination. In the first place, an irradiance H will make a positive contribution to dN/dt, proportional to H; that is, the light will raise electrons from the valence to the conduction band at a rate proportional to the irradiance, and each electron so raised will almost immediately become trapped in a region such as (a), and each hole left behind will be trapped in a region such as (b). Let this contribution to dN/dt be written as bH. In addition to this, there will be a recombination, the number of trapped holes or electrons recombining per unit time being a function of N. We may write this contribution to dN/dt as $-N/\tau$, where τ is of the dimensions of a time constant, but may in general be a function of N, as we shall immediately see. Provided we remember this, we can write the equation for the time rate of change of N in the form

$$\frac{dN}{dt} = bH - \frac{N}{\tau} \qquad (3)$$

Let us see why the quantity τ must depend on N, or why the rate of recombination N/τ will not be proportional to N. The trapped electrons will be found at those particular parts of the crystal, like (a), corresponding to a minimum energy for electrons or the top of a barrier for holes; and trapped holes will be found in positions (b), which represent potential minima for holes but barriers for electrons. Thus in either case the only mobile carriers which can combine with the trapped carriers are those which find themselves at the top of the barriers, or which can penetrate the barriers by the tunnel effect. As the barrier heights are lowered by increase of N, this will increase the number of mobile carriers at the tops of the barriers, and hence will increase the number of recombinations, or decrease τ. Thus we see that the "time constant" τ will decrease with illumination, or with increasing temperature, which also increases the number of carriers at the top of the barriers. This is just the sort of behavior found experimentally. We shall return later to the detailed question of the dependence of τ on N.

The quantity of N is not directly measureable; what we can measure is σ, the conductivity. Let us find the connection between these quantities. The number of electrons or holes per unit volume at the top of the barrier will be given by Eq. 2, in which ΔE is to represent the energy difference between the Fermi level and the top of the barrier; as we have seen, this is to be written as $\Delta E_o - aN$. The conductivity, as we see from Eq. 1, is $e(\mu_h + \mu_e)$ times this value, and this at once shows us how the photoconductive effect arises, since it contains the factor $\varepsilon^{aN/kT}$. That is, the conductivity is given by the formula

$$\sigma = (2/h^3)(2\pi mkT)^{3/2} \varepsilon^{-\Delta E_o/kT} \varepsilon^{aN/kT} e(\mu_h + \mu_e) \qquad (4)$$

There is no reason to think that the conductivity does not follow this value, even during a transient, when N and σ are both varying with time, for instance during the decay of photoconductivity. When we write σ, we shall always assume that it is this instantaneous function of N. The dark conductivity σ_D is the special case when N = 0. This will be the case in the dark, after sufficiently long time has elapsed for any previously existing photoconductive effect to have decayed. We see then that

$$\frac{\sigma}{\sigma_D} = \varepsilon^{aN/kT}, \quad N = \frac{kT}{a} \ln \frac{\sigma}{\sigma_D} \qquad (5)$$

Under steady illumination, dN/dt will be zero after the transient effects have ceased, and according to Eq. 3, we shall have

$$N = b\tau H \qquad (6)$$

This does not mean that N will be proportional to H, for we remember that τ depends on N, in a way so far only described qualitatively. Using

Eq. 5, we find that the conductivity is given by

$$\frac{\sigma}{\sigma_D} = \varepsilon^{ab\tau H/kT}, \tag{7}$$

or, taking the logarithm,

$$\frac{\tau H}{T \ln \sigma/\sigma_D} = \frac{k}{ab} \quad , \tag{8}$$

a constant. Since τ as well as σ is directly measurable, we can verify Eq. 8 experimentally. In order to verify this, we need not only the functional form of Eq. 8, but also estimates of the parameters a and b. We shall now ask how much information we can get, on general grounds, about their probable values.

