for the compact ion core orbitals. This procedure has been carried out for the Type III ground-state wave functions $\psi_n(\Gamma_1{}^e|\mathbf{r})$. The results are

$$(i|n)=\psi_n(\Gamma_1{}^e|\alpha)\frac{2^{p+1}(p+1)!}{[(2p)!]^{\frac{1}{2}}}\left(\frac{2\pi}{\delta^3}\right)^{\frac{1}{2}} \times\begin{cases}\left[1+\dfrac{(\eta^2-\xi^2)(p+3)(p+2)}{12\delta^2}+\cdots\right], & r_\alpha\leq a\\ \left[1+\dfrac{\eta^2(p+3)(p+2)}{6\delta^2}+\cdots\right], & r_\alpha>a\end{cases}$$

when ψ_i is the s function

$$\psi_i(1)=\left[\frac{2^{2p}\delta^{2p+1}}{2\pi(2p)!}\right]^{\frac{1}{2}} r_{\alpha 1}{}^{p-1}\exp(-\delta r_{\alpha 1})$$

and

$$(i|n)=\psi_n(\Gamma_1{}^e|\alpha)2^{p+1}(p+2)!\left[\frac{6\pi}{(2p)!\delta^5}\right]^{\frac{1}{2}} \times\begin{cases}\left[\dfrac{\eta+1}{3}-\dfrac{(\eta^2+\xi^2)(p+3)}{16\delta}+\cdots\right], & r_\alpha\leq a\\ \left[\dfrac{\eta r_\alpha+1}{3r_\alpha}+\cdots\right], & r_\alpha>a\end{cases}$$

when ψ_i is the p function

$$\psi_i(1)=\left[\frac{3(2)^{2p}\delta^{2p+1}}{2\pi(2p)!}\right]^{\frac{1}{2}} r_{\alpha 1}{}^{p-1}\exp(-\delta r_{\alpha 1})\cos\theta_{\alpha 1}.$$

If, when ψ_i is an s function, one uses only the first term in the asymptotic expansion for $(i|n)$, then

$$(i|n)=B_i\psi_n(\alpha),$$

where B_i is independent of ψ_n. This result was used in Sec. 5.

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Photoconductivity in Lead Selenide: Theory of the Dependence of Sensitivity on Film Thickness and Absorption Coefficients*

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Recently developed theoretical expressions for the responsivity R_s and noise of photoconductive films are examined. Assuming that the time constant is independent of film thickness we express R_s and signal/noise (S/N) in terms of the absorption coefficient α and thickness d. Using a curve of α *vs* λ for lead selenide obtained by Avery from crystal measurements, we calculate R_s *vs* λ for films of different thicknesses. These curves indicate that the photoconductive knee should lie near 5μ for PbSe films of all thicknesses. Experimentally, however, the position of the knee is observed to be a function of film thickness, being near 3.3μ in thin films and 5μ in thick films.

It is then shown from the theory that in very thin films the responsivity is a direct measure of α. Accordingly the wavelength dependence of α is calculated from responsivity data for thin films; the magnitude is determined from the crystal absorption data at 5μ. Curves of responsivity *vs* λ for various film thicknesses are computed, using the α *vs* λ curve derived from responsivity data on thin films. These curves agree with the observed responsivity data; they show the shift of the knee from 3.3 to 5μ with increased film thickness, and show that no increase in responsivity can be obtained at any wavelength by increasing the film thickness.

The dependence of signal/noise on λ and d is calculated, using the same α *vs* λ curve, and found to be in qualitative agreement with experiment. The curves show that for any given wavelength the signal/noise is a maximum at a certain value of film thickness. The maximum occurs at greater thicknesses for longer wavelengths. The dependence of S/N on d and α is given for any material fitting the same general photoconductive model. The same conclusion, that there is an optimum thickness for any particular absorption coefficient, holds in this general case.

Finally, the derived α *vs* λ curve is shown to be consistent with recent theories of indirect optical transitions.

INTRODUCTION

A RECENT experimental study[1] of photoconductive lead selenide films investigates the relationship of film thickness and method of sensitization to magnitude and spectral dependence of sensitivity. Previous workers had shown that at room temperature a knee in the spectral sensitivity curve occurs near 3.3μ in thin films,[2] but near 5μ in thicker films.[3] The sensitivity of the

* A portion of a dissertation submitted (by J.N.H.) to the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Part of this work was reported at the 1955 Washington meeting of the American Physical Society [J. N. Humphrey, Phys. Rev. **99**, 625(A) (1955)].

