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Spectral Distribution of Photoconductivity

H. B. DeVore
RCA Laboratories, Princeton, New Jersey

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A theoretical analysis of the shape of photoconductivity spectral distribution curves is presented, based upon the effects of surface and volume recombination of the charge carriers liberated by the light. Representative curves of photoconductivity *vs* absorption are computed and compared with experimental observations. As an application of this analysis, experimental data for antimony sulfide are compared with a theoretical curve, and the difference is found to be resolvable into two bands representing nonphotoconductive transitions.

INTRODUCTION

PHOTOCONDUCTIVE materials generally exhibit spectral distribution curves having a more or less sharp peak in the vicinity of the absorption edge. Characteristically, as one proceeds from the low-energy (long-wavelength) to the high-energy (short-wavelength) side of the absorption edge, the photoconductive response starts from zero, rises rapidly as the absorption edge is reached, goes through a maximum at some moderate value of absorption, falls again while the absorption coefficient is still rising, and usually appears to approach some asymptotic value greater than zero. This behavior is rather remarkable, since one would expect *a priori* that each absorbed photon would generate a pair of charge carriers and hence that the photoconductive response should have risen to a maximum value, corresponding to absorption of substantially all of the incident radiation, with no decrease for higher values of absorption coefficient.

It has been customary to explain the peak in the photoconductive response by asserting that for high values of absorption coefficient the radiation is all absorbed in a comparatively thin layer near the surface and that the high density of carriers in this region leads to more rapid recombination and hence to a reduced equilibrium concentration. This explanation, however, is completely invalidated by the observation, found in substantially all cases, that the photocurrent in all spectral regions is proportional to light intensity, at least for small intensities, while the peak in the spectral response curve remains. If the recombination of carriers were more rapid in the high-absorption region because of the high carrier density, the photoconductive current would have to approach proportionality to the square root of the light intensity in this region.

In the case of very thin layers of photoconductors, as, for example, in the case of evaporated films, the peak of the spectral response curve is found to be greatly broadened and the drop in the high-energy region is much less than is observed for thick speciments.

It is proposed that the spectral response curve may be explained by taking into account the recombination of carriers at the surface of the photoconductors. Thus, if the surface recombination rate is high, compared with that in the volume of the photoconductor, the equilibrium concentration of charge carriers will be less when these are generated close to the surface (high-absorption region) that when they are distributed through the body of the material (lower absorption).

ANALYSIS OF THE PROBLEM

For simplicity, consider the photoconductor to have the form of a large sheet with thickness l (Fig. 1). Let it be illuminated on one face by radiation having intensity I (photons/second). At each point through the specimen, the density of charge carriers is $n(x)$, and these charge carriers will diffuse in the positive or negative x direction because of the gradient of this density. It is assumed that the carrier pairs will undergo recombination in the volume of the material at a rate corresponding to a volume lifetime τ and further that they will recombine at the surface at a rate which may be represented by a surface recombination velocity S. The carrier pairs are being continuously generated at each point in the volume at a rate proportional to the intensity of the radiation at that point.

In a region at distance x from the surface on which radiation is incident, the rate of generation of carrier pairs is $dn/dt=Ae^{-\alpha x}$, where α is the absorption coefficient. To evaluate A, assuming that every photon absorbed creates a carrier pair, it is noted that for an infinitely thick specimen the number of pairs generated would be equal to the number of photons incident.

$$I=\int_0^\infty Ae^{-\alpha x}dx=\frac{A}{\alpha},\quad \text{i.e.,}\quad A=I\alpha.$$

The carrier pairs leaving the region by diffusion will decrease the carrier density according to the equation $dn/dt=-di/dx$, where $i=ndx/dt$ is the carrier current. The carrier pairs disappearing by recombination will be represented by $dn/dt=-n/\tau$, where τ is the volume recombination lifetime. Combining, we obtain an equation of continuity:

$$\frac{dn(x)}{dt}=-\frac{di}{dx}+I\alpha e^{-\alpha x}-\frac{n}{\tau}. \qquad (1)$$

