

Optical Properties of Lead Telluride*

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Optical constants of lead telluride films as a function of both temperature and oxygen content have been investigated. The films were evaporated onto sapphire disks subsequently exposed to air and also on sapphire disks maintained at pressures lower than 10^{-6} mm of Hg. Film thickness, determined by Tolansky interference techniques and by weighing techniques, indicated that the density of evaporated layers of PbTe is about 10 percent smaller than for bulk. The optical constants were calculated from the reflection and transmission curves of the film. The addition of oxygen to the film was shown to give rise to an increase in absorption and a slight increase in the index of refraction. The optical properties were then shown to be strongly dependent on the temperature of the film. A mechanism has been proposed to explain the results.

I. INTRODUCTION

THIN evaporated layers of PbTe are found to be photosensitive to radiation in the near infrared. The photoconductive properties have been described by Bode and Levinstein.¹ When the film is exposed to successive traces of oxygen, the resistance increases at first, then decreases, the thermoelectric power changes sign, and the material becomes sensitive to infrared radiation. The photosensitivity is low at room temperature, but when the film is cooled to liquid air temperature, the photosensitivity is increased by many orders of magnitude. The photoeffect at this temperature extends to about 5.5 microns. This upper wavelength limit shifts toward the visible as the temperature is raised.

The only detailed investigations of the optical properties of PbTe films reported to date were performed by Gibson.² He did not correlate them with the photoconductive properties of the films. Curve C of Fig. 1 shows the absorption coefficients of PbTe films as determined by Gibson.

The results of Vernier³ on the absorption and photoconductivity of PbS films should also be noted since many similarities have been found between PbTe and PbS. Vernier reported large variations among different films of both the spectral sensitivity and the absorption spectra and found a correspondence between the over-all shape of the sensitivity and absorption curves. He did not attempt experiments on unoxidized films nor did he perform experiments at temperatures other than room temperature.

Gibson theorized that the absorption by films in the long-wavelength region is mainly attributable to the scattering of light by individual crystallites in the film. This would render the true absorption undetectable. To eliminate this factor he began investigations on PbTe bulk crystals.⁴ This does not permit measurement of both absorption and photoconductivity on the same

sample since bulk PbTe crystals show no photoconductive properties. The main portion of his experiment was performed on thin cleaved or polished crystals. Absorption in these crystals for wavelengths below 4 microns is high and no measurement of the absorption coefficient could be made. The 4-micron edge moves linearly toward longer wavelength with temperature as the material is cooled. Gibson was able to obtain one extremely thin crystal, about 1 micron in thickness, and was able to measure the transmission to wavelengths below 2 microns. (Curve A, Fig. 1.)

Avery^{5,6} recently published two reports in which he

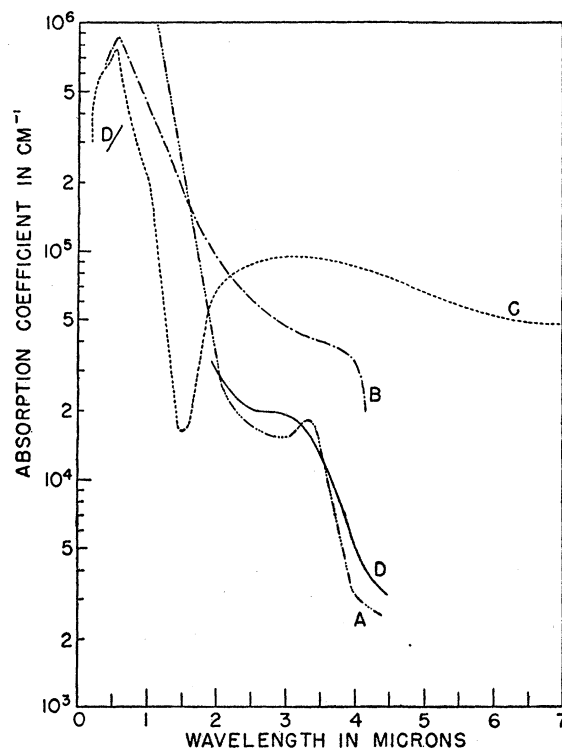


FIG. 1. Absorption coefficient as a function of wavelength: A. crystals (Gibson); B. crystals (Avery); C. films (Gibson); D. films (present work).