[1] J. N. Humphrey and W. W. Scanlon, Phys. Rev. **105**, 469 (1957).

[2] J. Starkiewicz, J. Opt. Soc. Am. **38**, 481 (1948); T. S. Moss, Proc. Phys. Soc. (London) **B62**, 741 (1949).

[3] Gibson, Lawson, and Moss, Proc. Phys. Soc. (London) **A64**, 1054 (1951).

thick films was reported to be considerably less than that of the thin films, but it was expected that it could be improved by further investigation of the sensitization procedure.

Absorption data[4–6] indicates that the photoconductive knee is to be expected near 5μ rather than at 3.3μ. Accordingly, it is of interest to determine whether more sensitive films could be prepared which would retain their high sensitivity out to 5μ.

Our experimental study[1] indicated that high responsivity (signal voltage output per volt bias per watt/cm^2 illumination) could only be achieved in thin films at short wavelengths. Thick films showing a knee at 4 to 5μ could be prepared, but invariably the level of responsivity in these films was low, even at short wavelengths. Signal/noise, on the other hand, was found to be greater in thick than in thin films, at long wavelengths, because of the lower noise in thick films.

The study further showed that under certain circumstances various sensitizers besides oxygen can produce sensitivity in PbSe films. The spectral distribution of the sensitivity is essentially independent of the sensitizer used. It was concluded that the electron transitions producing the photoconductivity are main-band transitions and not excitations from impurity states, since impurity states corresponding to various sensitizers could be expected to occur at various energies. This conclusion is in agreement with the situation in PbS,[7] in which thermal measurement of the energy gap agrees with the photoconductive limit.

In this paper we attempt to explain the observed wavelength dependence of the photoconductive response and signal/noise in terms of the absorption coefficient and film thickness.

A. RELATION BETWEEN ABSORPTION AND THE PHOTOCONDUCTIVE RESPONSE

The responsivity of a photoconductive detector is defined as

$$R_s=\Delta\sigma/4\sigma J, \tag{1}$$

where $\Delta\sigma$ is the change in conductivity σ resulting when J watts per cm^2 of radiation fall on the detector. The responsivity can be measured as the signal voltage across a load resistance equal to the cell resistance R_C, per unit biasing voltage and unit incident radiation intensity. In the general case (load not matched) this can be expressed as

$$R_s=\frac{V_s}{V_{dc}J}\frac{(R_C+R_L)^2}{4R_CR_L}. \tag{2}$$

One of us has recently shown[8] that this can be given in terms of fundamental parameters by

$$R_s=\frac{(1+B)\tau\eta}{4pdh\nu[1+(\omega\tau)^2]^{\frac{1}{2}}}, \tag{3}$$

where B is a coefficient of barrier modulation, η is the probability that an incident photon will create a hole-electron pair, τ is the lifetime of the majority carrier, p is the density of free majority carriers, d is film thickness, $h\nu=hc/\lambda$ is the energy per incident photon, and ω is the angular chopping frequency. η is given[9] by

$$\eta=(1-r)(1-e^{-\alpha d})/(1-re^{-\alpha d}), \tag{4}$$

where α is the absorption coefficient at the wavelength λ, and r is the reflection coefficient of the film. For simplicity this calculation will be made assuming r to be zero, since sample calculations showed no effect on the general form of the results. Thus,

$$\eta\cong(1-e^{-\alpha d}). \tag{5}$$

Since we found no variation in τ with thickness, we can write

$$R_s=K\lambda(1-e^{-\alpha d})/d, \tag{6}$$

where K is a constant independent of α, λ, and d.

B. PREDICTION OF PHOTOCONDUCTIVE RESPONSE FROM FILM AND CRYSTAL ABSORPTION DATA

Gibson[10] has reported absorption measurements on thin films of PbS, PbSe, and PbTe. Application of Eq. (6) to his data for PbSe does not give any indication of a photoconductive knee except at very short wavelengths (1μ). It is assumed that scattering due to the polycrystalline nature of the film produced a high apparent absorption at long wavelengths, masking the absorption edge.

