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Photoconductivity in the Infra-Red Region of the Spectrum. Part II. The Mechanism of Photoconductivity in Lead Telluride

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PHOTOCONDUCTIVITY IN THE INFRA-RED REGION OF THE SPECTRUM

PART I. THE PREPARATION AND PROPERTIES OF PHOTOCONDUCTIVE FILMS OF LEAD TELLURIDE

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PART II. THE MECHANISM OF PHOTOCONDUCTIVITY IN LEAD TELLURIDE

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PART I

The method of preparation of photoconductive films of lead telluride is described. Details are given of the construction of cells suitable for infra-red detection in spectroscopic applications. Lead telluride is not photosensitive at room temperature, but is strongly photoconductive at temperatures in the region of −190° C. The conductivity of lead telluride as a function of the applied voltage, and the wave-length and intensity of illumination has been investigated, for seven films of widely different conductivity, at liquid-air temperature. The application of the photoconductive effect to infra-red detection is discussed, and attention is drawn to the effect of any background of thermal radiation on the performance of a cooled photoconductor.

PART II

A method is described by which thin semi-conducting films of nearly stoichiometric lead telluride can be prepared by evaporation, in a sequence with increasing impurity of lead. The conductivity and infra-red photoconductivity of the specimens has been investigated as a function of temperature and of lead impurity. It is found that the magnitude of the photo-effect is a function of the dark conductivity, and depends only on the quantity of excess lead. The absorption of oxygen at room

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temperature is equivalent to the removal of excess lead; the presence of oxygen is not a requirement for the appearance of photoconductivity. These observations are used to draw conclusions concerning the mechanism of the photoconductivity. It is shown that all the phenomena can be explained by a single lattice model, without recourse to internal potential barriers or inhomogeneities in the composition of the samples.

I. THE PREPARATION AND PROPERTIES OF PHOTOCONDUCTIVE FILMS OF LEAD TELLURIDE

By O. Simpson and G. B. B. M. Sutherland, F.R.S.

Introduction

Photoconductivity in the infra-red region of the spectrum has been known for over 70 years, but it is only within the past 10 years that any use has been made of this phenomenon as a means of detecting infra-red radiation. The reason for this is that until recently, the limit of spectral sensitivity of such photoconductors was about $1{\cdot}2\mu$, and alternative methods (especially photographic and photoemissive) were effective just as far into the infra-red and were either more efficient or more suitable in practical applications. However, the discovery by Case (1917) that lead sulphide showed some photoconductivity stimulated research, initially in Germany and later in Britain and the United States, on the potentialities of this material as a detector. It was found that a very thin layer of lead sulphide, deposited either by evaporation or by chemical means, could be treated with oxygen in such a way that it became superior to any other detector in the region between 1 and 3μ. The motive for this work was to provide a detector for military applications, and naturally all of the work carried out between 1939 and 1945 was done under secrecy restrictions. Since 1945, brief accounts of the most important results achieved on lead sulphide have appeared in various journals. Oxley (1946) and Elliott (1947) have summarized the work done in Germany as far as available. The work in Britain was carried out at the Admiralty Research Laboratory by Starkiewicz, Sosnowski & Simpson (1946, 1947), while that in the United States was done by Cashman (1946*a*, *b*). It is clear from these publications that while satisfactory empirical procedures have been developed for the production of excellent lead sulphide photoconductive cells, and a possible theory has been proposed which accounts for certain of their properties in a formal way (Starkiewicz *et al.* 1947), many of the properties are unexplained, and the theory is such that it gives little help in a search for better infra-red photoconductors.

The present investigation was undertaken with two main objects in view. The first was to explore the potentialities of lead selenide and lead telluride as alternatives to lead sulphide. Fragmentary reports of war-time work in Germany indicated that layers of these materials were photosensitive as far as 4·5 and $6{\cdot}5\mu$ respectively, but no details were available to us of methods of preparation nor of properties. An efficient photoconductor which responds as far as $6{\cdot}5\mu$ is so superior to lead sulphide in nearly all applications that its method of preparation and *modus operandi* are worth intensive study. It is of particular importance in the field of infra-red investigation of molecular structure. Here the majority of the fundamental vibrations used in structural work give rise to bands in the infra-red between 2·6 and 14μ. Thus the lead sulphide cell can only be used for a minute fraction of them, but a cell sensitive to $6{\cdot}5\,\mu$ would cover the range of all fundamental stretching frequencies involving hydrogen atoms and most of the important bands associated with the presence of double bonds between carbon, oxygen and nitrogen atoms.

The second and even more important object was to obtain a better understanding of the precise mode of action of infra-red photoconductors. This forms an important branch of the physics of the solid state, which has been explored very little. It was hoped that a study of the conductivity, in addition to the photoconductivity, would lead to information about the energy-level scheme in such photoconductors and throw some light on the main factors which determine the distribution of the energy levels and the transitions between them which are operative in infra-red photoconductors. In this way one might hope to derive eventually a theory of infra-red photoconductivity which would make it possible to predict the ultimate limits of this method of infra-red detection and indicate the most promising practical method of approaching these limits.

Previous experience had made it appear that the attainment of an efficient photoconductor in the infra-red was almost more of an art than a science, because so many different factors apparently were concerned in determining the performance on any individual photocell. Thus from any given recipe for making a lead sulphide cell, the same worker seldom obtained cells of the same sensitivity, while workers in different laboratories often obtained quite contradictory results. One of our other aims was accordingly to try and make photoconductive layers in as simple and carefully controlled a manner as possible, and in particular, to see whether the oxygen treatment of a layer was essential, since the details of the oxygen treatment complicate so seriously the preparation and the theory of action of such detectors.

It should be added that in the initial stages of this work, films of lead selenide were also investigated. A brief account of their properties has already appeared (Blackwell, Simpson & Sutherland 1947). The lead selenide films were prepared in exactly the same manner as the lead telluride films dealt with here, and in general showed very similar properties. It was found, however, that lead selenide films frequently showed a drift towards increased conductivity over a period of several minutes during illumination, the relaxation time of the effect being sometimes as great as several hours, at liquid-air temperature. Lead telluride did not show this effect and was thus more amenable to quantitative investigation. It was therefore decided to concentrate attention on the latter substance.

Preparation of the photoconductive films

Purification of the materials

In any work with semi-conductors it is most important to be able to control the composition of the material under investigation, particularly with respect to the presence of impurities. For this reason the lead telluride used was made by direct combination of the elements, after each had been obtained in as high a state of purity as possible. The lead was a spectroscopically pure specimen obtained from Johnson Matthey and Company in the form of a rod. The rod was scraped to remove the oxide film and used immediately after scraping. The tellurium was a spectroscopically pure sample from the same source. It was found necessary to purify it still further (from traces of oxide) by distillation in a silica vessel at

600° C. Equivalent quantities of lead and tellurium, sufficient to make about 1 g. of lead telluride, were heated together *in vacuo* in a silica tube at 1000° C. This temperature was high enough so that the lead telluride was liquid and insured complete miscibility. The time allowed for completion of this process was 2 to 3 hr. The resulting lead telluride was sufficiently close to the stoichiometric ratio to use as a starting material. If a material was desired with an excess of tellurium, this could be added at the start of the operation or the original telluride could be heated up again with a known mass of tellurium. In order to obtain a material with an excess of lead it was found that each distillation of the original material *in vacuo* reduced the tellurium content. This distillation was carried out in a long silica tube, one end of which was electrically heated to 800° C and the other attached to a vacuum system. The lead telluride condensed a little way up the tube, while still higher, pure tellurium was found. In order to avoid contamination or oxidation, the tellurides were sealed off *in vacuo* immediately after preparation and stored there until required for use.

