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Photoconductivity in Lead Selenide. Experimental*

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The electrical and photoconductive properties of evaporated films of PbSe have been investigated using oxygen, sulfur, selenium, and the halogens as sensitizers. Each sensitizer acts as an acceptor impurity; increasing sensitizer concentration causes the film resistance to increase through a maximum and then decrease, the film changing from n to p type at the resistance maximum. Photoconductivity at room temperature could be produced only by treatment with oxygen; the time constant τ was of the order of 1 μsec. At $-195°$C photoconductivity ($\tau=15$ to 30 μsec) could be produced by any of the sensitizers, while oxygen treatment gave in addition a response with $\tau\sim 5$ msec. The spectral response extends to longer wavelengths in thick films than in thin films, but is independent of sensitizer used. It is concluded that oxygen introduces acceptor levels which are minority carrier traps, while the other sensitizers introduce acceptor levels which are not effective minority carrier traps.

A. INTRODUCTION

PHOTOCONDUCTIVITY was first observed in PbSe at liquid nitrogen temperature in Germany during World War II, but no reports were published in the open literature.[1] Subsequently, British workers reported spectral response curves obtained at room temperature[2,3] as well as at liquid nitrogen temperature.[2–4] The room-temperature spectral response curves showed a knee at about 3.3 μ, followed by a sharp drop at longer wavelengths. At $-195°$C the knee occurred variously at 3 to 5 microns. Sensitivity was obtained by baking in the presence of oxygen. Maximum sensitivity was found to occur when the oxygen treatment produced a maximum in the cell resistance at room temperature.

Infrared reflectivity measurements at room temperature by Avery,[5] in the range from 1 to 5 μ, and absorption measurements by Paul, Jones, and Jones[6] and by Gibson[7] from 4.5 to 9 μ both showed an absorption edge at about 5 microns in PbSe. This indicated that PbSe should be photoconductive out to 5 μ instead of only to 3.3. Following this lead Gibson, Lawson, and Moss[8] prepared a very thick PbSe film, in which the knee was found at 5 μ as predicted. However, the level of sensitivity achieved in the thick films was far below that in thinner films. Thus, one objective of this present work was to investigate the relations among film thickness, spectral distribution of sensitivity, level of sensitivity, and sensitization procedure.

A second important problem of photoconductivity in thin films concerns the sensitization process. It has not been understood what specific role oxygen plays in the the process, although its effect on the conductivity of PbS and PbSe was understood rather well. Hintenberger[9] was able to change the resistance and carrier sign of PbS films by heat treatment in vacuum, in sulfur vapor, or in air. He showed that the conductivity is a minimum for stoichiometric proportions, and that films containing excess lead were n type, while those containing excess sulfur were p type. Baking an n-type film in air increased the resistivity to a maximum and then reduced it; the film was converted to p type at or near the resistivity maximum. He did not relate his experiments to photoconductivity, however.

These experiments together with the conditions for producing photocoductivity in PbSe show that oxygen acts as an acceptor, converting n-type PbS or PbSe to p type and reducing the dark current in the film to a minimum by maximizing the film resistance. It has not been established whether the important action in producing photoconductivity is the increased dark resistivity,[1,10] or the conversion from n to p type,[11] or possibly some other factor. In this paper the mechanism is studied by following the oxygen sensitization in detail, measuring resistance, thermal emf, time constant, and

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[1] See O. Simpson, thesis, Oxford University, 1948 (unpublished) for a discussion of this.

[2] J. Starkiewicz, J. Opt. Soc. Am. **38**, 481 (1948).

[3] T. S. Moss, Proc. Phys. Soc. (London) **B62**, 741 (1949).

[4] Blackwell, Simpson, and Sutherland, Nature **160**, 793 (1947); T. S. Moss and R. P. Chasmar, Nature **161**, 244 (1948).

[5] D. G. Avery, Proc. Phys. Soc. (London) **B67**, 2 (1954).

[6] Paul, Jones, and Jones, Proc. Phys. Soc. (London) **B64**, 528 (1951).

[7] A. F. Gibson, Proc. Phys. Soc. (London) **B65**, 378 (1952).

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

[9] H. Hintenberger, Z. Physik **119**, 1 (1942); also Z. Naturforsch. **1**, 12 (1946).

[10] A. Von Hippel and E. S. Rittner, J. Chem. Phys. **14**, 370 (1946).