For steady-state conditions, $dn/dt=0$, and

$$di/dx=I\alpha e^{-\alpha x}-n/\tau.$$

For the diffusion carrier current, we have $i=-Ddn/dx$, where D is the diffusion constant. Differentiating and substituting,

$$\frac{d^2n}{dx^2}=\frac{n}{D\tau}-\frac{I\alpha}{D}e^{-\alpha x}.$$

For convenience, let $1/D\tau=\beta^2$ and $I\alpha/D=\gamma$.

$$d^2n/dx^2=\beta^2 n-\gamma e^{-\alpha x}.$$

This equation has the general solution

$$n=Be^{-\beta x}+Ce^{\beta x}+\left(\frac{\gamma}{\beta^2-\alpha^2}\right)e^{-\alpha x}. \tag{2}$$

Boundary conditions are determined by the assumption that recombination occurs at each surface at a rate which may be represented by a recombination current $i_R=n_sS$, where n_s is the pair density at the surface and S is the surface recombination velocity. Thus, at the first surface, $(i_R)_0=-D(dn/dx)_{x=0}=-n_0S$, and at the second surface, $(i_R)_l=-D(dn/dx)_{x=l}=n_lS$. Substituting these in Eq. (2) and solving for the constants B and C, we obtain

$$B=\frac{\gamma}{\beta^2-\alpha^2}\times\left\{\frac{(S-\alpha D)(D\beta-S)e^{-\alpha l}+(S+\alpha D)(D\beta+S)e^{\beta l}}{(D\beta-S)^2e^{-\beta l}-(D\beta+S)^2e^{\beta l}}\right\},$$

$$C=\frac{\gamma}{\beta^2-\alpha^2}\times\left\{\frac{(S-\alpha D)(D\beta+S)e^{-\alpha l}+(S+\alpha D)(D\beta-S)e^{-\beta l}}{(D\beta-S)^2e^{-\beta l}-(D\beta+S)^2e^{\beta l}}\right\}.$$

We assume that the increase in conductivity caused by the radiation is proportional to N, the total number of carrier pairs:

$$N=\int_0^l n(x)dx=\frac{1}{\beta}\{B(1-e^{-\beta l})+C(e^{\beta l}-1)\}+\frac{\gamma}{\alpha(\beta^2-\alpha^2)}(1-e^{-\alpha l})$$

$$=\frac{\gamma}{\beta^2-\alpha^2}\left\{\frac{1-e^{-\alpha l}}{\alpha}-\frac{1}{\beta}\frac{[S(1+e^{-\alpha l})+\alpha D(1-e^{-\alpha l})]\times[D\beta\sinh\beta l+S(\cosh\beta l-1)]}{(D^2\beta^2+S^2)\sinh\beta l+2D\beta S\cosh\beta l)}\right\}$$

$$=\frac{\gamma}{\beta^2-\alpha^2}\left\{\frac{1-e^{-\alpha l}}{\alpha}-\frac{1}{\beta}\frac{[S(1+e^{-\alpha l})+\alpha D(1-e^{-\alpha l})]}{D\beta+S\coth(\frac{1}{2}\beta l)}\right\}.$$

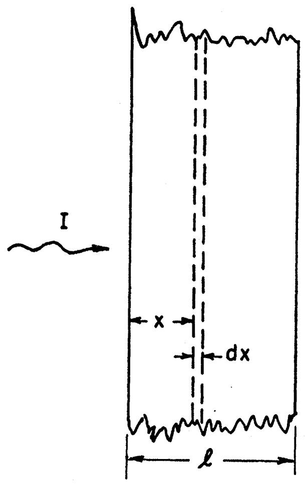

FIG. 1. Schematic arrangement.