Construction of the cell

A sublimation method was also used for the deposition of the photoconductive films and imposed certain restrictions on the construction of the cell, since a temperature of at least 550° C is needed to sublime a film of the type required in a reasonable time. The following were the essential conditions which governed the design of the cell:

(1) It must be made of a material capable of standing prolonged heating at 550 to 600° C when evacuated.

(2) Since the layer must be maintained *in vacuo*, the cell must either be made of material transparent to infra-red radiation between 1 and 7μ or contain a window transparent in this range through which a layer can be illuminated.

(3) The construction must be such that the film can be cooled to at least the temperature of liquid air and to various higher temperatures without obscuring the incident beam of infra-red radiation.

The final design of cell adopted is shown in figure 1, and is essentially a small Dewar flask into which the refrigerant is put for cooling the lead telluride layer. It is made from Pyrex or Hysil glass or a glass known as C 9 made by the British Thomson-Houston Company at Rugby. The choice is not critical so long as the softening point is above 550° C. The layer is deposited at E on the surface of the inner tube which is *in vacuo*. Since the above glasses do not transmit beyond about 2·8μ in the normal thickness required for a vacuum flask, it was essential to provide a window in the outer tube through which the infra-red radiation could reach the layer. Although materials exist which transmit radiation to 7μ and which can be sealed to Pyrex and the other glasses (e.g. sapphire), the practical difficulties in making such seals satisfactory are so great that it was found much simpler to thin down the outer glass wall of the cell until it gave good transmission to 7μ. A few experiments showed that a thickness of about 15μ gives satisfactory transmission (figure 2). Furthermore, it is possible to make a small window of this thickness in the outer wall provided it is hemispherical in shape. The method is to take a glass tube of 1·5 cm. diameter and close it at one end. This end is heated and the glass pulled away until it is very thin and uniform; it is then drawn into the tube by sucking and forms a uniform hemispherical shell which is well fused to the circumference of the tube and forms a vacuum joint of considerable mechanical strength. The hemispherical shape is important, since it ensures that the hydrostatic pressure is taken up as a pure tensile stress round the circumference of the joint. The optical distortion of such a window was found to be small and unimportant. In order to get the maximum aperture the surface of the inner tube was drawn out towards the window as far as was practicable. In earlier designs of such cells it had been customary to take the radiation in at the base of the cell; the present design is more convenient for most optical systems.

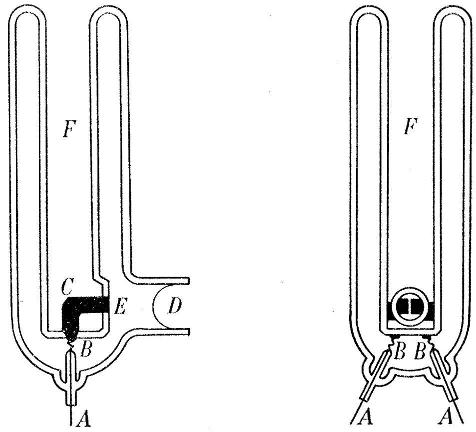

FIGURE 1. Construction of cell with infra-red transmitting window. *A*, tungsten leads; *B*, platinum connector; *C*, graphite line; *D*, bubble window; *E*, electrode surface; *F*, cavity for coolant.

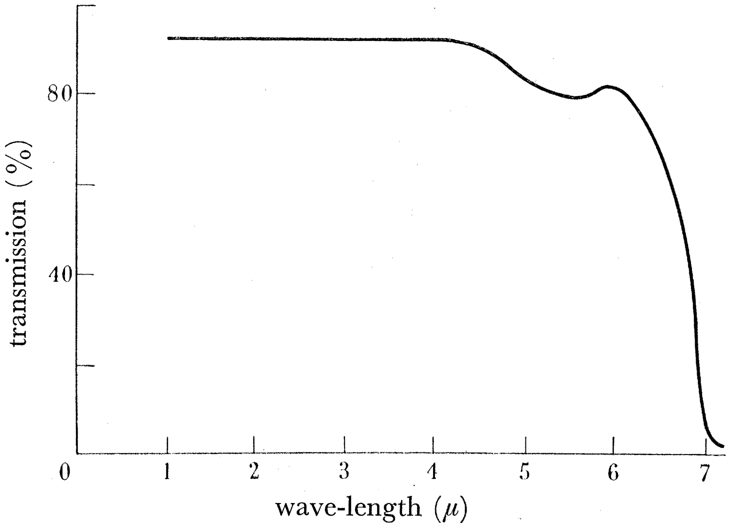

FIGURE 2. Transmission of cell window. Thickness of glass bubble approximately 20μ.

The electrodes were formed by a single strip of Aquadag 4 mm. wide, in which a gap of about 0·4 mm. was made opposite to the bubble window *D* by scratching with a fine glass stilo. The cut was flamed after scratching to remove any remaining traces of graphite and also to clean thoroughly the surface on which the film of lead telluride was to be deposited. External leads (*A*) of 1 mm. diameter of ground tungsten wire were sealed through the base of the cell. In order to avoid strain between the inner and outer walls of the cell, contact between the graphite electrodes and the tungsten leads was made by short platinum strips, spot-welded to the tungsten at one end and anchored to the inner tube by glass beads. This last joint was then covered with platinum paint, and finally connexion was made to the graphite electrode by painting Aquadag over the platinum paint. Occasionally trouble was experienced by the graphite flaking off the platinum, and an alternative procedure* is to use a thinner piece of tungsten wire instead of the platinum strip, grinding the junction of the thin tungsten wire flush with the glass of the inner tube and painting this over with Aquadag.

The cells were carefully cleaned by successive washing in hydrochloric acid and distilled water before the graphite electrodes were drawn. Immediately before the evaporation process, each cell was fired in air at 600° C to remove any organic dust which might have collected; it was then evacuated and thoroughly degassed by heating for about 4 hr. at 400° C. The evacuation equipment consisted of a Speedivac Rotary Pump working behind a mercury diffusion pump with a conventional McLeod gauge calibrated to 10^{-6} mm. This equipment was arranged in the lower portion of an iron framework which supported an electric oven, movable in the vertical direction. The asbestos base-plate of this oven contained a small hole through which projected the lead from the vacuum equipment. A liquid-air trap was inserted between the cell and the vacuum equipment to prevent contamination from the rest of the vacuum system. The cell blank was sealed on to this lead and the oven lowered on to the base-plate, a small window in the side of the oven making observation possible during the evaporation process.