[11] Sosnowski, Starkiewicz, and Simpson, Nature **159**, 818 (1947); H. James, Science **110**, 254 (1949); E. S. Rittner, Science **111**, 685 (1950); Mahlman, Nottingham, and Slater, in *Photoconductivity Conference*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 489; J. C. Slater, Phys. Rev. **103**, 1631 (1956).

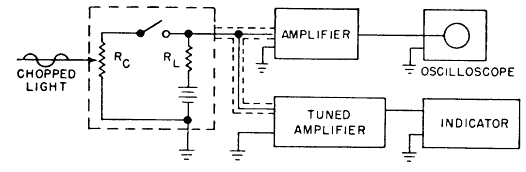

FIG. 1. Circuit used for ac photoconductive response measurements. R_c represents the photoconductive element. R_L is the load resistance.

spectral sensitivity in various stages of preparation of the film.

Extending Hintenberger's work, it should be possible to use selenium and perhaps sulfur in place of oxygen as a sensitizer, if the function required is to increase the film resistivity or convert it from n to p type. Also, since the halogens are active oxidizers (highly electronegative) it is possible that they might serve a similar purpose. Accordingly we have also studied the effect of these materials on the various electrical properties of PbSe films, to obtain further information regarding the sensitization process.

B. METHOD AND APPARATUS

For weak illumination the observed photoconductive response is exponential in time. Thus the conductivity change $\Delta\sigma$ will satisfy a differential equation of the form

$$d\Delta\sigma/dt = JA - \Delta\sigma/\tau, \tag{1}$$

where A is a constant depending on the film, J is the intensity of illumination, and τ is the observed response time. If the illumination is turned on at time $t=0$, the solution of (1) is

$$\Delta\sigma = JA\tau(1-e^{-t/\tau}). \tag{2}$$

If the illumination is chopped at the angular frequency ω, the maximum change in conductivity is given by

$$\Delta\sigma(\omega) = JA\tau/[1+(\omega\tau)^2]^{\frac{1}{2}}. \tag{3}$$

If $\omega \ll 1/\tau$, this reduces to

$$\Delta\sigma|_{\omega\to 0} = JA\tau. \tag{4}$$

Photoconductive sensitivity may be defined in any of a number of ways. The fractional change per unit incident radiation flux is called the responsivity, and defined as $R_s = \Delta\sigma/4\sigma J$. Thus, from Eq. (4) we have

$$R_s = A\tau/4\sigma. \tag{5}$$

Another expression for sensitivity is the signal-to-noise ratio. This has been normalized in various ways in the past. We shall refer to the signal-to-noise voltage ratio per unit radiation energy density. The term spectral sensitivity will imply the spectral dependence of either responsivity or signal-to-noise ratio.

The PbSe used in this study was prepared by fusion of spectroscopically pure lead and selenium. Single crystals[12] were grown by the Stockbarger method. Pyrex cell blanks were constructed with Pyrex bubble windows transparent to 6.5 μ. Sensitivity, time constant, and noise were measured using the circuit of Fig. 1. Spectral response was obtained using a Leiss (rock salt) monochromator. Carrier sign was determined by thermoelectric measurements. A more complete discussion of the method and apparatus will be found elsewhere.[13] A general discussion of the preparation and