On the other hand, his crystal absorption measurements[5] show absorption edges at 3, 5, and 4μ for PbS, PbSe, and PbTe, respectively, at room temperature. Reflectivity measurements made on PbSe crystals by Avery[6] showed high absorption up to an edge at 5μ (in PbSe at room temperature) in agreement with Gibson's crystal data. Avery's data (converted to absorption coefficient[11]) together with Gibson's data are reproduced in Fig. 1.

Figure 2 shows the variation of R_s with λ and d calculated from Eq. (6), using Avery's data for α *vs* λ (Fig. 1). The predictions for thick films agree qualitatively with experiment, in that the knee is at 5μ. However, because of the steepness of the edge there is only a very slight shift of position of the knee with thickness. Accordingly, no knee is predicted at 3.3μ in

[4] Paul, Jones, and Jones, Proc. Phys. Soc. (London) **B64**, 528 (1951).
[5] A. F. Gibson, Proc. Phys. Soc. (London) **B65**, 378 (1952).
[6] D. G. Avery, Proc. Phys. Soc. (London) **B67**, 2 (1954).
[7] W. W. Scanlon, Phys. Rev. **92**, 1573 (1953).
[8] R. L. Petritz, Phys. Rev. **104**, 1508 (1956).
[9] T. S. Moss in *Photoconductivity Conference*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 427.
[10] A. F. Gibson, Proc. Phys. Soc. (London) **B63**, 756 (1950).
[11] D. G. Avery reported by R. P. Chasmar, in *Photoconductivity Conference*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 463.

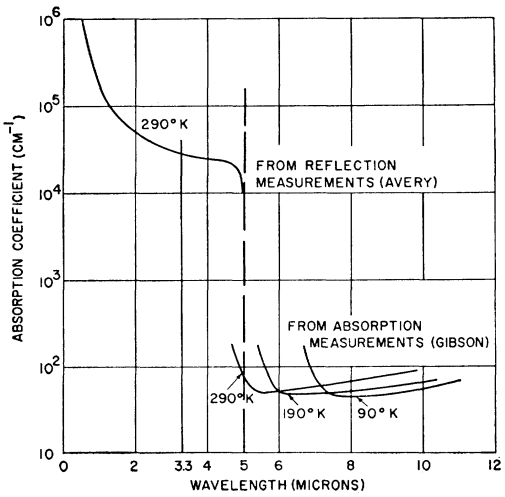

FIG. 1. Absorption coefficient measurements on PbSe crystals.

thin films comparable to that normally seen in the photoconductive data. Thus the crystal reflectivity measurements do not adequately predict the photoconductive data for thin films. There are several possible explanations for this.

It is well known that many properties of films do not agree with the corresponding crystal properties. For example Fan, Shepherd, and Spitzer[12] point to a difference between their absorption measurements on germanium crystals and similar measurements of Briggs[13] on films. The crystal absorption curve shows a sharp rise not seen in the film data. They attribute the difference to inhomogeneities in the films.

Reflection measurements on germanium[14] have been found to yield an absorption coefficient a factor of 2 to 5 higher than that obtained by transmission measurements[15]; and reflection measurements on silicon[16] give an absorption coefficient which is a factor of 10 to 20 higher than that obtained by transmission measurements.[15] (These curves have been collected on a common graph by Burstein.[17])

It is also possible that the total absorption in the photoconductive region includes a large component which does not contribute to the photoconductivity. For example, free-carrier absorption is of this nature, but not of sufficient magnitude to account for the effect. Whatever the explanation, however, it is clear that the available absorption data do not predict the thin-film photoconductive data. Furthermore, we have no data for absorption coefficients of 10^2 to 10^4 cm^{-1}, which is a region of particular interest in the study of photoconductivity in thin films.

C. USE OF THIN-FILM PHOTOCONDUCTIVITY DATA TO CALCULATE AN ABSORPTION CURVE FOR FILMS

The difficulties described above make it clear that it may not be possible to obtain complete correlation between photoconductivity and absorption as measured by purely optical methods (transmission or reflection). However, we are concerned here with only that absorption which produces photoconductivity: main-band absorption, in this case.

It is possible that the absorption coefficient for main-band transitions in films could be appreciably different from that in crystals; for example, indirect transitions (see Sec. E) may be favored by the polycrystalline nature of films. However, it does not seem probable that the coefficient should vary radically with film thickness, in films which are prepared under similar conditions. The difference between a thin and a thick film should be less than the difference between a film and a single crystal.