In the first place, a was introduced by the statement that the barrier height ΔE in the presence of trapped electrons was equal to $\Delta E_o - aN$. Since the trapped charge results in a volume charge density, it is a simple problem of electrostatics to compute the resulting modulation of the height of the barrier. This has been done on the assumption that the charge density varies sinusoidally with position, and that the distance between successive n-type regions (or successive p-type regions) is 0.1μ. The quantity b occurs in the statement that the number of electrons excited per second, and hence the number of particles trapped per second, equals bH, where H is the irradiance. This has been calculated on the assumptions that all photons are absorbed and that each one excites an electron. When these assumptions are made, we find that

$$k/ab \simeq 3.8 \times 10^{-10} \text{ joules/cm}^2 \text{ - degree} \quad . \tag{9}$$

For a good many cells, we have measurements of conductivity as a function of irradiance and temperature, and time constants measured under the same circumstances. Hence we are able to substitute these values into Eq. 8, so as to verify in the first place the constancy of the quantity k/ab, and in the second place to see if the values of this quantity approximate the expected value given in Eq. 9. In Table 1 we present results of this type for Cell 111X, a typical cell for which we have a good deal of data. Other cells for which similar calculations have been made show similar results.

TABLE 1

CHECK OF THE CONSTANCY OF $\tau H/(T \ln \sigma_L/\sigma_D)$, FOR CELL R111X

$1/T$	H	τ	σ_L/σ_D	$\tau H/(T \ln \sigma_L/\sigma_D)$ (10^{-10})
0.005	3×10^{-5}	4×10^{-3}	1.33	20.0
	2×10^{-4}	2×10^{-3}	3.3	16.3
0.006	7×10^{-6}	9×10^{-3}	1.6	7.8
	3×10^{-5}	5.5×10^{-3}	3.6	7.7
	2×10^{-4}	2×10^{-3}	11.5	9.7
0.013	7×10^{-6}	1.4×10^{-2}	17.0	4.6
	3×10^{-5}	6.6×10^{-3}	42.0	7.0
	2×10^{-4}	2×10^{-3}	150.0	10.0

From the results of Table 1, we see that the quantity which should equal k/ab shows a surprising constancy, as a function of irradiance and of temperature. Furthermore, the values found are not very far from the value 3.8×10^{-10} which we calculated as an approximate value in Eq. 9. Since that calculation contained several rather arbitrary assumptions, in particular the distance between p- and n-type barriers, there is a possible variation of a small numerical factor in this quantity k/ab, and the value found in Table 1 for Cell R111X clearly lies within the reasonable range. Furthermore, similar calculations for other cells all give values of the same quantity lying in this same general range, not differing from the values of Table 1 by more than perhaps a factor of 5. This gives a strong support for the general correctness of our theory. If the numbers had come out many orders of magnitude different from the predicted value, we could hardly have upheld this general picture of the phenomenon.

One aspect of the measurements which has a close connection with these calculations is the question of the deviation from linearity of the response. In some cases the conductivity varies superlinearly with the irradiance, in other cases sublinearly, as is shown by our data. Let us inquire whether our theory gives the possibility of such variability. We can answer this question best, perhaps, by looking at Eq. 7. In that equation, we see that if τ were independent of the irradiance, the conductivity would vary exponentially with irradiance; that is, in a very superlinear manner. On the other hand, experimentally the time constant decreases with the irradiance. In other words, in Eq. 7, which is $\sigma/\sigma_D = \exp(ab\,\tau H/kT)$, the product τH increases less rapidly than H, and hence the conductivity will vary less superlinearly with irradiance than the exponential curve would suggest. In fact, if the time constant were to vary inversely as the conductivity, as we shall discuss in the next section, we can show that the conductivity would vary sublinearly with the irradiance. In other words, the theory is flexible enough to allow anything from a superlinear to a sublinear variation, and the experimental results vary all through this range.

4. The Time Constant and its Dependence on Irradiance and Temperature

We have already mentioned one possible explanation of the dependence of time constant on irradiance and temperature: the possibility that the recombination resulted from mobile carriers at the tops of the barriers, combining with the trapped charges of the opposite sign located at the barriers. We have pointed out that these mobile carriers will decrease in number as the barriers become higher, so that the recombination time would depend on N, or on the irradiance and temperature. In the present section we shall first examine the consequences of this simple hypothesis, shall then show that it does not represent the actual facts very quantitatively, and shall inquire as to the nature of modification which we must make to get closer agreement with experiment.