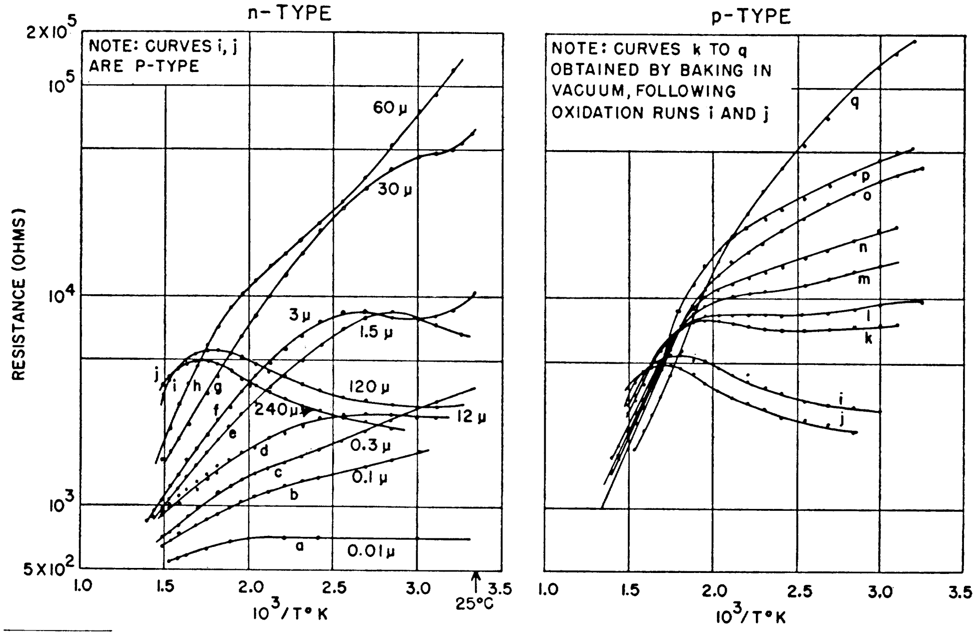

FIG. 2. Resistance-temperature data for a PbSe film heated in air at reduced pressures. The air pressure indicated in microns μ was maintained during entire cooling curve.

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[12] Prepared by R. F. Brebrick of the U. S. Naval Ordnance Laboratory.

[13] J. N. Humphrey, Doctoral dissertation, U. S. Naval Ordnance Laboratory Report NAVORD 3922 (unpublished).

properties of PbS, PbSe, and PbTe photoconductive films and an extensive bibliography has been given by Moss.[14]

C. SENSITIZATION PROCEDURE AND EXPERIMENTAL RESULTS—OXYGEN TREATMENT

1. Resistance-Temperature Measurements

The resistance of a PbSe film depends on the purity of the original material, the temperature at which it was deposited, its subsequent heat treatment, and its thickness and surface dimensions. We have found, however, that by suitable choice of starting materials and heat treatment a standard initial condition could be obtained. A film so prepared exhibits reproducible resistance-temperature behavior during subsequent treatment. The film is deposited by evaporating in a vacuum small crystallites freshly cleaved from a crystal of *n*-type PbSe. This may produce either *n*- or *p*-type films. A film can be converted from *p* to *n* type by repeated short bakes at 350°C to 450°C, at pressures of 10^{-5} mm of mercury or less. If this treatment is continued, the room-temperature resistance will be reduced gradually. For the film dimensions used, a resistance of 100 to 600 ohms is normally found as the limiting value. No photoconductivity is found in a film in this condition.

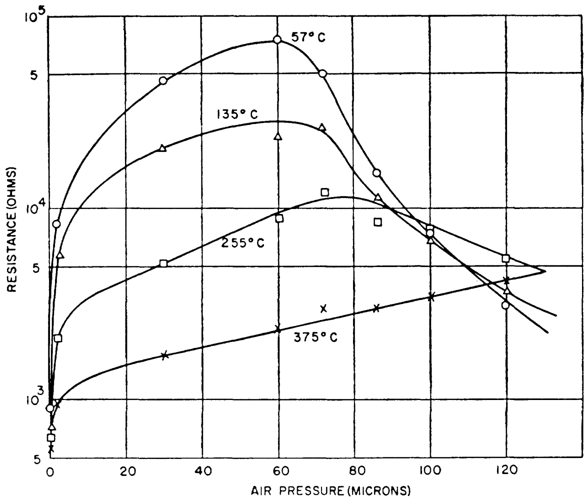

FIG. 3. Resistance-pressure isotherms for a PbSe film heated in air.

The effect of heat treatment on the resistance *vs* reciprocal temperature curves of a film originally brought into the standard condition is shown in Fig. 2. The resistance of a film in this condition is essentially independent of temperature, as shown by curve *a*. Curves *b–j* show the effect of oxygen (dried air) on the film. Each curve is obtained by heating the film to approximately 400°C, establishing the air pressure (as indicated in microns on each curve), and then cooling the film under constant pressure. It is seen that successive treatments at higher pressures result in a general increase of the slope of the curve until some maximum room-temperature resistance is attained. Further oxygen treatment produces a drop in resistance as shown by curves *i* and *j*, and a reversal of the sign of the thermoelectric power, indicating *p*-type material. If the process is now reversed and the film repeatedly baked at 400°C in vacuum the resistance changes will reverse their course; curves *k* to *q* show the effect of successive vacuum bakes.