Our problem then is to evaluate α *vs* λ for main-band transitions directly from film data. As discussed in Sec. B optical absorption data on films is not satisfactory for this because of the scattering from crystallites. We therefore consider the possibility of obtaining α from photoconductive data. For the case of a very thin film, we have from Eq. (6)

$$\alpha=\frac{1}{K\lambda}(\lim_{d\to 0} R_s). \tag{7}$$

Thus we can calculate the wavelength dependence of α from the wavelength dependence of R_s in a very thin film. The calculation can be put on an approximate

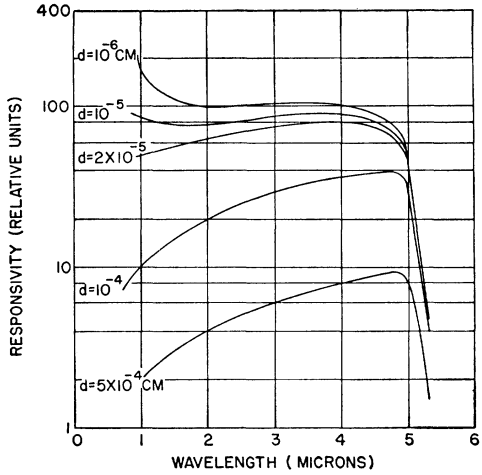

FIG. 2. Effect of PbSe film thickness on responsivity, calculated from Avery's crystal reflection data by Eq. (6). (The calculated curves for thin films are not in agreement with experiment.)

[12] Fan, Shepherd, and Spitzer in *Photoconductivity Conference*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 184.
[13] H. Briggs, J. Opt. Soc. Am. **42**, 686 (1952).
[14] D. G. Avery and P. L. Clegg, Proc. Phys. Soc. (London) **B66**, 512 (1953).
[15] Dash, Newman, and Taft, Phys. Rev. **98**, 1192(A) (1955), and W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).
[16] G. Pfestorf, Ann. Physik **81**, 906 (1926).
[17] E. Burstein, *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1955), Vol. VII, p. 1.

absolute scale by evaluating K from crystal absorption data at one wavelength.

We have therefore determined α *vs* λ by Eq. (7), using thin-film photoconductive data for R_s *vs* λ, and Gibson's directly measured value of α at 5μ; Fig. 3 contains a plot of the resulting curve.

We then use Eq. (6) to calculate R_s *versus* λ for films of different thicknesses, using the data calculated above for α *vs* λ. The resulting curves of R_s *versus* λ are also shown in Fig. 3. The general behavior predicted by these curves is in agreement with experiment. In particular, the shift[1,3] of the knee from three microns for very thin films to five microns for thick films is predicted. Furthermore, the responsivity monotonically decreases with increased film thickness (see Fig. 5, reference 1). We therefore conclude that making a film thicker cannot increase the responsivity at any wavelength so long as τ remains constant.

D. DEPENDENCE OF SIGNAL/NOISE ON FILM THICKNESS

An expression for the noise in a photoconductive film has recently been presented by one of us.[8] It is shown that under normal biasing conditions the cell noise can be represented by a short-circuit noise generator of the form

$$G(I^2)=\frac{4kTAd}{\rho L^2}+\frac{a_1\tau I_{dc}^2}{Ad[1+(\omega\tau)^2]}+\frac{a_2 I_{dc}^2}{Ad\omega}, \qquad (8)$$

where A is the sensitive area of the cell, k is the Boltzmann constant, T is the absolute temperature, ρ is the resistivity of the cell material, L is the cell length between electrodes, I_{dc} is the bias current through the cell, and a_1 and a_2 are constants depending on the cell but independent of cell geometry.