* This work was supported by the Wright Air Development Center.

¹ D. Bode and H. Levinstein, *Phys. Rev.* (to be published).

² A. F. Gibson, *Proc. Phys. Soc. (London)* **B63**, 756 (1950).

³ P. Vernier, *J. phys. radium* **14**, 175 (1953).

⁴ A. F. Gibson, *Proc. Phys. Soc. (London)* **B65**, 378 (1952).

⁵ D. G. Avery, *Proc. Phys. Soc. (London)* **B66**, 133 (1953).

⁶ D. G. Avery, *Proc. Phys. Soc. (London)* **B67**, 2 (1954).

obtained values for the optical constants of single crystals by means of a reflection technique. Curve *B* in Fig. 1 shows his results on the absorption constant. Avery also found that heating of a PbS crystal caused a decrease in both the absorption and the index of refraction at longer wavelengths. The measurements of the effects of temperature were restricted to PbS, since Avery was unable to obtain cleavage faces of PbTe crystals smooth enough to give reproducible data.

Thin films have been used in the present study of the optical constants because they have the following advantages over bulk crystals of PbTe.

1. It is possible to obtain correlations between photo-sensitivity and absorption on the same samples. Photo-sensitivity has not been found in bulk crystals of PbTe.
2. The absorption coefficients in the region examined are high. This gives rise to very low percentages of transmission in crystals.
3. If reflection measurements of bulk crystals are used to determine the optical constants, surface conditions seriously affect the results.
4. It is possible to control the amount of oxygen impurities added to thin layers. The present arrangement allows for the measurement of the optical constants with different oxygen impurity concentrations.

II. EXPERIMENTAL TECHNIQUES

The optical constant measurements were performed on a Model 12B Perkin-Elmer Spectrometer. Preliminary measurements of the optical constants were made on PbTe films evaporated in a bell jar on sapphire disks.

The major part of the work, however, was done on films that were never exposed to the atmosphere. For this purpose, a cell in which the films could be formed was mounted on the spectrometer. A detailed drawing of the cell used is shown in Fig. 2. Sapphire was used for the front window and substrate since it is transparent in the near infrared. The transmission of a disk 1 mm thick is constant (88 percent) to wavelengths up

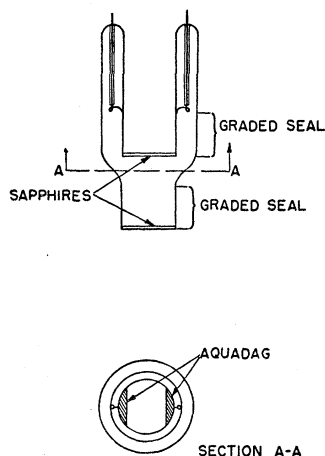


FIG. 2. Sketch of cell blank.

to 4 microns and then falls slowly to about 50 percent at 6 microns.

Approximately 5 mg of powdered PbTe was introduced into the cell. The cell was attached to an all-glass vacuum system which used a three-stage oil diffusion pump backed by a Welch forepump. A glass reservoir of oxygen was separated from the system by stopcocks such that pulses of oxygen could be admitted. The system was trapped with liquid oxygen. Pressures lower than 5×10^{-7} mm of Hg could be obtained. The pulses were adjusted to produce a pressure increase of about 1 micron.

Before the film was formed, the cell was heated to 550°C for over an hour in order to outgas the cell. Some of the PbTe was vaporized in the process but it condensed outside of the cell. An air stream was then directed against the inside sapphire, cooling it to about 50°C, thus allowing the PbTe to condense on the substrate. This process was continued until a desired thickness was obtained. The thickness was determined by noting the wavelength of the interference peaks. A film of 5000Å thickness could be formed in about 2 hours.