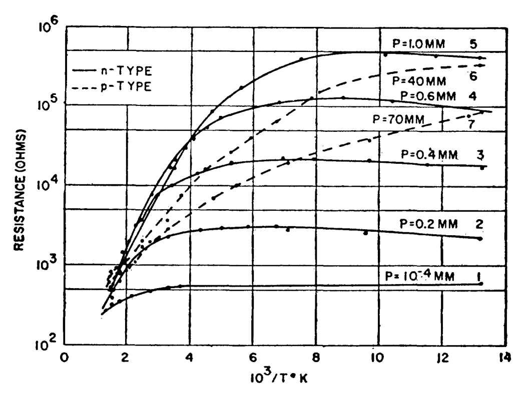

FIG. 4. Resistance-temperature data for a PbSe film heated to 400°C in air at pressure *P* for 15 sec; pressure was reduced to 10^{-5} mm before obtaining cooling curve.

The data of Fig. 2 have been replotted as isotherms in Fig. 3. We see that except at the highest temperatures the resistance passes through a peak as the pressure is increased, dropping off at high pressures. The peak resistivity at room temperature was found to be of

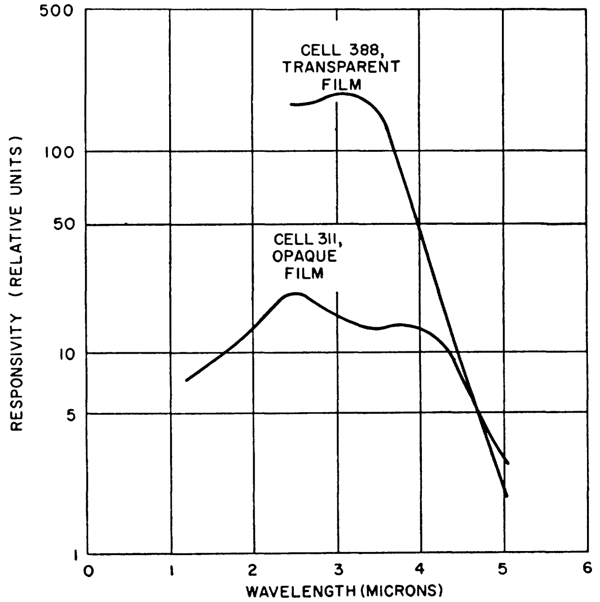

FIG. 5. Responsivity at 25°C for PbSe films sensitized with air.

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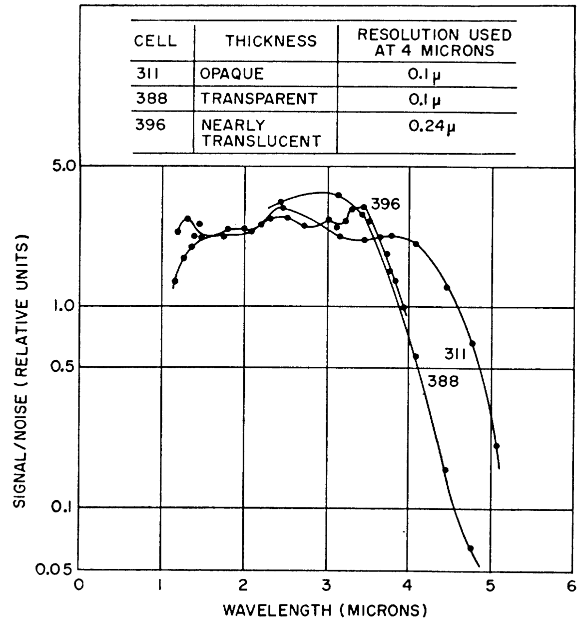
[14] T. S. Moss, Proc. Inst. Radio Engrs. 43, 1869 (1955).



CELL	THICKNESS	RESOLUTION USED AT 4 MICRONS
311	OPAQUE	0.1 μ
388	TRANSPARENT	0.1 μ
396	NEARLY TRANSLUCENT	0.24 μ

Fig. 6. Signal/noise at 25°C for PbSe films sensitized with air.

the order of 3 ohm cm. Intrinsic bulk resistivity at room temperature would be about 0.1 ohm cm.

In Fig. 4, resistance-temperature curves are shown for another cell in which the measurements were extended down to −195°C. In this case oxygen was introduced by 15-sec bakes at 400°C and the cooling curves were taken after re-evacuating the cell.