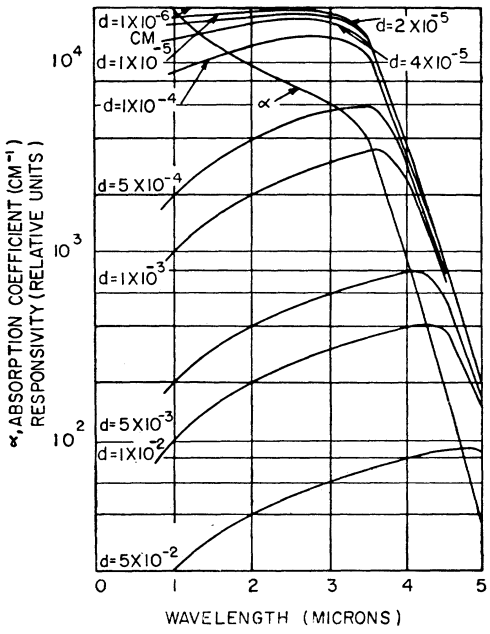

FIG. 3. PbSe absorption coefficient α derived from thin-film photoconductive data [Eq. (7)]; effect of film thickness on responsivity as calculated from the derived absorption coefficient by Eq. (6).

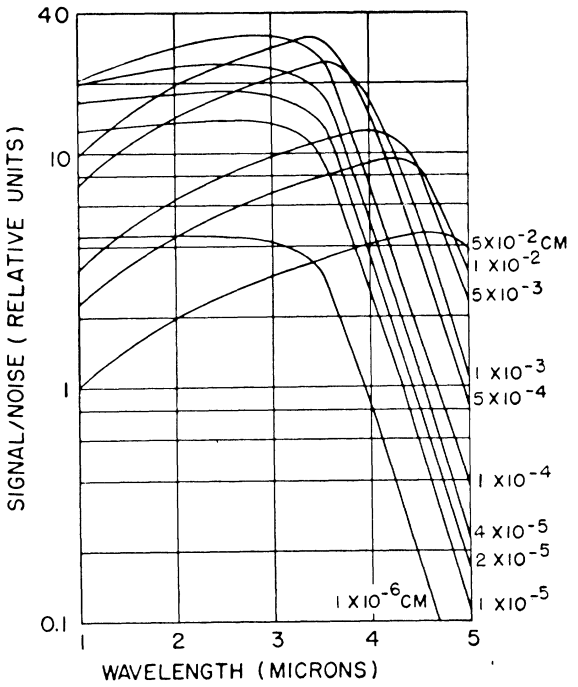

FIG. 4. Signal/noise per unit radiation intensity in PbSe films *vs* wavelength, calculated from photoconductive data by Eq. (12). Parameter is film thickness.

The first term is the Nyquist noise which arises from fluctuations in the rate at which carriers cross barriers within the film. The second term arises from fluctuations in the number of charge carriers and includes effects of radiation and lattice vibration noise. This term establishes the intrinsic limit of sensitivity of the detector. The third term is the $1/f$ noise which is observed in most evaporated photoconductive films. All models for $1/f$ noise so far investigated depend on cell geometry as given by the above equation.[18]

The noise voltage output from the generator $G(I^2)$ having a source impedance R_C and feeding a load resistance R_L is

$$V_n=[G(I^2)\Delta f]^{\frac{1}{2}}R_C R_L/(R_C+R_L). \qquad (9)$$

According to Eqs. (2) and (6), the signal voltage from the cell is

$$V_s=4K\lambda J V_{dc}(1-e^{-\alpha d})R_C R_1/(R_C+R_1)^2 d. \qquad (10)$$

When current flows, the Nyquist term in Eq. (8) is normally negligible. To show the dependence on geometry, the remaining terms can be written as

$$G(I^2)=I_{dc}^2 f(\omega,\tau)/(Ad). \qquad (11)$$

[18] See references 17, 19, 20, 21, and 22 of reference 8.