Replacing the values of β and γ,

$$N=\frac{\tau I}{1-\alpha^2D\tau}\left\{(1-e^{-\alpha l})-\frac{[\alpha S\tau(1+e^{-\alpha l})+\alpha^2D\tau(1-e^{-\alpha l})]}{1+S(\tau/D)^{\frac{1}{2}}\coth[l/2(D\tau)^{\frac{1}{2}}]}\right\}. \tag{3}$$

It is convenient to make use of the following dimensionless parameters:

$l/(D\tau)^{\frac{1}{2}}\equiv\lambda$($\sim$ thickness of photoconductor),

$\alpha(D\tau)^{\frac{1}{2}}\equiv\zeta$($\sim$ absorption coefficient),

$S(\tau/D)^{\frac{1}{2}}\equiv\xi$($\sim$ ratio of surface to volume recombination rates).

Hence, $\alpha l\equiv\lambda\zeta$. Then

$$N=\frac{\tau I}{1-\zeta^2}\left\{(1-e^{-\lambda\zeta})-\frac{[\zeta\xi(1+e^{-\lambda\zeta})+\zeta^2(1-e^{-\lambda\zeta})]}{1+\xi\coth(\frac{1}{2}\lambda)}\right\}. \tag{4}$$

Letting $Z\equiv\lambda\zeta=\alpha l$, and expressing the photoconductivity in the form $P=N/I\tau$,

$$P=\frac{N}{I\tau}=\frac{1}{\lambda^2-Z^2}\left\{\lambda^2(1-e^{-Z})-\frac{[\xi\lambda Z(1+e^{-Z})+Z^2(1-e^{-Z})]}{1+\xi\coth(\frac{1}{2}Z)}\right\}$$

$$=\frac{1-e^{-Z}}{1+\xi\coth(\frac{1}{2}\lambda)}\times\left\{\frac{\lambda^2+\xi\lambda^2\coth(\frac{1}{2}\lambda)-\xi\lambda Z\coth(\frac{1}{2}Z)-Z^2}{\lambda^2-Z^2}\right\}$$

$$=\frac{1-e^{-Z}}{1+\xi\coth(\frac{1}{2}\lambda)}\times\left\{1+\frac{\xi\lambda[\lambda\coth(\frac{1}{2}\lambda)-Z\coth(\frac{1}{2}Z)]}{\lambda^2-Z^2}\right\}. \tag{5}$$

It is of interest to examine several limiting cases.

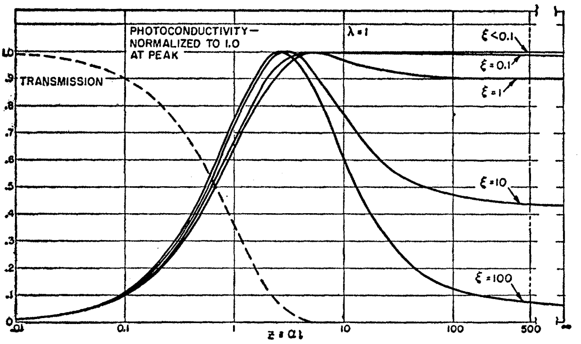

Fig. 2. Photoconductivity-absorption curve, $\lambda=1$, $\xi=0.01$ to 100.

1. Small absorption. $\alpha\to 0$. Therefore $Z\to 0$. Hence $1-e^{-Z}\to Z$, $Z\coth(\frac{1}{2}Z)\to 2$. Then

$$P\to\frac{Z}{1+\xi\coth(\frac{1}{2}\lambda)}\left\{1+\frac{\xi\lambda(\lambda\coth(\frac{1}{2}\lambda)-2)}{\lambda^2}\right\}\to 0 \quad\text{as}\quad Z\to 0.$$

This result is essentially trivial; if light is not absorbed, then there can be no conductivity.