2. Spectral Sensitivity—Film Thickness

When the sensitivity of the film is checked after each heat treatment it is found that the highest sensitivity is achieved only near the condition of the maximum resistance; this is the condition where the sign of the carrier is found to reverse. Figure 5 shows the results obtained for the spectral responsivity of two cells at room temperature. Cell 388 is a thin film, estimated to be 0.1 μ thick, and cell 311 is a very thick film, estimated to be about 5 μ thick. The responsivity at short wavelengths (1 to 3 μ) is seen to be considerably greater in a sensitized thin film than in a sensitized thick film. However, in the thin film (cell 388) the knee occurs at 3.3 μ, while in the thicker film (cell 311) it occurs at about 4 μ, with the result that responsivity at long wavelengths is not significantly changed by increasing film thickness.

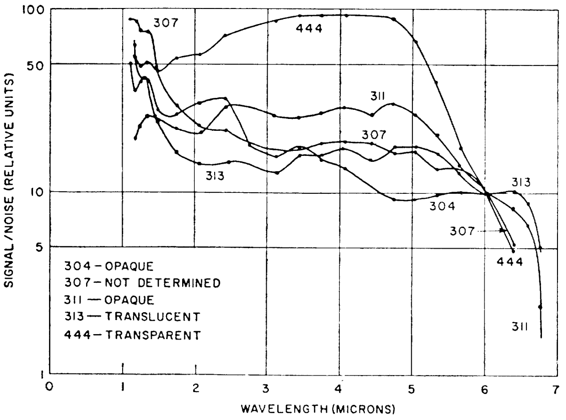


Fig. 7. Spectral response at −195°C for PbSe films sensitized with air. Curves are normalized at 6 microns.

Figure 6 shows the signal/noise curves for these two cells and another cell, 396, about 0.5 μ thick. Since the noise level is decreased by increasing the film thickness, signal/noise is greater in thick films than in thin ones, at long wavelengths. The sensitization procedure was found to be the same for thin and thick films.

In general it is found that the cell becomes more sensitive and the knee moves to longer wavelengths as it is cooled from room temperature to −195°C. Many cells show no sensitivity at all at 25°C, but are quite sensitive at −78°C and −195°C. The spectral response curves at −195°C also show a variation in position of the long wavelength limit with thickness (Fig. 7). Cell 444, a transparent film, has a knee at 5 μ while each of the thicker films 311 and 313 has its knee near 6.5 μ. At this temperature, just as at room temperature, we find that responsivity at short wavelengths decreases with increasing film thickness, responsivity at long wavelengths is essentially independent of film thickness, and signal/noise at long wavelengths increases with increasing film thickness.

3. Time Constants

At room temperature τ was too short to be measured accurately with the equipment available. From Eq. (3) τ is found to be less than 3 μsec, since the response was flat out to the limit of our frequency measurements, 16 kc.

At −195°C response times in three ranges were observed. In *n*-type samples τ was of the order of 15 to 30 μsec. The square-wave response of one such sample is shown in Fig. 8(A); the value of τ can be obtained from the variation of response with chopping frequency, curve *b* of Fig. 9. In films which were made *p* type by oxygen treatment, τ was of the order of 5 msec [Fig. 8(B)]. When a film in this condition is baked in vacuum to a condition near maximum resistivity, a combination of the above responses is seen. The re-

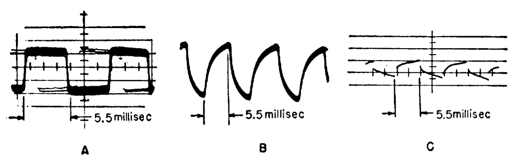


Fig. 8. Square-wave response characteristics at −195°C for PbSe films sensitized with air. Chopping frequency is 90 cps. (A) *n* type; $\tau = 30$ μsec. (B) *p* type; $\tau \sim 5$ msec. (C) nearly stoichiometric; $\tau_1 = 20$ μsec, $\tau_2 \sim 5$ msec.

sponse to a 90-cps square wave is shown in Fig. 8(C), while the variation of response with chopping frequency is shown in curve *a* of Fig. 9.

Finally, films showing the 5-msec response frequently showed an additional very long recovery time: the resistance decreased under illumination with white light, and failed to recover significantly within a period of hours. Warming the cell and recooling was found to re-establish the original high resistance.