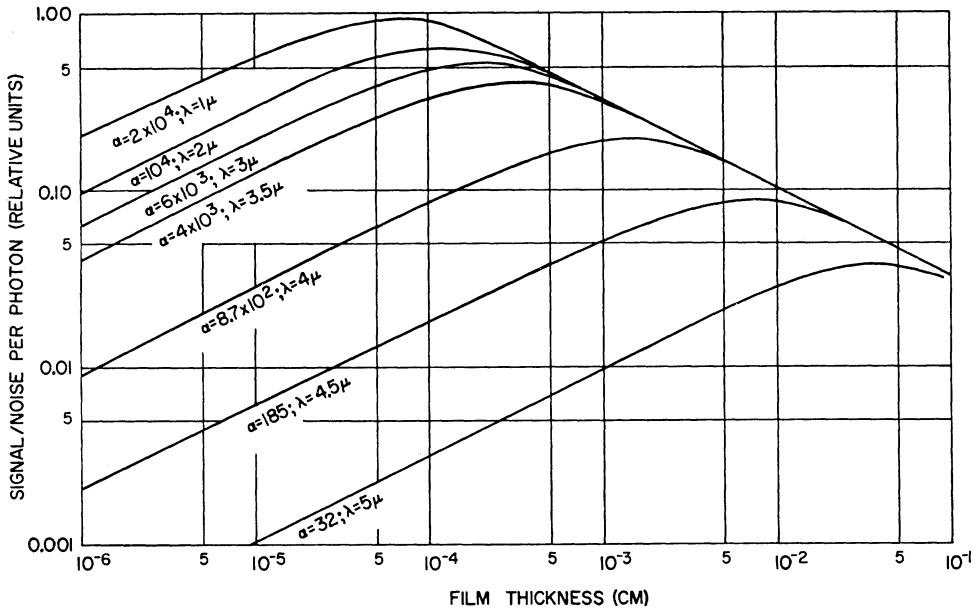

FIG. 5. Signal/noise per photon *vs* film thickness, for any photoconductor which obeys Eq. (13). Parameter is absorption coefficient α. The wavelength at which PbSe exhibits the specified absorption coefficient is also indicated on each curve.

Thus combining Eqs. (9), (10), and (11), the signal/noise per unit radiation intensity is

$$V_s/V_nJ=K_2(A/d)^{\frac{1}{2}}\lambda(1-e^{-\alpha d}), \qquad (12)$$

where K_2 is independent of film geometry. Note that whereas thickness d appeared as $(1-e^{-\alpha d})/d$ in the responsivity, Eq. (6), it appears as $(1-e^{-\alpha d})/d^{\frac{1}{2}}$ in signal/noise.

V_s/V_nJ *versus* λ has been calculated for films of various thicknesses, using Eq. (12) and the absorption coefficient of Fig. 3. Figure 4 shows V_s/V_nJ *vs* λ, using thickness as a parameter. We see that at short wavelengths the signal/noise increases with increasing thickness to a maximum, and then decreases; at longer wavelengths a similar but lower maximum occurs. To produce maximum signal/noise at long wavelengths requires thicker films than at short wavelengths. This is in qualitative agreement with experiment.[1-3] Specifically, Fig. 6 of reference 1 shows the increase in signal/noise obtained at long wavelengths (beyond 4μ) in thicker films. The increase results from the combination of two effects, the displacement of the responsivity knee toward longer wavelengths and the decrease in noise with increased thickness.

The above description applies to any photoconductive material for which the same general assumptions are valid; the numerical values will be different. However, a generalized family of curves can be obtained for the signal/noise per incident photon,

$$V_s/V_nJ\lambda=K(1-e^{-\alpha d})(A/d), \qquad (13)$$

since this contains only two independent parameters, α and d. This is plotted in Fig. 5, with film thickness as a continuous variable and α as parameter. Each curve is also labeled with the appropriate wavelength at which PbSe exhibits that particular α.

This plot can be used to determine the theoretical optimum film thickness for any given absorption coefficient. To determine the wavelength at which this value would hold for a particular photoconductor one would need the appropriate α *vs* λ curve for that material. Aside from this, however, the curves apply to any photoconductor whose responsivity and noise dependence on thickness are of the form given by Eqs. (6) and (8), respectively. These equations are quite general in respect to their dependence on thickness. Therefore Fig. 5 should be useful for a large class of photoconductors. Possibly the most important limitation is that the derivation assumed the experimental observation that in PbSe the time constant is independent of thickness. This is in contrast to the cases calculated by DeVore[19] who discussed the effect of surface recombination velocity on responsivity.

E. MAIN-BAND ABSORPTION EXPRESSIONS

In order to see whether the absorption coefficient calculated in the preceding sections is meaningful, we will compare it with predictions of recent theory. Expressions for absorption based on the transition probability for creating an electron-hole pair across an energy gap E_i have been developed by Dexter,[20] and by Bardeen, Blatt, and Hall.[21] They show that radiation of energy E, greater than the band gap energy E_i by an

[19] H. B. DeVore, Phys. Rev. **102**, 86 (1956).

[20] D. L. Dexter, in *Photoconductivity Conference*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 155.