Brattain and Briggs⁷ have derived equations for the transmission and reflection of radiation incident on a film of index n , extinction coefficient k , and thickness t .

The equation for transmission is:

$$T = \frac{16n_1n_2(n^2 + k^2)}{r^2\{[e^x - (\rho/r)e^{-x}]^2 + 4(\rho/r)\sin^2[y + \frac{1}{2}(\phi - \theta)]\}}, \quad (1)$$

where

$$r^2 = [(n_1 + n)^2 + k^2][(n_2 + n)^2 + k^2],$$

$$\rho^2 = [(n_1 - n)^2 + k^2][(n_2 - n)^2 + k^2],$$

$$\tan\phi = \frac{[-k(2n + n_1 + n_2)]}{[(n_1 + n)(n_2 + n) - k^2]},$$

$$\tan\theta = \frac{[-k(2n - n_1 - n_2)]}{[(n_1 - n)(n_2 - n) - k^2]},$$

$$x = 2\pi kt/\lambda,$$

$$y = 2\pi nt/\lambda,$$

where n_1 represents the index of refraction of air and n_2 is the index of refraction of the nonabsorbing film substrate.

For very large k the e^x term in the denominator is much greater than either the e^{-x} term or the sine term. Equation (1) thus reduces to

$$T = Ae^{-4\pi kt/\lambda}. \quad (2)$$

Hammer⁸ has shown that for the reflected energy only, in the range of values of optical constants found in this experiment, the use of the relationship $2nt = m\lambda$

⁷ W. H. Brattain and H. B. Briggs, Phys. Rev. **75**, 1705 (1949).

⁸ K. Hammer, Z. tech. Phys. **24**, 169 (1943).

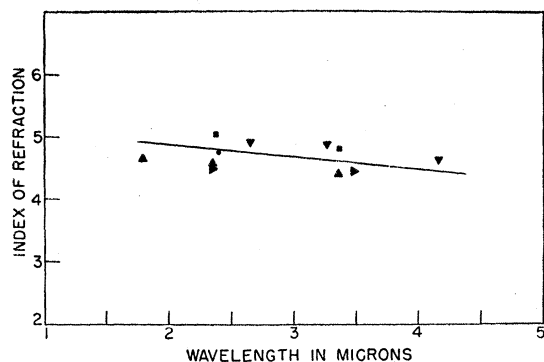


FIG. 3. Room temperature index of refraction as a function of wavelength (thickness determined by Tolansky method).

to determine the locations of maxima and minima is valid.

Since the determination of the index of refraction requires a knowledge of the thickness of the film, this thickness had to be carefully measured. Two different accepted methods of thickness determination were used. One method consists of weighing the film and determining the film thickness by assuming a bulk density of PbTe. The other method makes use of the Tolansky interference technique.

Thicknesses of films determined by the Tolansky method averaged about 10 percent greater than those determined by the weighing method. This result indicates that the density of the material when it is evaporated and then condensed in the form of films is less (by about 10 percent) than the density of bulk crystals. Since Wilman⁹ has found from x-ray data that lattice constants in films of PbS and PbSe are the same as in the bulk crystals, the change in apparent density is probably attributable to the presence of spaces between the crystallites.

The thickness of films formed inside of the cell cannot be measured directly. However, if the index of refraction is known from the measurements above, the thickness can be calculated from the location of the interference peaks.

Equation (1) was used for the calculation of the extinction coefficient k . The evaluation of k at wavelengths where the absorption is not large enough to damp out the effect of interference is based on the assumption that both n and t at a given wavelength are known, being found as above. Thus we have an equation with one unknown which cannot be solved explicitly for k .