2. Large absorption. $\alpha\to\infty$. Therefore $Z\to\infty$, $e^{-\lambda Z}\to 0$, $\coth(\frac{1}{2}Z)\to 1$. Then

$$P\to\frac{1}{1+\xi\coth(\frac{1}{2}\lambda)}\left\{1+\frac{\xi\lambda(Z-\lambda\coth(\frac{1}{2}\lambda))}{Z^2}\right\}\to\frac{1}{1+\xi\coth(\frac{1}{2}\lambda)}.$$

The photoconductive response approaches a constant value.

3. Surface recombination negligible compared with volume recombination. I.e., $S\ll D/\tau$ or $\xi\ll 1$. Then

$$P\to(1-e^{-Z})\left\{1+\frac{\xi\lambda(\lambda\coth(\frac{1}{2}\lambda)-Z\coth(\frac{1}{2}Z))}{\lambda^2-Z^2}\right\}\to(1-e^{-Z}).$$

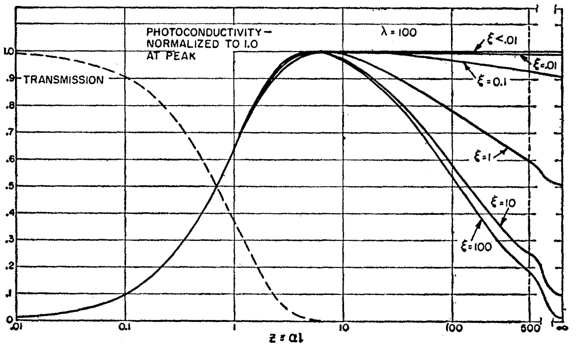

Fig. 3. Photoconductivity-absorption curve, $\lambda=100$, $\xi=0.01$ to 100.

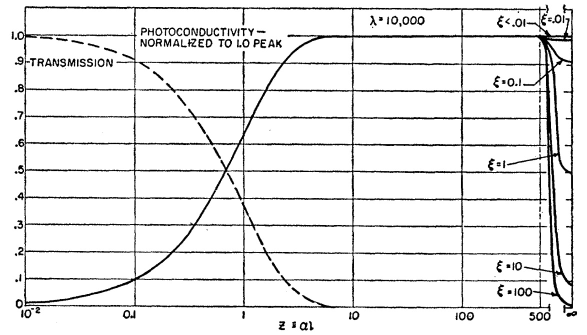

Fig. 4. Photoconductivity-absorption curve, $\lambda=10\,000$, $\xi=0.01$ to 100.

Here P increases monotonically from 0 for small α to 1 for large α. There is no peak in the photoconductivity curve.

4. Surface recombination large compared with volume recombination. $\xi\gg 1$. Then

$$P=\frac{1-e^{-Z}}{\xi\coth(\frac{1}{2}\lambda)}\left\{1+\frac{\xi\lambda(\lambda\coth(\frac{1}{2}\lambda)-Z\coth(\frac{1}{2}Z))}{\lambda^2-Z^2}\right\}.$$

This approaches 0 as $\alpha\to 0$ and approaches $1/\xi\coth(\frac{1}{2}\lambda)$ for large α. For intermediate values of α, there is a peak which may be approximated as follows: For λ and Z greater than about 3, $\coth(\frac{1}{2}\lambda)$ and $\coth(\frac{1}{2}Z)$ both approach unity. Then

$$P=\frac{(1-e^{-Z})}{\xi}\left\{1+\frac{\xi\lambda(\lambda-Z)}{\lambda^2-Z^2}\right\}=\frac{1-e^{-Z}}{\xi}\left\{1+\frac{\xi\lambda}{\lambda+Z}\right\}.$$

This quantity has a maximum given by $dP/dZ=0$; i.e.,

$$e^{-Z}+\frac{\xi\lambda(\lambda+Z)e^{-Z}-\xi\lambda(1-e^{-Z})}{(\lambda+Z)^2}=0,$$

which reduces to $e^Z=1+\lambda+Z$ for $(\lambda+Z)^2\ll\xi\lambda$. For $\lambda=3$, 10, 100, and 1000, this equation gives $Z_{\max}=1.75$, 2.61, 4.7, and 6.9, respectively. For this case there will be a peak in the photoconductivity response corresponding to small values of Z.