Evaporation of the film

Approximately half a milligram of lead telluride was required for each film. This was introduced into a well-degassed cell blank in the form of a fine powder; the cell was immediately re-evacuated to 10^{-6} mm. Hg pressure and heated to 550° C. After heating at this temperature for about 20 min. the material evaporated completely from the powder and condensed as a diffuse patch on the coolest part of the wall of the envelope; owing to a slight temperature gradient in the oven this was usually the lowest part of the cell. By means of a fine jet of compressed air it was possible to apply local cooling to any part of the wall. As soon as the part of the envelope cooled by compressed air had a lower temperature than any other part of the wall, condensation occurred and the material was collected as a dense patch at that point. During the heating at 550° C a certain amount of lead telluride was continuously being lost from the cell by condensation in the liquid-air trap. This was, however, only a small fraction of the material, because the rate of diffusion through the narrow lead from the cell to the trap was very slow on account of the low vapour pressure of lead telluride.

In order to obtain a uniform film over the electrodes it was found more convenient to employ two stages of evaporation, rather than to collect the material directly on to the electrode surface. In the first stage local cooling was applied to the outer wall of the cell, opposite to the electrodes, until all the lead telluride was collected; the whole cell was then allowed to cool to room temperature. The second stage consisted of re-evaporating the lead telluride by applying a gas-air flame for a few seconds to the outside of the envelope. As a result of the second evaporation a uniform highly reflecting film was formed over the electrode surface and the surrounding parts of the inner wall of the cell. It was usual for

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* This modification was suggested by Dr W. Scanlon of the U.S. Naval Ordnance Laboratory.

some of the material to be deposited also on the thin window, whence it could be removed by gentle flaming. Throughout the preparation the cell was pumped continuously and the pressure maintained below 10^{-6} mm. Hg. Successive films could be formed from the same material by repeating the cycle of operations. Finally, the cell was sealed off from the vacuum system and the film preserved indefinitely *in vacuo*.

Many modifications of this method of preparation are possible; in particular, the rate at which the second evaporation is performed, and the temperature of the surface on which the film is condensed are obvious variants. No significant differences were observed between the properties of films deposited on surfaces at room temperature and those at liquid-air temperature; similarly, the rate of evaporation did not appear to be critical. However, it was found that the results were most reproducible when the preparation was as described above, and for the sake of uniformity a standard procedure was observed by which the whole evaporation was performed as rapidly as possible, less than 10 sec. being required, the electrode surface being maintained at room temperature.

The effective dimensions of a film were governed by the geometry of the graphite electrodes. The thickness of the films was calculated from the area of the deposit and the weight of material used. It was found that $0{\cdot}1\,\mu$ was convenient and gave reproducible results. Consequently, except where specifically stated, all films may be assumed to be of approximately this thickness. A rough estimate of the thickness can be obtained from the transmission in the visible region of the spectrum. Lead telluride of $0{\cdot}1\,\mu$ thickness appears a dark blue by transmitted light; films much thicker than $0{\cdot}1\,\mu$ were opaque to visible light.

Film characteristics

The reflexion, transmission and absorption in the infra-red of a film of lead telluride of thickness about $0{\cdot}1\,\mu$ is shown in figure 3. The material was evaporated from a quartz tube

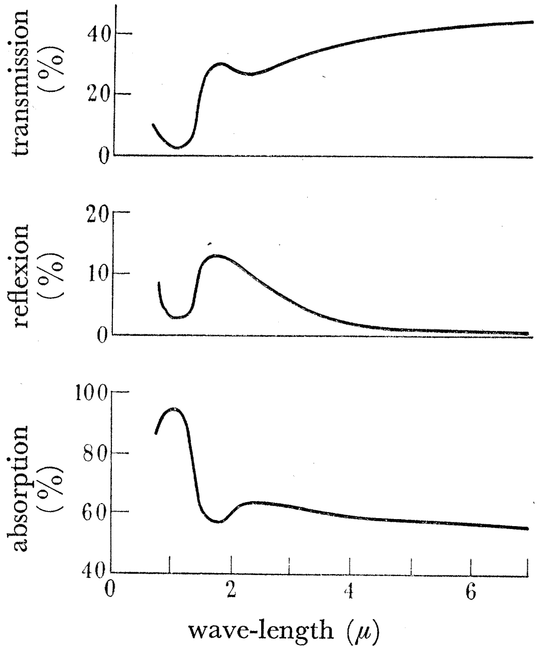


FIGURE 3. Reflexion, transmission and absorption of a lead telluride film of thickness 10^{-5} cm. approximately.

heated by a tungsten spiral, *in vacuo*, in a cylindrical cell; the two ends of the cylinder were closed by calcium fluoride plates and the film was deposited on one plate. It was thus possible to make measurements of both transmission and reflexion without passing the radiation through glass. This permitted the measurements to extend into the infra-red as far as 7μ. The results shown in figure 3 were obtained without exposing the film to air at any time; measurements with films deposited on rock-salt but then exposed to air gave similar results. The maximum reflexion occurs at $1{\cdot}6\mu$, where the optical thickness of the film is equal to a quarter wave-length; there is a corresponding minimum in the absorption at the same wave-length. If this is an interference effect it may be inferred that the refractive index of the specimen was approximately 4·0.

VARIATION OF PHOTOCONDUCTIVITY WITH THE INTENSITY AND NATURE OF INCIDENT RADIATION

Experimental arrangements

In order to assess the value of lead telluride films as photoconductive detectors in the infra-red, it is necessary to shield them as far as possible from the ordinary temperature radiation of the room, since the intensity of the radiation lying within the range of sensitivity of the film (i.e. below $5{\cdot}5\mu$) is quite appreciable. This may be estimated from the Planck radiation formula to be about 4×10^{-4} W/cm.^{2}. To minimize the effects of this background of thermal radiation, the cell was partially immersed upside down in a Dewar flask containing liquid nitrogen as shown in figure 4. It was surrounded by a brass cylinder C which dipped into the liquid nitrogen. This cylinder contained a side tube 7 cm. long, opposite the bubble window of the cell, with a small aperture, B, 2·0 mm. wide and 1·5 cm. long, through which the film could be irradiated. The cold dry nitrogen evaporating from the Dewar flask prevented frost from forming on the cell window. This arrangement proved

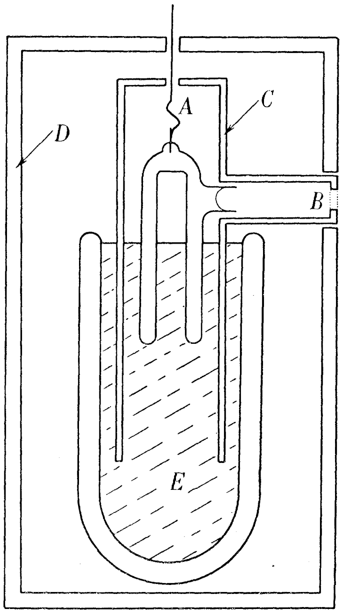


FIGURE 4. Arrangement for measuring photoconductivity with the film shielded from room-temperature radiation. *A*, electrode leads; *B*, slit; *C*, brass cylinder; *D*, lagged box; *E*, liquid air.

much more satisfactory than the more obvious one of immersing the cell completely in the liquid air and taking the radiation through the liquid air.