In order to obtain an approximation solution, the transmission equation is divided into a number of parts and the individual relationships are plotted as a function of n for different values of k . The three relationships are: $16n_1n_2(n^2+k^2)/r^2$, ρ/r , and $\frac{1}{2}(\phi-\theta)$. Through the choice of a value of k and the assumption that the values of the above three relationships calculated from

it are correct, the only equation remaining to be solved for k is: $e^x - (\rho/r)e^{-x} = C$, where ρ/r is found from the graph of this value and C is calculated from T and values obtained from all the graphs.

Graphs of $16n_1n_2(n^2+k^2)/r^2$ and ρ/r show that these relationships do not depend strongly on k . The phase angle is proportional to k but the evaluation of Eq. (1) is not affected greatly by the value of the phase angle.

The method, therefore, was to assume a value of k at a given n , t , and λ and then solve $e^x - (\rho/r)e^{-x} = C$ for k . If this calculated value of k was greatly different from the value assumed, it in turn could be used as the assumed value. It was usually found that this process did not have to be repeated more than once, the two calculated values agreeing closely.

III. RESULTS

A. Films Exposed to Air

1. Index of Refraction

The values of n as a function of wavelength obtained from the thicknesses determined by the Tolansky method are shown in Fig. 3. The value of the index calculated from the thickness determined by the weighing technique was found to be higher than the index based on the Tolansky thickness method. The error in both methods is not greater than ± 5 percent. This error is believed to be based almost entirely on the uncertainty of the thickness calculations.

Values of index based on the assumption of bulk densities (weighing methods) agree within experimental error with the values found by Avery on bulk crystals. Avery found that n increases slightly with increasing wavelength, while the present results show a definite decrease in index at longer wavelengths.

2. Extinction Coefficient

Since the value of the extinction coefficient in the visible region is found to be high, Eq. (2) is valid in

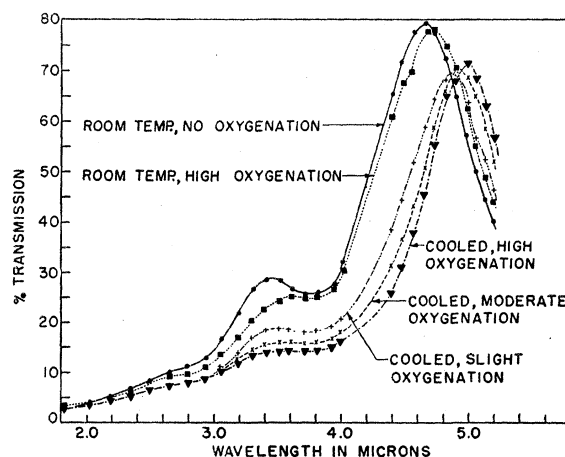


FIG. 4. Percent transmission of a typical film for different temperatures and different degrees of oxygenation.

⁹ H. Wilman, Proc. Phys. Soc. (London) **60**, 117 (1948).

this region. A Welch Densichron with three different Wrattain Filters was used to determine the percentage transmission at wavelengths of 0.45, 0.53, and 0.65 micron. The values of $\ln T$ vs t were plotted for the three wavelengths measured. The values of the extinction coefficient determined from the slopes of these curves are: 1.03 at 0.45 micron, 1.32 at 0.53 micron, and 1.82 at 0.65 micron. These values, expressed in terms of the absorption coefficient α , where $\alpha = 4\pi kt/\lambda$, are shown in curve *D* of Fig. 1. The measurements in this region were performed only to obtain an order of magnitude value of the absorption constant, so that these values could be compared with the absorption measured at longer wavelengths.

B. Films in High Vacuum

1. Effects of Oxygen and Temperature on Transmission Properties

A typical transmission curve of a film maintained in vacuum is shown in Fig. 4. The transmission peaks at 3.4 microns and at 4.7 microns arise from the presence of interference. When the substrate was cooled to -158°C (the lowest temperature achieved with the cooling techniques used) there was no appreciable change in either the transmission curve or the resistance. However, if one pulse of oxygen was allowed to enter the cell, the following very noticeable effects on both the electrical and optical properties of the film were obtained:

- The resistance of the film suddenly increased from 150 to 300 ohms.
- The transmission in the 3-micron wavelength region decreased about 10 percent.
- The wavelength at which the 4.7-micron interference peak appeared was shifted about 0.02 micron toward longer wavelengths. This shift is below the resolving power of the instrument, but the change in peak can definitely be seen for all samples investigated.