On this simple hypothesis, let us proceed as follows. We assume the mobile carriers to be moving with thermal velocity, $(kT/2\pi m)^{1/2}$. Let the trapping cross section for trapping of a mobile carrier by a fixed carrier be c. That is, when an electron at the top of a barrier comes within an area c surrounding a hole trapped in that region, it will be trapped by the hole, thus neutralizing the electrostatic effect of the hole, and effectively reducing N by one unit; the same situation is assumed to hold if a mobile hole is trapped by a fixed electron. The time rate of decrease of N by recombination of this type then equals the number of mobile carriers per unit volume times the thermal velocity. This equals N/τ. In other words,

$$\frac{1}{\tau} = (2/h^3)(2\pi mkT)^{3/2}\ \varepsilon^{-\Delta E_0/kT}\ \varepsilon^{aN/kT}\ c(kT/2\pi m)^{1/2} \quad . \qquad (10)$$

This shows us how τ depends on N, as well as on the temperature. We can at once combine Eqs. 4 and 10 to obtain the equation

$$\sigma\tau = \frac{e(\mu_h + \mu_e)}{c\sqrt{kT/2\pi m}} \quad . \qquad (11)$$

In other words, the product of conductivity and time constant should be independent of N, or independent of illumination, and should depend on temperature only through slowly varying quantities, not involving exponentials. We cannot precisely predict this temperature dependence, for the trapping cross-section c most likely will depend on the thermal velocity of the mobile carrier in a way which we cannot predict without understanding the trapping mechanism more completely. As for the order of magnitude of the trapping cross-section c, it is hard to estimate it theoretically, but our trapping mechanism is not completely different from that in silicon discussed by Haynes and Hornbeck.[4] They find experimental trapping cross-sections of the order of magnitude of 10^{-13} cm^2. We should not be surprised, then, to find c coming out to this order of magnitude, even though it is a good deal larger than the geometrical cross-section of an atom.

When we examine the experimental data, we find that there is a tendency for the time constant to increase when the conductivity decreases, either on account of reduction of temperature or reduction of irradiance. In some cases the inverse proportionality between the two seems to hold rather accurately. When it does not, the time constant in general does not vary as much as the conductivity. In particular, the time constant never gets very much greater than 10 or 20 msec, whereas if we took Eq. 11, determined a constant of proportionality from the high-temperature values, and extrapolated to low temperatures for very high-resistance material, we should compute values of the time constant, from the conductivity, which might even be of the order of magnitude of seconds. The fact that these very long time constants are not observed might be a result of failure of experimental techniques. More likely, however, it is an indication that some additional recombination mechanism may be at work, resulting in time constants of the order of magnitude of a hundredth of a second, and producing a recombination probability in addition to that arising from the mobile charge carriers surmounting the barriers.

Such an additional mechanism might, for instance, be the tunnel effect. If we had barriers of the order of magnitude of those indicated in Fig. 7, the maximum electric fields set up would be of the order of magnitude of a million volts per centimeter. Such fields would create appreciable, though not large, probabilities that electrons at the bottom of the conduction band at locations like (a), in Fig. 7 could tunnel through the barrier to combine with holes trapped at locations like (b), and vice versa. Simple calculations of such tunnel effect probabilities indicate that it is not out of the question that this mechanism could come into competition with the direct recombination process, provided the latter became very unlikely, which would be indicated by time constants of a hundredth of a second. We have not tried, however, to analyze our results further on the basis of such a hypothesis.