The source of illumination for intensities between 10^{-6} and 10^{-4} W/cm.^{2} was an ordinary $\frac{1}{2}$ W tungsten filament lamp under-run so that the colour temperature was about 1500° C. This source was calibrated against a black body and the intensity was varied by altering the distance between the source and the cell. For higher intensities (from 10^{-4} to 10^{-2} W/cm.^{2}) a 60 W short-filament lamp was used. Experiments were also carried out in this intensity range with radiation of wave-length $2{\cdot}2\mu$ from a monochromator.

Results

If σ_d denotes the conductivity of the cooled film in radiative equilibrium with its surroundings before illumination is applied, and σ_i the conductivity during illumination, then the photoconductivity is defined as $\sigma_i - \sigma_d$ and the photoconductive ratio as σ_i/σ_d. In order to find σ_d, it is necessary to close the aperture B with a shutter which is at the temperature of liquid nitrogen. If the shutter was not so cooled, the temperature radiation, even from such a small solid angle (6×10^{-3} steradian), was sufficient to increase σ_d by a factor as large as 2. Thus in measuring σ_i there was always a background of temperature radiation of at least 4×10^{-7} W/cm.^{2} (i.e. the background energy $<5{\cdot}5\mu$).

The experimental results are illustrated in figures 5, 6 and 7, where the square of the photoconductive ratio $(\sigma_i/\sigma_d)^2$ is plotted against the incident intensity I and is seen to fit a straight line in all cases. This experimentally determined relation may first be expressed by the equation

$$(\sigma_i/\sigma_d)^2 = 1 + a + bI, \tag{1}$$

where the term a represents the effect of background temperature radiation, so that $\sigma_i \to \sigma_d$ when the illumination and background radiation both tend to zero. The constant b is found to depend on the spectral distribution of the illuminating radiation. If for monochromatic radiation of wave-length λ it is denoted by b_λ, then

$$a = \int b_\lambda I_\lambda d\lambda,$$

where the integration is over all wave-lengths present in the background radiation. This leads to an undesirably clumsy form of the equation when comparison with theory comes to be made. Accordingly, we assume that a can be replaced by bI_0, where I_0 represents that intensity of the illuminating radiation which is equivalent to the background radiation. The equation then has the convenient form

$$(\sigma_i/\sigma_d)^2 = 1 + b(I + I_0). \tag{2}$$

The experimental justification for the assumption comes from the results in figure 6. The lower line corresponds to a series of observations under the conditions just described for keeping background radiation to a minimum. For the upper line, the observations were made with all shielding removed so that temperature radiation from a solid angle of 2π was incident on the film. Since the upper curve is parallel to the lower, the effect of the background radiation must be purely additive, and the assumption that the effect of background radiation may be replaced by a virtual shift of the zero of the abscissa I is justified.

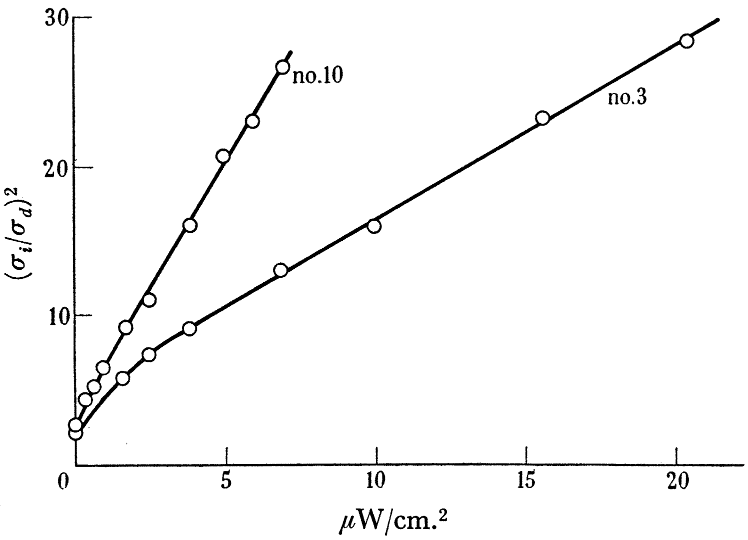


FIGURE 5. Photoconductive ratio of lead telluride at −190° C against intensity of illumination. Incandescent lamp source.

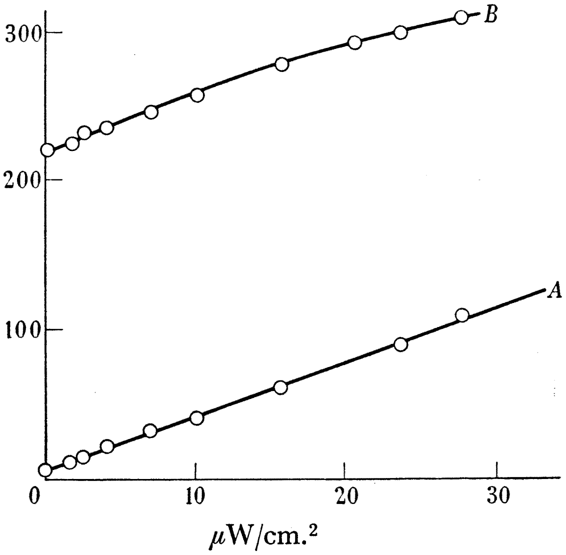


FIGURE 6. Photoconductive ratio of lead telluride at −190° C against intensity of illumination. Curve A is the response of film no. 10 when shielded from room-temperature radiation; curve B is the response of the same film when the applied intensity is superimposed on a background of 15° C radiation in a solid angle of 2π.

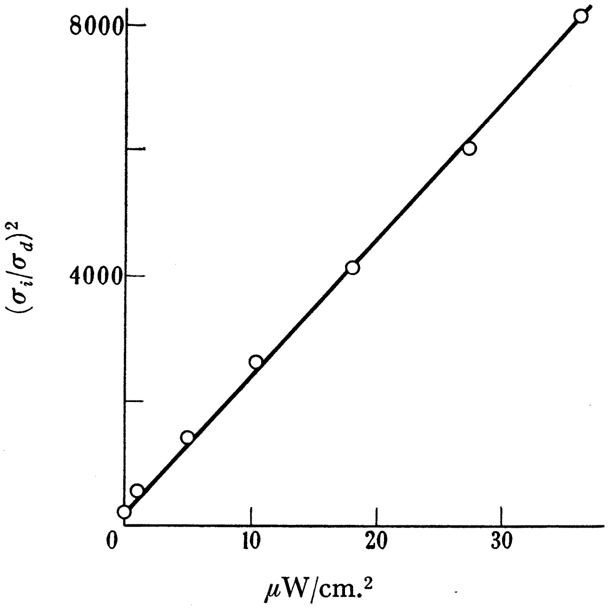


FIGURE 7. Photoconductive ratio of a lead telluride film at −190° C, at high intensities of illumination. Monochromatic source of wave-length $2{\cdot}2\mu$.