When the film was cooled below room temperature the above effects all increased considerably. The resistance value doubled, the transmission decreased to about 65 percent of its original value, and the long-wavelength interference peak moved about 0.15 micron toward longer wavelengths. (See curve marked "cooled, moderate oxygenation" in Fig. 4.)

If additional pulses of oxygen were admitted to the cell, further increases in peak shift, absorption, and resistance were noted. The energy transmitted as a function of wavelength is shown in Fig. 4, designated "high oxygenation." The room temperature resistance was 11 000 ohms, increasing to 1.7 megohms when the film was cooled to -158°C .

It should be pointed out that the effect of oxygen on the location of the room temperature long-wavelength interference peak is small in magnitude (less than 1 percent). The shift in interference peak that probably

occurs on the sapphire disks when they are exposed to air at room temperature, therefore, would not significantly affect the determination of either the index of refraction or the thickness. It is this result which makes it possible to use the value of the index of refraction determined on the exposed sapphire for the calculation of thicknesses of films maintained in vacuum.

Heating of the films produced reverse effects on the electrical and optical properties, decreasing the resistance and the wavelength at which the long-wavelength interference appears, and increasing the transmission at shorter wavelengths. It is difficult to obtain accurate values for films at elevated temperatures, since heating of the film for the time required to take transmission measurements usually changed the properties of the films. Only a few cases were found where it was possible to raise the temperature of the film without producing a permanent change in film properties.

Although no careful measurements were made on the film in the vacuum cell at wavelengths below 1.8 microns, experiments were performed to see if additions of oxygen and changes in temperature affected the transmission between 1 and 1.8 microns. Within the limits of oxygenation and temperature variations used in the present investigation, no effects have been noted in this region below 1.7 microns.

2. Effects of Oxygen and Temperature on the Index of Refraction

Figure 5 is a plot of the index of refraction as a function of wavelength for films at different temperatures and with different oxygen content. The addition of oxygen did not affect the index of a film at room temperature sufficiently to make it observable on the graph. As indicated in the curves, the index variation begins at wavelengths near 2.5 microns and increases with wavelength. The change in index, therefore, could not be due to a thickness change of the film, since this

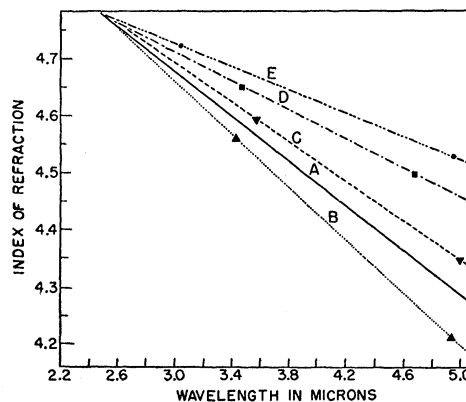


FIG. 5. Index of refraction as a function of wavelength for different degrees of oxygenation: A. Room temperature; B. heated -225°C (slight oxygenation); C. cooled -158°C (slight oxygenation); D. cooled -158°C (moderate oxygenation); E. cooled -158°C (high oxygenation).

would give rise to a peak shift in all regions of the spectrum investigated. Since the thickness does remain constant, and the location of the peaks is given by the relationship $2nt=m\lambda$, the change in index is proportional to the change in wavelength. On the basis of this fact the values shown in Fig. 5 were determined. Figure 6 shows the linear decrease in the index with temperature, at a particular wavelength. This result is in contrast to germanium, where the index increases with increasing temperature as reported by Briggs¹⁰ for crystals and as measured on films of germanium in this laboratory.