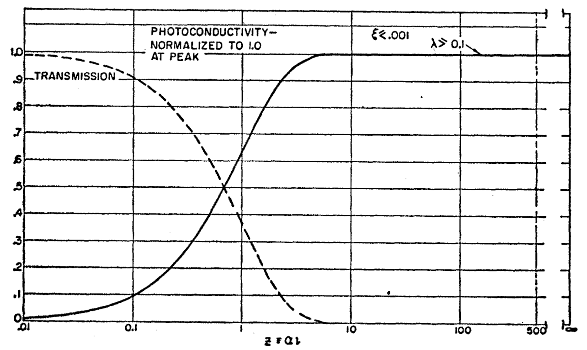

Fig. 5. Photoconductivity-absorption curve, $\xi\pm 0.001$, $\lambda\geqslant 0.1$.

TABLE I. Values of $P_\infty/P_\lambda \equiv$ ratio of photoconductivity at high absorption coefficient to peak photoconductivity.

ξ	=	0.001	0.001	0.01	0.1	1	10	100
$\lambda =$	0.1	1.0000	1.0000	1.0000	0.9993	0.9921	0.8967	0.4278
	1	1.0000	1.0000	0.9993	0.9922	0.8981	0.4317	0.0684
	10	1.0000	0.9996	0.9951	0.9447	0.6073	0.1261	0.0141
	100	0.9999	0.9991	0.9910	0.9167	0.5159	0.0957	0.0105
	1000	0.9999	0.9990	0.9903	0.9100	0.5025	0.0917	0.0100
	10 000	0.9999	0.9990	0.9901	0.9092	0.5003	0.0910	0.0099
	100 000	0.9999	0.9990	0.9901	0.9091	0.5001	0.0909	0.0099

5. Small sample thickness. $\lambda \rightarrow 0$. Then

$$P=\frac{1-e^{-Z}}{2(\xi/\lambda)}\left\{1+\frac{\xi\lambda(2-Z\coth(\frac{1}{2}Z))}{-Z^2}\right\}\sim\frac{\lambda}{2\xi}(1-e^{-Z}).$$

As in the case of small surface recombination velocity, there is a monotonic increase in P from small to large α, but the magnitude of the photoresponse is also small and proportional to the sample thickness.

For the general case, the equation for photoconductivity response was evaluated numerically. For convenience in computation, Eq. (5) may be modified to give

$$P=\frac{N}{I\tau}=\frac{2}{[1+\coth(\frac{1}{2}Z)][1+\xi\coth(\frac{1}{2}\lambda)]}\times\left\{1+\frac{\xi(\frac{1}{2}\lambda)[(\frac{1}{2}\lambda)\coth(\frac{1}{2}\lambda)-(\frac{1}{2}Z)\coth(\frac{1}{2}Z)]}{(\frac{1}{2}\lambda)^2-(\frac{1}{2}Z)^2}\right\}.$$

The spectral response curves have been computed over a wide range of parameters. Specifically, the ranges considered are:

Thickness of photoconductor:
$l=10^{-3}$ cm to 10^{-1} cm.
Diffusion constant: $D=10^{-1}$ cm^2/sec to 10 cm^2/sec.
Volume recombination time:
$\tau=10^{-11}$ sec to 10^{-5} sec.
Surface recombination velocity:
$S=10^2$ cm/sec to 10^4 cm/sec.