If it had been possible to exclude all background radiation coming from surfaces not in temperature equilibrium with the layer then equation (2) would take the form

$$(\sigma_i/\sigma_d)^2 = 1 + b_\lambda I_\lambda, \tag{3}$$

where I_λ is the intensity of the illuminating monochromatic radiation of wave-length λ. At very low intensities of illumination (where $\sigma_i - \sigma_d \ll \sigma_d$) one might expect that the photoconductivity would approximate to the following relation:

$$\sigma_i - \sigma_d = \sigma_d b_\lambda I_\lambda/2. \tag{4}$$

It was not possible to test such a relation experimentally because the background term I_0 was always so large that $(\sigma_i - \sigma_d) \sim \sigma_d$ as soon as the cooled shutter was removed to admit the illuminating radiation.

TABLE 1. PHOTOSENSITIVITY OF LEAD TELLURIDE AT $-190°$ C. $\lambda = 2{\cdot}2\,\mu$

film no.	σ_d (ohm^{-1}cm.$^{-1}$)	σ_0 (ohm^{-1}cm.$^{-1}$)	b_λ (W^{-1}cm.^{2})	τ (μ-sec.)	$I_{0\lambda}$ (μ-W cm.$^{-2}$)
9	$1{\cdot}8 \times 10^{-3}$	$8{\cdot}3 \times 10^{-3}$	$6{\cdot}0 \times 10^5$	400	38
3	$1{\cdot}1 \times 10^{-3}$	$6{\cdot}7 \times 10^{-3}$	$1{\cdot}7 \times 10^6$	400	20
5	$4{\cdot}0 \times 10^{-4}$	$4{\cdot}1 \times 10^{-3}$	$1{\cdot}8 \times 10^6$	300	55
6	$9{\cdot}3 \times 10^{-5}$	$1{\cdot}3 \times 10^{-3}$	$4{\cdot}0 \times 10^6$	150	49
10	$9{\cdot}1 \times 10^{-6}$	$1{\cdot}3 \times 10^{-4}$	$6{\cdot}8 \times 10^6$	100	30
8	$1{\cdot}6 \times 10^{-7}$	$3{\cdot}9 \times 10^{-6}$	$1{\cdot}0 \times 10^7$	40	59
7	$1{\cdot}0 \times 10^{-7}$	$1{\cdot}6 \times 10^{-6}$	$9{\cdot}2 \times 10^6$	40	28

We conclude that equation (2) gives the best representation of the experimental results in the range of σ_i/σ_d between 2 and 1000, although it is not possible to exclude the presence of an additional linear term in σ_i/σ_d with a small coefficient. Such a term would only be important when σ_i/σ_d is not much greater than 1. Plots of $(\sigma_i/\sigma_d)^2$ for a range of I between 0 and 2×10^{-5} W/cm.^{2} are given in figure 5 for two films of very different σ_d at $-190°$ C. Film number 3 had $\sigma_d = 1{\cdot}1 \times 10^{-3}$ ohm^{-1}cm.$^{-1}$, while film number 10 had $\sigma_d = 9{\cdot}1 \times 10^{-6}$ ohm^{-1}cm.$^{-1}$. In figure 6 the range of I is between 0 and 3×10^{-5} W/cm.^{2} and demonstrates the effect referred to earlier of allowing the full background radiation to be present. In each of these experiments the illuminating radiation was from the 'white' source; in figure 7 are shown the corresponding results using monochromatic radiation of wave-length $2{\cdot}2\,\mu$ in a film with $\sigma_d = 9{\cdot}3 \times 10^{-5}$ ohm^{-1}cm.$^{-1}$ over a range of I from 0 to 10^{-2} W/cm.^{2}. The detailed results for a series of observations of this kind on seven different films are collected in Table 1. The films are arranged in decreasing order of σ_d given in the second column. The third column σ_0 gives the conductivity when the full background radiation was incident but no applied illumination. It will be noticed that σ_0 is from about 5 to 25 times greater than σ_d, emphasizing the magnitude of the effect of background radiation. The values of b_λ are given in column 4, and it is significant that although σ_d varies by a factor of over 10^4, the variation of b_λ is only between 1×10^7 and $6{\cdot}0 \times 10^5$ W^{-1}cm.^{2}. The response times (τ), defined as time required for photoconductivity to decay to half-value, were measured with the films unshielded from background radiation and are listed in column 5. The variation here is still smaller, being only by a factor 10; films with high σ_d are much slower in response than films with low σ_d. The time of response is only given to one significant figure, since it is found to depend to some extent on the conditions under which it is measured. Thus the time of response decreases as the intensity of applied illumination is increased and is therefore sensitive to the amount of background radiation. The response time always decreases with rise of temperature, and all measurements quoted here were made with the films at −190° C.

In the last column of table 1 are given values for $I_{0\lambda}$, the amount of $2\cdot2\,\mu$ radiation equivalent to the background radiation as obtained from the equation

$$(\sigma_0/\sigma_d)^2 = 1 + b_\lambda I_{0\lambda}. \tag{5}$$

The mean value of these is 4×10^{-5} W/cm.^{2}. It is of some interest to try to get an independent estimate of the quantity by another method. This can be done by combining the Planck black-body curve for 15° C with the spectral sensitivity curve of a lead telluride cell as shown in figure 8. The spectral sensitivity curve was obtained from a cell in a spectrometer by comparing its response with that of a thermocouple of known sensitivity

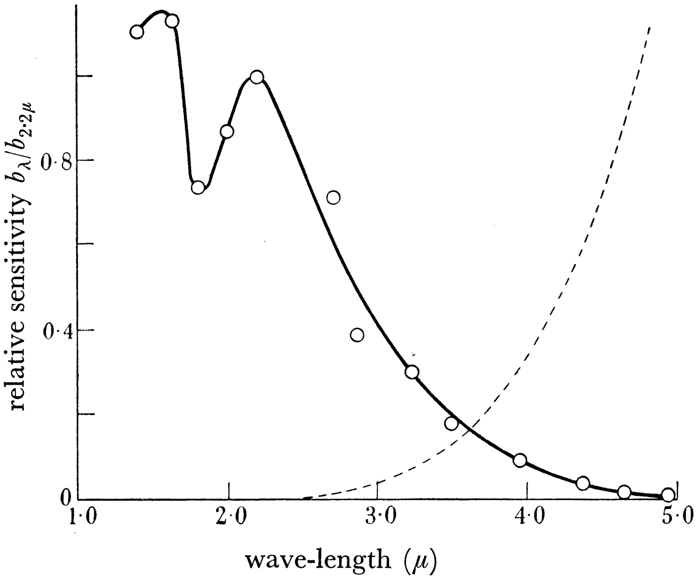


FIGURE 8. The spectral distribution of photosensitivity in lead telluride at −190° C. The film was not shielded from thermal radiation; the broken curve represents the Planck curve for 15° C.

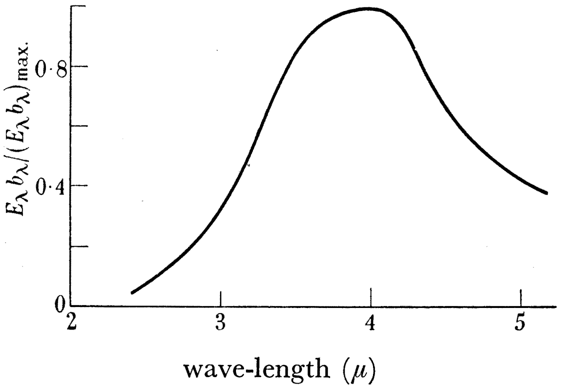


FIGURE 9. Photoconductive response of lead telluride at −190° C to the radiation from a black body at 15° C. The data are taken from figure 8, E_λ is the energy in unit wave-length interval for 15° C radiation.