[21] Bardeen, Blatt, and Hall, in *Photoconductivity Conference*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 146.

amount ϵ, will be absorbed and create an electron-hole pair with a probability

$$K \propto \epsilon^n, \quad \epsilon = E - E_i; \tag{14}$$

n is a positive exponent whose value depends on the shape of the energy-momentum surfaces and the type of transition involved. Transitions in which the selection rules are obeyed are termed direct; those in which they are violated are termed indirect. Direct transitions require the values $n=\frac{1}{2}$ and $n=\frac{3}{2}$, while integral values of n from 1 to 3 are predicted for the indirect cases, depending on the details of the wave functions. Since the absorption coefficient is proportional to the transition probability, this gives us

$$\alpha = C\epsilon^n = C[(hc/\lambda) - E_i]^n. \tag{15}$$

Fan, Shepherd, and Spitzer[12] reported an $\epsilon^{2.5}$ dependence in their experimental absorption measurements in germanium.

MacFarlane has calculated[22] E_i in PbSe by fitting the free carrier portion of the crystal absorption of Gibson[5] by a quadratic in λ, and extrapolating back to short wavelengths. Subtracting the extrapolation from the measured values yielded a curve which agreed well with Eq. (15) for $n=3$. He obtained $E_i=0.22$ ev corresponding to a cut-off wavelength $\lambda_c=5.6\mu$ at room temperature.

To see if our photoconductive data fits this expression we plot observed values of R_s/λ at long wavelengths against $\epsilon=(hc/\lambda)-E_i$, on a logarithmic plot (Fig. 6). MacFarlane's value of 0.22 ev was taken for E_i. The long-wavelength data for a given cell can be represented by a straight line, indicating a power law $R_s/\lambda \propto \epsilon^n$; n ranges from 3 to 5 in the five cells shown. From this we conclude that our absorption curve derived from photoconductive data is consistent with current theories of optical absorption.

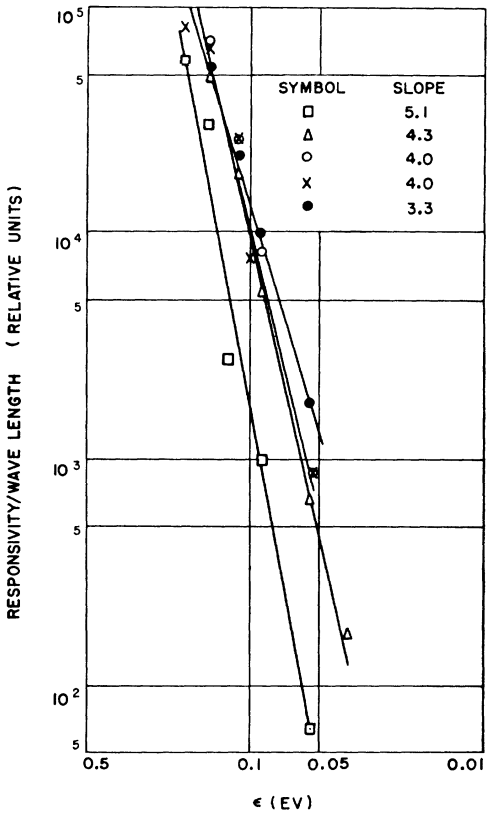

FIG. 6. Experimental values of responsivity/wavelength *vs* $\epsilon=(hc/\lambda)-E_i$ for five PbSe cells. ($E_i=0.22$ ev.)

F. CONCLUSIONS

We conclude that the wavelength dependence of the absorption coefficient of a photoconductor can be calculated from the photoconductive spectral response of thin films of that material. The wavelength dependence of the absorption coefficient so calculated is consistent with that predicted from the theory of indirect main-band transitions. It explains the observed change of long-wavelength limit of sensitivity of PbSe produced by a change in film thickness. It shows that no improvement in responsivity at any wavelength can be achieved by increasing film thickness, but that for any particular wavelength a specific thickness can be found which will yield a maximum signal/noise. Specifically, the lower the absorption coefficient the thicker the film must be to yield maximum signal/noise. Thus, in the region of the long wavelength cut-off of the photoconductor, the longer the wavelength the thicker the film must be to yield the maximum signal/noise.

[22] G. G. MacFarlane, as reported by R. A. Smith, Physica **20**, 910 (1954).