Corresponding to various possible combinations of these values, the dimensionless parameters have the following ranges:

$$\lambda=10^{-1} \text{ to } 10^5, \quad \xi=10^{-4} \text{ to } 10^2.$$

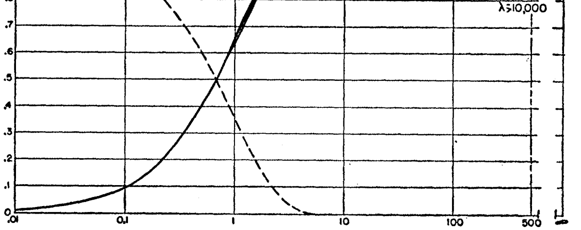

FIG. 6. Photoconductivity-absorption curve, $\xi=0.1$, $\lambda=0.1$ to 10 000.

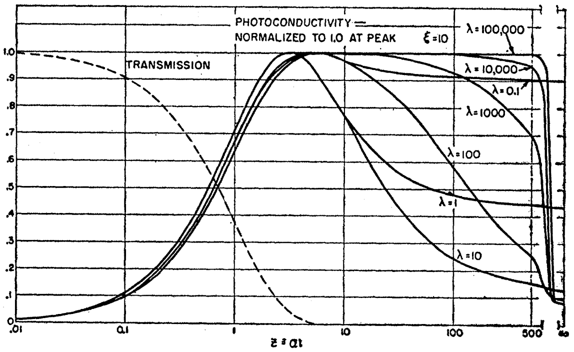

FIG. 7. Photoconductivity-absorption curve, $\xi=10$, $\lambda=0.1$ to 100 000.

In order to exhibit the forms of the computed photoconductivity curves, each curve was normalized to a value of 1.000 at its peak.

Figures 2 to 7 show the manner in which the photoductivity curves vary with recombination rate (ξ) for fixed sample thickness (λ) and the variation with thickness for given recombination rate. The abscissas of the curves are $Z=\zeta\lambda=\alpha l$ and the curves, representing photoconductive response as a function of absorption coefficient, are equivalent to spectral curves of photoconductivity. They differ in shape from such curves, as normally presented, with either wavelength or photon energy as abscissa, in being greatly stretched out beyond the absorption edge. This stretching in the horizontal direction occurs because after the absorption edge is reached, the absorption coefficient changes very

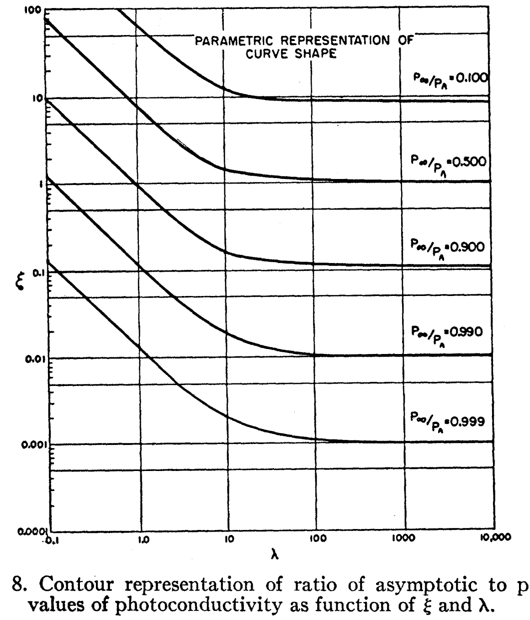

FIG. 8. Contour representation of ratio of asymptotic to peak values of photoconductivity as function of ξ and λ.

rapidly for small change in wavelength or photon energy. For convenient reference, the optical transmission is also plotted ($T=e^{-\alpha l}$).

Characteristically, each curve approaches an asymptotic value of photoconductive response for large values of absorption coefficient, and perhaps the most conspicuous distinguishing feature of a curve is the ratio of this asymptotic response to the peak response. Table I gives the values of these ratios for the ranges of λ and ξ used herein. It is notable that, for small values of λ and ξ (small thickness, small surface recombination), this ratio is practically unity, and no peak exists. For large values of λ and/or large values of ξ, there is a peak, which becomes more pronounced very rapidly in the case of increasing ξ and more slowly for increasing λ, with the peak shape becoming constant for large values of λ. Figure 8 shows a contour map of the asymptote-to-peak ratio as a function of ξ and λ.