To the extent to which Eq. 11 holds, we can compute the values of $\sigma\tau$ determined experimentally, and hence check our estimate of the quantities on the right side of Eq. 11; and we can assume the constancy of $\sigma\tau$, and investigate the behavior of a film having this characteristic. If we put in for $\mu_h + \mu_e$ the value of 370 cm^2 v^{-1} sec^{-1}, indicated by our empirical material;

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[4] J. R. Haynes and J. A. Hornbeck, Phys. Rev. 90, 152 (L) (1953)

for c the value 10^{-13} cm^2; for T, room temperature; then Eq. 11 would give the value

$$\sigma\tau = 2.2 \times 10^{-10} \text{ sec/(ohm - cm)} \qquad (12)$$

To check the order of magnitude, we give in Table 2 values of $\sigma\tau$ for different temperatures, and for the dark conditions and a rather highly irradiated condition, for Cell R19X, a typical cell for which the constancy of the product $\sigma\tau$ is not well obeyed. We see a variation of this quantity by nearly two orders of magnitude between the low and high temperature ranges; a variation, moreover, which cannot well be explained by temperature dependence to be expected from the right side of Eq. 11. In other words, the constancy of the product is certainly not a quantitatively accurate relation. Nevertheless, the product even in this case is staying much more nearly constant than either of its factors separately. Further, the numerical value given by Eq. 12 lies not far from those found in Table 2 so that our hypotheses do not seem to be grossly unreasonable. The products found in Table 2 run considerably larger than the numerical value of Eq. 12 which could be explained by a cross-section c considerably smaller than the value 10^{-13} cm^2 assumed in the calculation for Eq. 12; this certainly is a deviation in the direction which we should expect.

TABLE 2

PRODUCT $\sigma\tau$ FOR CELL R19X

1/T	$\sigma_D\tau_D$	$\sigma_L\tau_L$
0.004	4.5×10^{-8}	5.0×10^{-8}
0.006	1.5×10^{-9}	2.3×10^{-9}
0.008	1.4×10^{-10}	4.0×10^{-10}
0.011	1.0×10^{-10}	7.2×10^{-10}

We have mentioned that if the product $\sigma\tau$ were constant, the dependence of conductivity on irradiance would be sublinear. We can show this by introducing Eq. 10 into Eq. 7, and taking the logarithm. We then find

$$\sigma \ln \frac{\sigma}{\sigma_D} = \frac{abH}{kT}\,\frac{e(\mu_h + \mu_e)}{c\sqrt{kT/2\pi m}} \quad . \qquad (13)$$

That is, if we let $x = \sigma/\sigma_D$, we find $x \ln x$ to be proportional to H. This equation cannot be solved analytically for x as a function of H. However, if we plot $y = x \ln x$, and then turn the graph around to find x as a function of y, we see that the dependence is decidedly sublinear. In other words, the con-