(Simpson, Sutherland & Blackwell 1948). In this case the layer was exposed to a large amount of background radiation at room temperature, although the layer itself was at the temperature of liquid nitrogen. The relative sensitivity curve has been adjusted to make the ordinate at $2\cdot2\,\mu$ unity. It follows that the expression

$$\frac{1}{b_{2\cdot2\mu}}\int E_\lambda b_\lambda\, d\lambda \tag{6}$$

evaluated over the range of overlap should give the total effective background radiation expressed in terms of an equivalent amount of radiation of wave-length $2\cdot2\,\mu$. The curve of figure 9 represents the product $E_\lambda b_\lambda$ calculated from the curves of figure 8, and indicates that it is that part of the room-temperature radiation which lies between 2·5 and 5μ, which contributes most strongly to the background effect in these lead telluride cells. The expression (6) may now be evaluated by measuring the area under the curve of figure 9 graphically in terms of absolute energy. The result so obtained gives $I_{0\lambda}$ as $1{\cdot}5\times10^{-5}$ W/cm.^{2} in terms of 2·2μ radiation. The agreement with the earlier figure of 4×10^{-5} W/cm.^{2} is quite satisfactory, considering the approximations and assumptions involved. In particular, it must be remembered (1) that the curve for the spectral sensitivity was obtained from a film which is not represented in table 1, and that considerable variations occur in such curves of spectral sensitivity; (2) that the figure $1{\cdot}5\times10^{-5}$ W/cm.^{2} must be a lower limit since the contributions from wave-lengths greater than 5μ could not be estimated from figure 9. It was remarked earlier that the total background radiation at 15° C in wave-lengths less than 5μ was 4×10^{-4} W/cm.^{2}, which is roughly ten times the value of I_0 expressed as 2·2μ radiation. This is to be expected, since b_λ decreases rapidly from a maximum at 2·2μ to nearly zero at 5μ, and the mean value over the range 2·5 to 5μ must be much less than the peak value at 2·2μ.

Deviations from Ohm's law

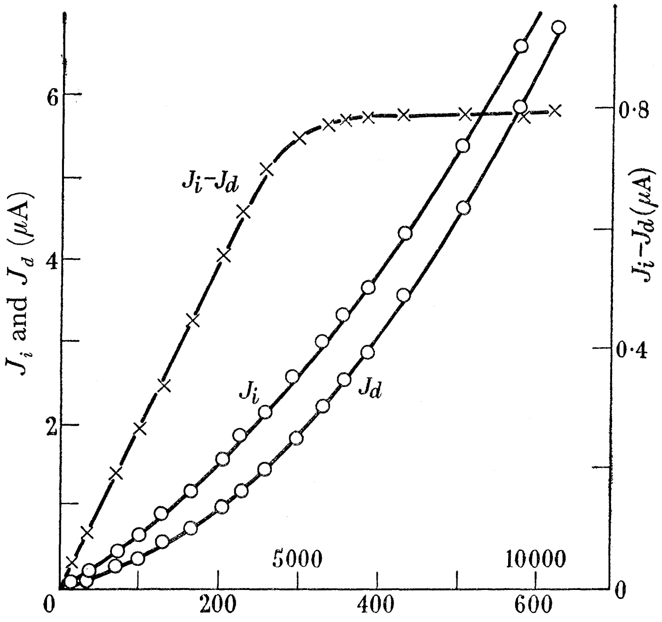
At room temperature, lead telluride films showed strict proportionality between current and voltage as long as the current density did not exceed about 100 A/cm.^{2}, which in the case of the films we investigated corresponded to an absolute current value of about 500μA. At somewhat higher values, the Joule heating led to increased conductance, and when the heating became excessive, breakdown occurred, the film disintegrating along with the graphite at the cathode. Presumably a new effect was taking place here with ion transport, the positive ions having the greater mobility.

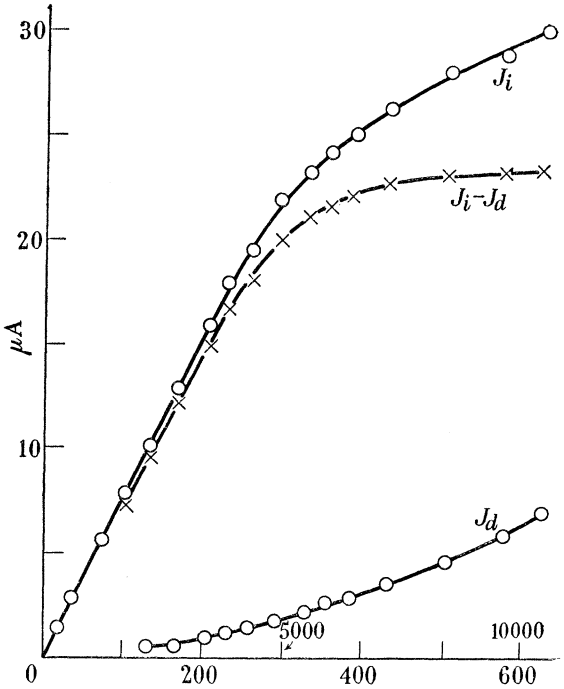
Much more important were the deviations from Ohm's law which were found with the film at liquid-nitrogen temperatures. These were of various types.

(1) With no illumination, Ohm's law held until the applied field exceeded 500 V/cm., but for higher values (up to 10,000 V/cm.) the dark current J_d increased disproportionately, although no instability or breakdown took place, provided the current density was less than 20 A/cm.^{2}.

(2) Under illumination, it was found that the photocurrent, $J_i - J_d$, was strictly proportional to the applied voltage, until the latter reached a value of a few thousand V/cm. Thereafter, the photocurrent decreased disproportionately and quickly reached a steady saturation value. These phenomena are illustrated in figures 10 and 11. The field strength at which saturation occurred seemed to depend inversely on the dark conductivity σ_d. Thus films of very low σ_d (around 10^{-7} ohm^{-1}cm.$^{-1}$ at −190° C) showed only small deviations from Ohm's law up to 10,000 V/cm., while films of high σ_d (around 10^{-3}ohm^{-1} cm.$^{-1}$ at −190° C) began to saturate at about 2000 V/cm. It was not easy to investigate the characteristics of the latter very fully, because the current densities were close to being excessive and breakdown through Joule heating occurred rather readily. Accordingly, there was only a narrow range of film resistances suitable for the study of saturation effects.

For all films the saturation voltage appeared to be nearly independent of the intensity of illumination. This is also illustrated by comparing figures 10 and 11, where J_i, J_d and $J_i - J_d$ are plotted against the applied field for two widely different intensities of illumination,





upper scales: volts/cm.; lower scales: applied voltage

FIGURE 10. Saturation of photocurrent at −190° C under intensity of illumination of $2{\cdot}4 \times 10^{-7}$W/cm.^{2}.