COMPARISON WITH EXPERIMENTAL RESULTS

Detailed comparison of the predictions of this theory with experiment is rather difficult, in view of the meager data on absorption on the short-wavelength side of the absorption edge. The general shapes of observed photoconductivity spectral distribution curves are in reasonable agreement with those predicted by this theory, when due account is taken of the non-uniform variation of absorption coefficient through the spectrum.

One general observation that has been made is that photoconductivity curves obtained for thick specimens (of the order of magnitude of 1 mm or greater) invariably show a peaked form, with a tendency to approach an asymptotic value in the high-absorption region. On the other hand, thin films of the same materials (thickness in the micron range) show either no peak or a very broad peak with small drop in the high-absorption region. These characteristics are in good agreement with this theory.

On the low-absorption (long-wavelength) side of the peak, experimental curves generally show less photoconductive response, corresponding to a given absorption coefficient, than would be expected from this theory. The situation is exemplified by the experimental curve for a crystal of antimony sulfide (Sb_2S_3),[1] shown in Fig. 9, together with the theoretical curve (for $\lambda=1000$, $\xi=1$) which seemed most nearly to match the location of the peak and the ratio of peak height to asymptotic value at large α. The disparity apparently arises from the assumption that every photon absorbed creates a pair of charge carriers—i.e., the assumption that only band-to-band transitions occur. However, it is substantially never true that photoconductors are of such purity and perfection that no other type of transition can occur. Absorption in the long-wavelength tail may arise from a variety of electronic transitions, not all of which are of such nature that they give rise to photoconductivity.

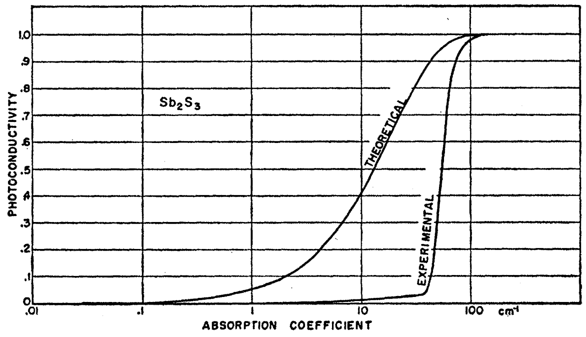

FIG. 9. Photoconductivity-absorption curves for antimony sulfide.

This divergence between experimental data and theoretical predictions may be utilized to obtain information concerning electronic transitions, occurring in the long-wavelength tail, which do not give rise to photoconductivity. Such an analysis was carried through for the Sb_2S_3 data. By subtracting the absorption values of the theoretical curves from the corresponding experimental values, a curve for "excess" absorption is obtained. Figure 10 shows the tail of the experimental absorption curve and the corresponding curve of excess absorption. This excess-absorption curve was then resolved into absorption bands, assumed to have Gaussian form, and these bands are also shown in Fig. 10. No great accuracy is claimed for the second absorption band, since the absorption data in the neighborhood of $h\nu=1.6$ ev, corresponding to very low light transmission by the samples available, have considerable uncertainty.

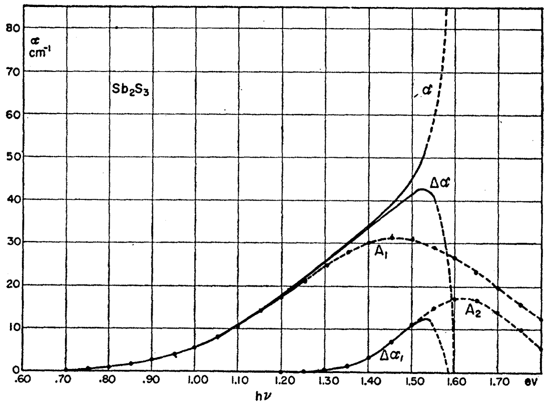

FIG. 10. Low-energy tail of absorption curve for antimony sulfide. α—experimental absorption curve; $\Delta\alpha$—difference between experimental and theoretical curves; A_1—first absorption band; $\Delta\alpha$—difference between $\Delta\alpha$ and A_1 curves; A_2—second absorption band.