3. Effects of Oxygen and Temperature on the Extinction Coefficient

Typical values for the extinction coefficient are shown in Fig. 7. The curves were calculated on the basis of values for the refractive index and thickness determined by the Tolansky method. Curves calculated on the basis of index and thickness values obtained from the weighing technique are very similar.

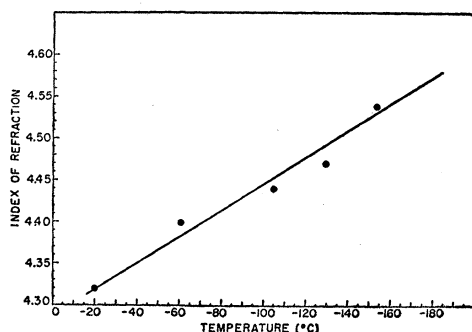


Fig. 6. Index of refraction at $\lambda = 4.9$ microns as a function of temperature for a film after high oxygenation.

The absorption curves for different films show one common characteristic. The long-wavelength absorption edge moves toward longer wavelengths when the film is cooled. This is very similar to the effect on bulk crystals observed by Gibson.¹¹ In Fig. 1 the magnitude of a typical absorption curve of a photosensitive cell is compared with the results obtained, by both Avery and Gibson, on bulk crystals. Avery's values were obtained from radiation reflected from bulk crystals; Gibson obtained his results from measurements of transmitted radiation. The present results agree more closely with those of Gibson, but it should be pointed out that Gibson does not claim very good accuracy in his results. The similarity of the magnitudes and shapes shown in all three curves indicates that absorption obtained in bulk and films is essentially due to the same mechanism, and that scattering by crystallites does not play a significant role at the wavelengths under consideration.

¹⁰ H. B. Briggs, Phys. Rev. **77**, 287 (1950).

¹¹ A. F. Gibson, Proc. Phys. Soc. (London) **B65**, 378 (1952).

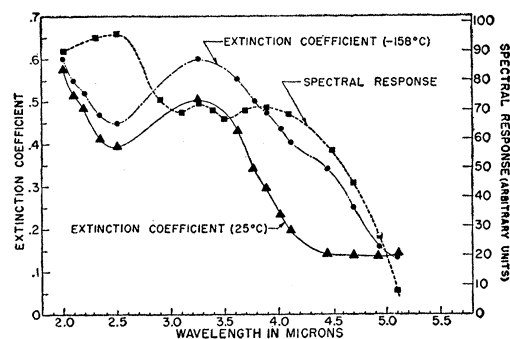


Fig. 7. Extinction coefficient and spectral response as a function of wavelength.

IV. DISCUSSION

The similarity between the absorption curves at low temperatures and the spectral sensitivity curves indicates that the two are related. The sensitivity curves are displaced toward longer wavelengths, but Moss¹² shows that this is often to be expected in regions where the absorption is high. The fact that the absorption cutoff at long wavelengths varies with temperature in much the same way as the long-wavelength limit of sensitivity as reported by Bode and Levinstein¹ also helps to substantiate the theory that absorption and sensitivity are interrelated.

The results indicate that the absorption below 1.7 microns is intrinsic in nature, the absorption arising from excitation of electrons from the valence band to the conduction band. Two mechanisms are conceived as possible causes of the absorption at longer wavelengths. The first is that the absorption in this longer wavelength region is still intrinsic. This assumption is supported by the high absorption values and also by the comparatively small variations of both the absorption and spectral response from their respective values in the shorter-wavelength region.

This long-wavelength region may also be considered an impurity region, the absorption being caused by excitation of electrons either from the valence band to impurity centers or from impurity centers to the conduction band. Impurity absorption is indicated since the absorption in this region varies with the oxygen content and the temperature of the film.