D. EFFECT OF OTHER SENSITIZING AGENTS

1. Selenium Treatment

PbSe films were prepared in the standard initial condition (low resistance *n*-type films). Care was taken to avoid oxygen contamination. A small quantity of selenium in a side arm was kept in liquid nitrogen during the preparation. Then the nitrogen was removed and the selenium heated until a small quantity of selenium vapor entered the cell. The resistance and sensitivity to white light were checked at room temperature and liquid nitrogen temperature following each addition of selenium. The results are shown in Fig. 10(a). The addition of selenium caused the resistivity to increase to a maximum, and then decrease. The peak resistivity at room temperature was equal to that found by oxygen treatment. The sign of the thermoelectric power reversed when the resistance passed through the maximum.

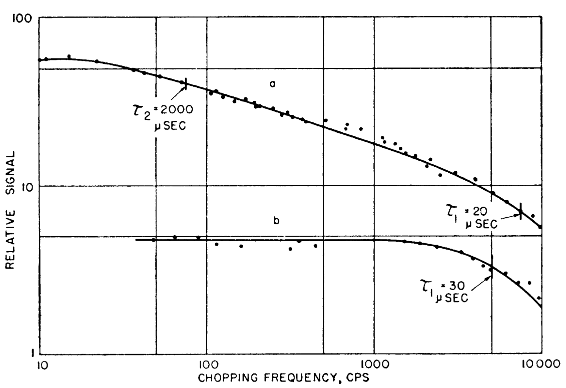


FIG. 9. Dependence of photoconductive response on chopping frequency at −195°C. (a) cell with two time constants; (b) cell with single time constant.

No photoconductivity was found at room temperature at any stage of the treatment with selenium. At liquid nitrogen temperature, sensitivity ($\tau=20$ μsec) was found when the resistance was high; the very long recovery from white light illumination observed in heavily oxidized films also was evident after the sixth and seventh selenium vapor addition.

2. Sulfur Treatment

The same procedure was followed with sulfur vapor. Figure 10(b) shows the effect on resistance over the range from −195°C to 400°C. Again, the resistivity increased to a maximum comparable to that found with oxygen treatment, and ultimately decreased as more and more sulfur was added. The sensitivity was too low

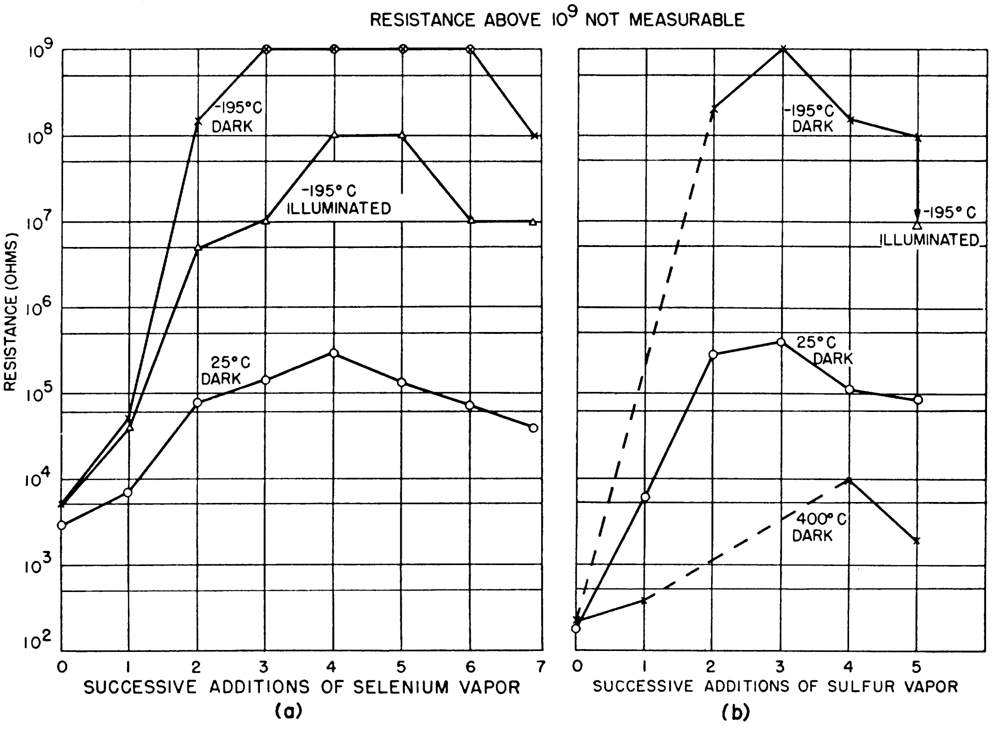


FIG. 10. Resistance of PbSe films treated with selenium and sulfur vapor.