Applying Smakula's[2] formula to the absorption bands,

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[1] This crystal was prepared by E. L. Lind.

[2] See F. Seitz, *Modern Theory of Solids* (McGraw Hill Book Company, New York, 1940), p. 664.

we obtain values for densities of impurities responsible for these two bands. The calculated values are about 8×10^{16} cm^{-3} and 3×10^{16} cm^{-3}, respectively. These results are plausible values.

ACKNOWLEDGMENTS

The author wishes to express his indebtedness to Dr. L. S. Nergaard, of these Laboratories, who initially proposed this approach to the problem and who has given advice and assistance at many stages of the development.

APPENDIX

The technique of resolving the absorption curve into absorption bands having Gaussian form may be of interest. The absorption band has the equation $\alpha=A\exp[-k(h\nu-h\nu_0)^2]$. For convenience of computation, we use logarithms to the base 10: $\log\alpha=\log A-K(h\nu-h\nu_0)^2$.

The problem is then that of determining the constants A, K, $h\nu_0$, such that this curve will fit as well as possible to the experimental curve. A number of experimental points $\alpha_n(h\nu_n)$ are selected. The assumption is made that the first of these, $\alpha_1(h\nu_1)$, lies on the Gaussian, and the fit of the others is checked. Writing $\log\alpha_n=\log A-K(h\nu_n-h\nu_0)^2$ and $\log\alpha_1=\log A-K(h\nu_1-h\nu_0)^2$, and subtracting, we find

$$\log\alpha_n-\log\alpha_1=-K(h\nu_n-h\nu_1)(h\nu_n+h\nu_1-2h\nu_0).$$

Define

$$z_{n,1}\equiv\frac{\log\alpha_n-\log\alpha_1}{h\nu_n-h\nu_1}=-K(h\nu_n+h\nu_1-2h\nu_0).$$

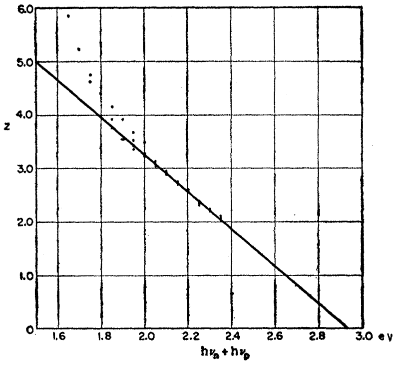

FIG. 11. Plot of $Z\equiv(\log\alpha_n-\log\alpha_1)/(h\nu_n-h\nu_1)$ vs $(h\nu_n+h\nu_1)$.

If, now, z_n is plotted on a linear scale against $(h\nu_n+h\nu_1)$, a straight line should be obtained. Its zero intercept will be $2h\nu_0$ and its slope will be $-K$.

The computation of z_n is repeated with each of the selected points in turn being assumed to lie on the curve and a plot will be obtained similar to that shown in Fig. 11. It is seen that a straight line can be found which fits well to most of the points. Those points departing widely from the line are associated with experimental points which do not fall on the curve sought. From the line so determined, mean values of K and $h\nu_0$ are found. These are then substituted in the equation $\log A=\log\alpha_n+K(h\nu_n-h\nu_0)^2$ for each of the experimental points and the mean of the values of $\log A$ is found.

Having determined a first absorption band in this fashion, it is plotted together with the experimental absorption curve and subtracted, point-by-point, from the experimental curve to give a residual which may then be analyzed in the same manner for further absorption bands.