FIGURE 11. Saturation of photocurrent at 190° C under intensity of illumination of $5{\cdot}4 \times 10^{-5}$ W/cm.^{2}.

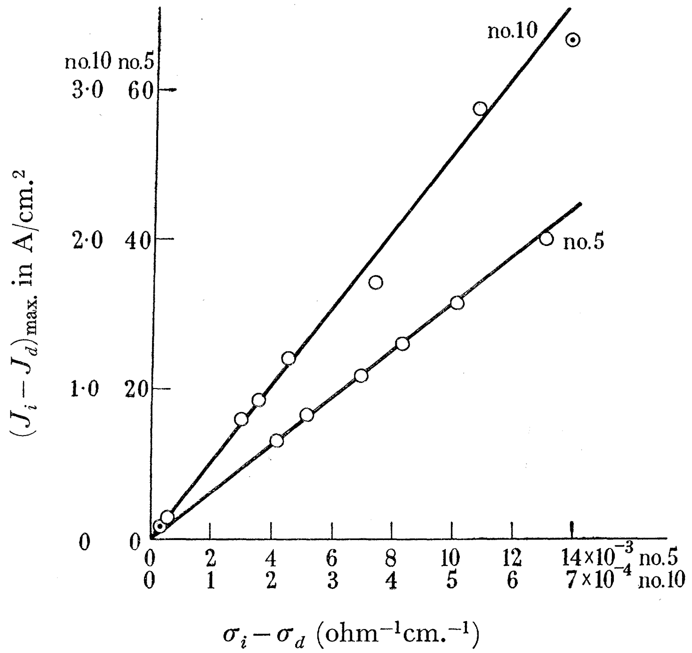


FIGURE 12. The saturation photocurrent density plotted against the photoconductivity. The saturation photocurrent is proportional to $\sigma_i - \sigma_d$ measured in the voltage range where Ohm's law is valid, and not to the intensity of illumination. The slope of the curves gives the approximate saturation field strength. The two points ⊙ correspond to the saturation currents deduced from the curves in figures 10 and 11.

viz. $2{\cdot}4\times10^{-7}$ and $5{\cdot}4\times10^{-5}$ W/cm.^{2}. Using figures obtained in the region for which Ohm's law still holds, the corresponding photoconductivities are computed as $2{\cdot}4\times10^{-5}$ and $7{\cdot}05\times10^{-4}$ ohm^{-1}cm.$^{-1}$. Although saturation occurred a little more sharply for the weaker illumination, the ratio of the saturation photocurrents $23{\cdot}3/0{\cdot}8=29{\cdot}1$ is very close to the ratio of the respective photoconductivities, viz. 29·8. This proportionality between the saturation photocurrent and the photoconductivity for low applied fields was found to be a general property of all films which showed saturation effects.

By definition we should expect in the region where Ohm's law holds

$$\sigma_i-\sigma_d=(J_i-J_d)l/VA=\sigma^*,$$

where V is the applied voltage, l is the distance between electrodes and A the cross-sectional area of the film. Accordingly

$$(J_i-J_d)/A=V\sigma^*/l,$$

and if the saturation takes place over the same narrow range of V, for various incident intensities, we should expect a plot of $(J_i-J_d)_{\text{sat.}}/A$ against σ^* to yield a straight line through the origin, the slope of which gives the voltage gradient at which saturation occurs. That this is indeed the case is illustrated by figure 12, in which the two lines represent two different films, while the points ⊙ in no. 10 film are derived from the data in figures 10 and 11.

The use of lead telluride films as infra-red detectors

The performance of any new device for the detection of infra-red radiation can be judged in two ways: (*a*) by substituting it for the best of the earlier devices in a given apparatus and comparing the practical performance of the two, (*b*) by comparing its basic characteristics with those of earlier devices. The results of the first method, which is useful in getting a rough idea of applicability in a given field, have already been published (Simpson *et al.* 1948) and show that lead telluride cells are superior to thermocouples and bolometers for spectroscopic work at least as far as 5μ. We shall now consider those properties of the lead telluride films described earlier which determine their usefulness as detectors of infra-red radiation particularly of low intensity, viz. responsivity, noise and speed of response.

The *reponsivity* of an infra-red detector is defined (Sutherland & Lee 1948) as the output of the detector per unit of incident radiation power. It is usually given in microvolts per microwatt and may be deduced from the preceding experimental data in the following manner. Consider a photoconductive film of uniform thickness x cm. between electrodes of length l cm., separated by a distance of d cm., and illuminated by radiation of wavelength λ and intensity I_λ W/cm.^{2}. If the film is in series with a high resistance, so that a current of J amperes is maintained independently of the photoconductivity, then the voltage drop across the electrodes is

$$V=Jd/\sigma_i xl, \tag{7}$$

where σ_i is the conductivity under the given illumination. From (3) above, we have

$$\sigma_i=(1+b_\lambda I_\lambda)^{\frac{1}{2}}\sigma_d.$$

This may be substituted in (7), whence by differentiation we obtain the responsivity

$$R_\lambda=\frac{dV}{dI_\lambda}=-\frac{Jdb_\lambda}{2xl\sigma_d}\frac{1}{(1+b_\lambda I_\lambda)^{\frac{3}{2}}}. \tag{8}$$

It is to be remembered that I_λ includes any thermal background radiation, since the responsivity is very much affected by the degree to which the film is shielded from such radiation. Thus the responsivity of a completely shielded film to which only the exciting radiation dI_λ is admitted would be

$$R=\left(\frac{dV}{dI}\right)_{\text{shielded}}=-\frac{Jdb}{2xl\sigma_d}.$$

This differs from the responsivity in the unshielded condition by a factor $(1+b_\lambda I_{0\lambda})^{\frac{3}{2}}$, where $I_{0\lambda}$, the thermal background radiation, has been shown earlier to be equivalent to about 3×10^{-5} W/cm.^{2} (table 1). Thus there can be a variation by a factor of the order of 1000 in the responsivity of a lead telluride cell depending on the degree of shielding from background temperature radiation. In table 2 are given values for responsivities of four different films, evaluated from the data in table 1, assuming the intensity of the exciting illumination is equivalent to 10^{-7} W/cm.^{2} of 2·2μ radiation, and that the current throughout is kept constant at 10^{-6} A. The film dimensions in these cases were $x=1\times10^{-5}$ cm., $l/d=10$, while the responsivity is computed under conditions of complete shielding (column 5) as well as conditions of no shielding (column 6). It has to be remembered that in the case of films of highest resistance, the conditions for which these figures were computed are not attainable in practice, as the linearity between current and voltage would have broken down before a current of 10^{-6} A was reached. In such cases, the voltages and responsivities should be scaled down by the ratio of the actual current, J, to 10^{-6} A. Furthermore, the responsivities are applicable only in the region of low illumination ($I<10^{-6}$ W/cm.^{2}), since at high intensities the output voltage is not directly proportional to the incident intensity.