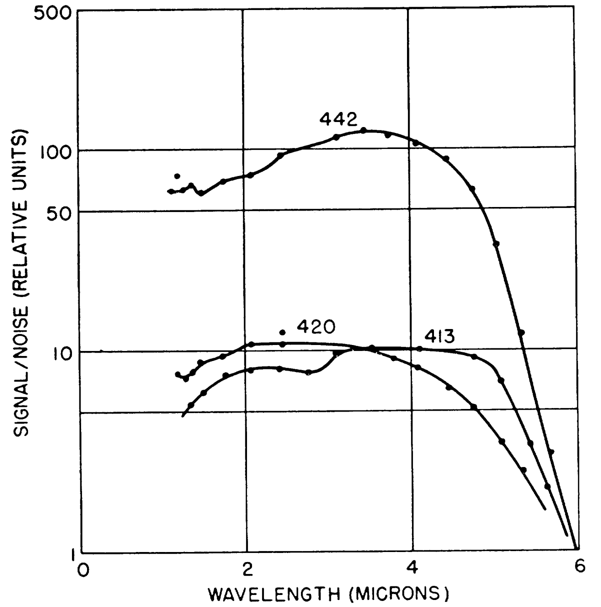


FIG. 11. Spectral response at $-195°C$ for PbSe films sensitized with sulfur (420, 442) and fluorine (413). All curves are normalized at 6 μ. All films were transparent.

to be measured at room temperature. At $-195°C$, however, sensitivity was obtained, with a time constant of about 5 msec. Figure 11 includes the spectral sensitivity of two such samples, one (442) quite thin ($<0.1\ \mu$), the other (420) somewhat thicker ($\sim 0.2\ \mu$).

3. Halogen Treatment

Fluorine vapor was obtained by the use of CoF_3 powder. At room temperature a fluorine pressure of about 1 mm of mercury is found above the CoF_3. Chlorine gas (bottled) and bromine and iodine vapors were used. Approximate pressure readings were obtained by using a thermocouple gauge as calibrated for air. Pressure readings were not attempted for iodine.

Figure 12 gives the dependence of resistance of a PbSe film on temperature for various chlorine treatments. Note that the curves are very similar to those for oxygen treatment, Fig. 2. A change from *n*-type to *p*-type conductivity occurs when the film resistance at room temperature is near its maximum. One of the *p*-type curves (No. 8) was obtained by pumping on a heavily treated film at high temperature, rather than by continuing the step-by-step addition of the halogen.

Figure 13 shows resistance-pressure isotherms for the chlorine treatment. The character of this set of curves is quite similar to that for oxygen.

Similar behavior was observed with fluorine, bromine, and iodine treatments.

As in the case of the sulfur and selenium, photosensitivity at liquid nitrogen temperature was produced by the halogens. The spectral sensitivity of a typical cell is given in Fig. 14. The response times observed were of the order of 20 μsec; the very slow response to white light (recovery only when warm) was also present.