An explanation in terms of impurity levels still does not account for the high absorption coefficient. It is perhaps possible that the films would contain a large enough number of impurities to give rise to the high extinction coefficient. If, however, the absorption is considered as arising from the same mechanism as in bulk crystals, where the impurity concentration is much smaller, the similarity of shape and magnitude of absorption curves is not easily explained. Figure 1 shows a comparison of the absorption in films as obtained in this study.

¹² T. S. Moss, Proc. Phys. Soc. (London) **A64**, 590 (1951).

If the long-wavelength absorption is assumed to be intrinsic, no simple description of the conduction band can be proposed. A simple model will not illustrate how changes in temperature and oxygen contamination affect the absorption. To explain these effects the conduction band should have a structure that is sensitive to changes in temperature and oxygen content.

Such a proposal might be avoided if it is assumed that a new oxide is formed when oxygen is added, the high absorption at 3 microns being due to intrinsic absorption of the oxide itself. Temperature variations of the film and the oxide might cause the changes in absorption noted, but it is difficult to see how the various effects reported would be explained. If it is assumed that the absorption characteristics in the film do arise mainly from an oxide, the similarity with absorption in bulk crystals is also not easily understood.

The supposition that the absorption spectra result from structure of the conduction band therefore appears to be the only way to describe an intrinsic phenomenon. In order to explain the long-wavelength cutoff at about 5 microns at low temperatures, the energy gap between the valence and the conduction band must be of the order of 0.25 ev. This value disagrees with the results of Hall measurements as reported by Chasmar and Putley.¹³ However, Scanlon¹⁴ has recently pointed out that the energy gap derived from Hall constant measurements at high temperatures may be in error.

By producing purer crystals of PbS, Scanlon can measure the activation energy of PbS at lower temperatures, and he finds that it is about 0.37 ev as compared with earlier results of 1.17 ev obtained at temperatures above 900°K.¹⁵ It could therefore be expected that when purer crystals of PbTe are available with

activation energies measurable at lower temperatures, a similar decrease in activation energy will be observed.

To explain the observed effects, one might assume a conduction band which would lie 0.25 ev above the valence band. The density of states might be quite low to a point about 0.7 ev above the valence band, at which point the density would increase rapidly. The tail in the conduction band could thus explain the decreased absorption beyond 2 microns. Since freshly evaporated films are always *n* type,¹⁶ part of the tail of the conduction band would be filled with electrons, probably excited from interstitial Pb centers, close to the conduction band. Oxygen added to the film is adsorbed on the film surface,¹⁷ and, by acting as a trap for electrons, removes them from the tail of the conduction band, thus increasing absorption beyond 2 microns. A decrease in temperature prevents thermal excitation from the valence band to the tail of the conduction band, resulting in both an increase in absorption and an extension of the high absorption region to longer wavelengths. Photoconductivity is then produced when the electron and hole density is increased as electrons are excited to the conduction band.

Although this picture disagrees with the interpretation suggested by Chasmar and Putley,¹⁸ a model of this type can still explain their results. Their high value of activation energy (0.62 ev) would arise from thermal excitation from the valence band to the region above the tail of the conduction band. The value of 0.62 ev determined thermally is to be compared with the approximate value of 0.7 ev determined in this experiment by optical measurements.

We are indebted to Mr. Eric Ellis and Mr. Donald Cole for their assistance in the performance of this work.

¹³ R. P. Chasmar and E. H. Putley, *Semiconducting Materials* (Butterworth Scientific Publications, London, 1951), p. 216.

¹⁴ W. W. Scanlon, *Phys. Rev.* **92**, 1573 (1953).

¹⁵ E. H. Putley and J. B. Arthur, *Proc. Phys. Soc. (London)* **B64**, 616 (1951).

¹⁶ S. J. Silverman and H. Levinstein, *Phys. Rev.* **94**, 871 (1954).

¹⁷ R. A. Smith, *Semiconducting Materials* (Butterworth Scientific Publications London, 1951), p. 198.

¹⁸ R. P. Chasmar and E. H. Putley, *Semiconducting Materials* (Butterworth Scientific Publications, London, 1951), p. 216.