TABLE 2. RESPONSIVITY OF LEAD TELLURIDE FILMS AT −190° C UNDER ILLUMINATION OF INTENSITY 10^{-7} W/cm.^{2} 2·2μ RADIATION FOR CONSTANT EXCITING CURRENT OF 10^{-6} A

film no.	measured dark resistance $d/xl\sigma_d$ (ohms)	output (shielded) (V)	output (unshielded) (V)	responsivity (shielded) (μV/μW)	responsivity (unshielded) (μV/μW)
9	$5·6\times10^{6}$	$1·7\times10^{-1}$	$1·7\times10^{-3}$	$1·7\times10^{6}$	$1·7\times10^{4}$
6	$10·8\times10^{7}$	$2·2\times10^{1}$	$7·5\times10^{-3}$	$2·2\times10^{8}$	$7·5\times10^{4}$
10	$11·0\times10^{8}$	$3·0\times10^{2}$	$1·3\times10^{-1}$	$3·7\times10^{9}$	$1·3\times10^{6}$
7	$10·0\times10^{10}$	$4·6\times10^{4}$	$2·9\times10^{+1}$	$4·6\times10^{11}$	$2·9\times10^{8}$

It is of some interest to consider how the responsivity varies with the linear dimensions of the film. These occur explicitly in equation (8) and implicitly in the value of b_λ. The area of the film ld is arbitrary (provided l/d remains constant), but if the total radiation available is limited, it is advisable to concentrate it on as small an area as possible in order to get a high intensity. Although it is desirable to make l/d as small as possible, this may be controlled by the particular application of the detector. Thus in infra-red spectroscopy l/d is the ratio of the length to the width of the slit, and this must be kept large to admit as much radiation as possible for a given separating power (Daly & Sutherland 1949).

The dependence of dV/dI on the film thickness is more complicated, because b_λ itself depends on x. This may be seen qualitatively by considering a film which is thick compared with the characteristic absorption thickness; the majority of the radiation is absorbed at the surface of such a film, the rest of the film acting only as a conductor in parallel and thus decreasing the overall responsivity. This problem will be discussed in more detail in the following part (Simpson); it is sufficient here to mention that dV/dI is maximum for a film of vanishing thickness. The practical problem of the optimum thickness is, however, further complicated by the fact that the noise necessarily increases as the linear dimensions are decreased, so that it is not profitable to decrease the thickness beyond a certain limit.

Although the responsivity is the first important characteristic of any detector, at low intensities of illumination, the noise is equally important. Noise may arise from three main sources:

(1) Johnson noise, controlled by the resistance and temperature of the film $\phi_1 = (4kTR\Delta f)^{\frac{1}{2}}$.

(2) Current noise, ϕ_2, which is generally lower at high frequencies, and increases as some unknown positive power of the current.

(3) Radiation noise, ϕ_3, due to statistical fluctuations in the radiation field to which the detector is exposed and dependent only on the temperature.

This last controls the ideal performance towards which one strives, but in practice other sources of noise generally are much more effective in controlling the signal/noise ratio. These sources of noise are independent and the resultant noise voltage ϕ is given by

$$\phi = (\phi_1^2 + \phi_2^2 + \phi_3^2)^{\frac{1}{2}}.$$

Decreasing the temperature of the film and its surroundings will decrease ϕ_3 but will increase ϕ_1, since the resistance of the film becomes higher very rapidly at low temperatures. Much more experimental work must be devoted to the special problem of how the noise in a lead telluride film varies with temperature, current and frequency before any guidance can be given in choosing the conditions for the maximum signal/noise ratio.

It may be of some interest to quote a noise measurement made on film no. 6, since it provides a basis for comparison with other infra-red detectors. The r.m.s. noise output of this film measured at liquid-air temperature when exposed to room-temperature radiation was $2{\cdot}5 \times 10^{-6}$ V in a band width of 20 c./sec. at 1000 c./sec. From table 2 the intensity of $2{\cdot}2\mu$ radiation equivalent to this is $1{\cdot}65 \times 10^{-10}$ W/cm.^{2}. Since the area of the film was $0{\cdot}02$ cm.^{2} the equivalent noise input for a band width of 1 c./sec. can be compared with those quoted for thermocouples, bolometers and superconducting bolometers (Sutherland & Lee 1948). It is important to notice that the lead telluride cell has a lower radiation noise limit than the thermocouple or bolometer, since it is not appreciably sensitive to wave-lengths beyond $5{\cdot}5\mu$. A rough comparison of the lead telluride cell against a good vacuum thermocouple (Hilger-Schwarz) showed that (as might be expected from the above figures) its effective performance in an infra-red spectrometer was greatly superior (Simpson *et al.* 1948) to the thermocouple in the range 2 to $4{\cdot}5\mu$. Experiments by Moss (1948) indicate that this range may be increased somewhat to longer wave-lengths by using the lead telluride film at liquid-hydrogen temperatures. However, the full possibilities of these new detectors will not be realized until some means is found of shielding them during use from room-temperature radiation.

The speed of response of the lead telluride detector is the other important factor in determining its usefulness. The greater the speed of response the greater will be the signal/noise ratio for a given time of observation. Furthermore, it becomes practicable to scan a reasonable portion of an infra-red spectrum in a time of the order of 0·005 sec. and so to follow reactions in flames, and more generally to study the spectra of molecules and radicals with short life-times. Some progress has already been made in this field with lead sulphide cells (Bullock & Silverman 1949). Table 1 indicates that the speed of response was highest for films with the lowest σ_d. However, films with excessively high resistance which therefore seem desirable for several different reasons have associated with them special problems in the design of amplifiers to deal with the output from such a high impedance. Further work is also required in this field before the ultimate limit of these detectors can be established.

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II. THE MECHANISM OF PHOTOCONDUCTIVITY IN LEAD TELLURIDE

By O. Simpson

Introduction

There are three principal classes of semi-conducting solids, namely, the stoichiometric excess or defect type, the foreign impurity type, and the amphoteric semi-conductors. The first class includes most of the metallic oxide semi-conductors, of which zinc oxide containing an excess of metallic zinc is typical of the excess or *N*-type; and cuprous oxide with a stoichiometric defect of copper is typical of the defect or *P*-type. The second class includes monatomic solids in which the semi-conducting properties are attributed to the presence of atoms of a foreign species; thus, germanium may behave either as an *N*-type or a *P*-type semi-conductor according as the number of valence electrons of the substituted atoms is greater or less than that of germanium itself. The third class of semi-conductors comprises the sulphides, selenides and tellurides of metals such as tin, lead and bismuth. Of the three classes of semi-conductors the properties of the last are the least well understood. Hintenberger (1942), Anderson & Morton (1945) and others have shown that amphoteric semi-conductors may acquire an excess of either the metallic or the non-metallic constituent. As the name implies, a given compound will be either an *N*-type or a *P*-type semi-conductor depending on whichever of the constituents happens to be in excess. There are, however, few reliable data concerning the dependence of photoconductivity on the stoichiometric excess in amphoteric semi-conductors. It was shown in part I that lead telluride, when prepared in the form of thin films, shows some of the characteristics of a semi-conducting solid. Attention was focused primarily on the photoconductive properties of lead telluride at the fixed temperature of −190° C, and investigations were made of the dependence of conductivity on the applied field, and the intensity and wave-length of illumination. Of equal importance is the variation of conductivity and photoconductivity