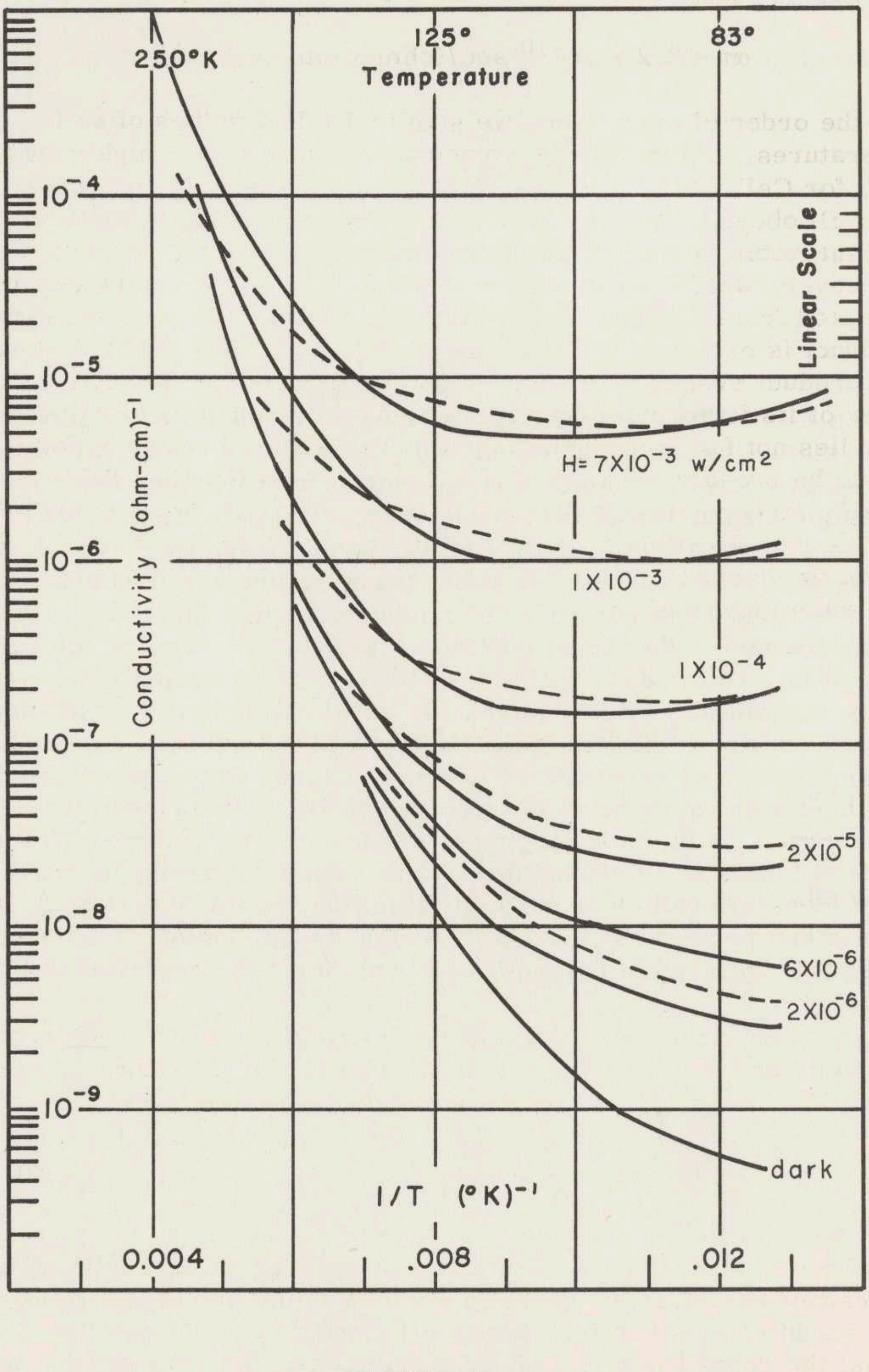

FIGURE 8
CONDUCTIVITY vs 1/T FOR VARIOUS IRRADIANCES FOR CELL R19X
Full curves: experimental; dashed: Eq. 15

ductivity in this case is a sublinear function of the irradiance, as we stated in the preceding section.

If we wish to disregard the dependence on temperature of the quantity

$$A = \frac{ab}{kT} \frac{e(\mu_h + \mu_e)}{c\sqrt{kT/2\pi m}} \quad , \tag{14}$$

then we would have in Eq. 13 which becomes

$$\sigma \ln \frac{\sigma}{\sigma_D} = AH \quad , \tag{15}$$

a very simple equation giving the dependence of conductivity on irradiance and temperature (the temperature entering through the empirical dependence of σ_D on temperature). Even this simple equation works surprisingly well in predicting the behavior of the conductivity. Thus, in Fig. 8, we have taken the experimental data for Cell R19X, have chosen the constant A so as to fit the observed conductivity at one temperature and irradiance, and then have used Eq. 15 to compute the conductivity as a function of temperature and irradiance. We cannot compute this quantity directly, since we cannot solve Eq. 15 for σ, but it is easy to work out a numerical procedure for getting the solution. It is remarkable how well this very crude approximation works in predicting the general nature of the curves of conductivity versus temperature at various irradiances. Closer examination shows that the agreement with experiment is improved if we use measured time constants in the calculation, rather than trying to predict the time constant from the relation $\sigma\tau$ = constant, which is known to be rather far from the truth. The success of even this rather crude approximation should be enough to indicate that the present theory is at least on the right track, though it undoubtedly needs far more refinement before it can explain all the experimental details of the problem.