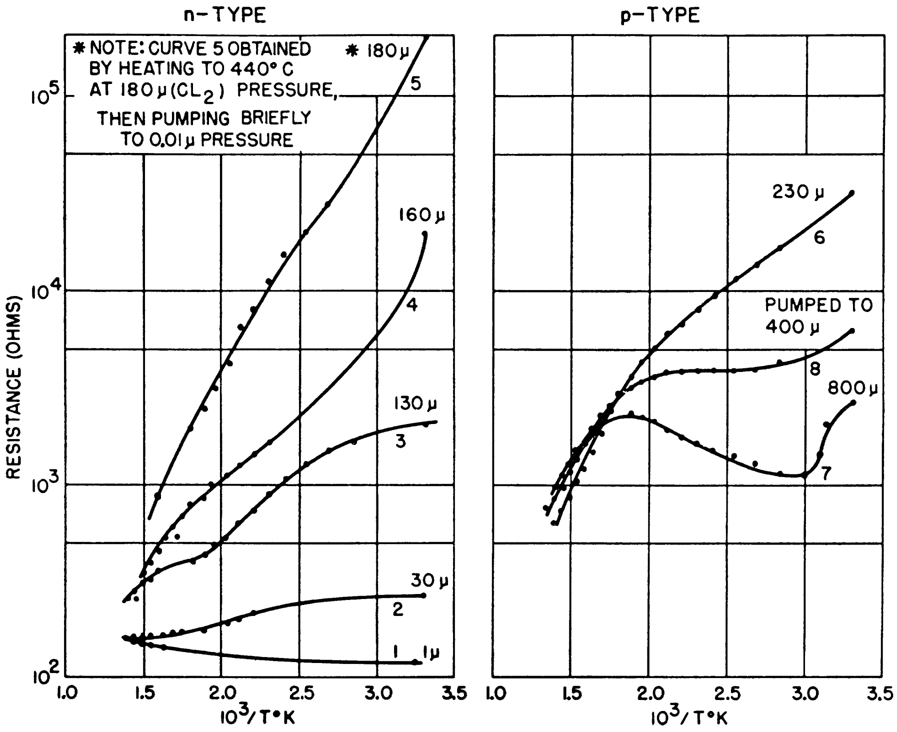


FIG. 12. Resistance-temperature data for a PbSe film heated in chlorine.

When adequate care was taken to exclude oxygen no photosensitivity was found at room temperature with any of the halogens, in spite of the fact that the maximum resistivity in each case was essentially equal to that produced by oxygen, and conversion from *n* type to *p* type took place at the maximum.

4. Oxygen-Halogen Sensitization

If the film was first oxidized until photosensitivity occurred, then baked in vacuum until the standard initial conditions were apparently restored, and finally the treatment repeated with the pure halogen, room-temperature photoconductivity was found to occur near the resistivity maximum. This photoconductivity shows essentially the same properties as that produced with oxygen alone as regards magnitude, time constant, and spectral limit. Spectral response curves for two cells treated with air and bromine and one each treated with air and fluorine, air and chlorine, and air and iodine are shown in Fig. 14. The time constant was found to be too short to affect the wave forms of 15-μsec pulses in a typical cell treated with bromine at 250°C. The long wavelength knee is seen at about 3.3 μ in each case. (Because of the wide slits and correspondingly poor resolution used with iodine the position of the knee is not well defined for cell 349.) The fluorine-sensitized cell (392) shows a strong increase of sensitivity at short wavelengths. This tendency was noted with all the halogens to a limited extent.

E. DISCUSSION AND CONCLUSIONS

We have shown that oxygen, selenium, sulfur, and the halogens act as acceptor impurities in PbSe, converting *n*-type material to *p*-type and causing the resistivity to increase to a maximum and then decrease; essentially the same maximum of resistivity is found in each case. At low temperatures each of these sensitize PbSe films, giving in each case a time constant of 20 to 40 μsec and a very long time constant of several hours. The oxygen-sensitized films showed the presence of an additional time constant of about 5 msec. Sensitivity at room temperature could be obtained only if oxygen was used, alone or together with another sensitizer. The long wavelength limit of sensitivity was independent of sensitizer.

The responsivity at short wavelengths was less in thick films than in thin films. However, the knee (long-wavelength limit of sensitivity) occurs at longer wavelengths in thick films than in thin, with the result that the responsivity at long wavelengths was essentially independent of film thickness. Thus no improvement in responsivity could be achieved by increasing the film thickness. On the other hand, because of the lower noise in thick films the signal-to-noise ratio at long wavelengths could be improved somewhat by increasing film thickness. No difference in method of sensitizing was required for thick films as compared to thin. The effect of film thickness on sensitivity will be further analyzed in a following paper.[15]

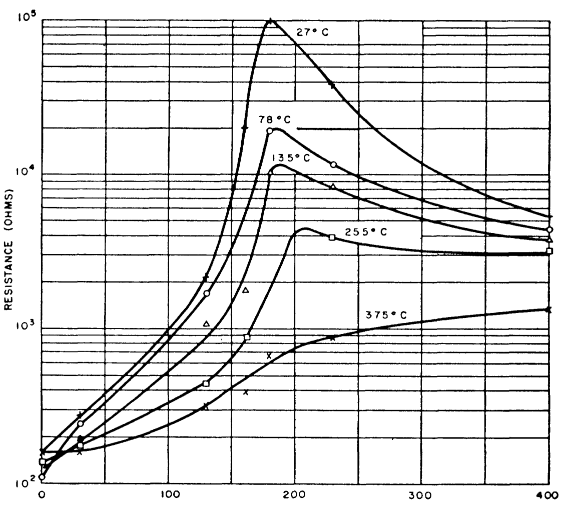


FIG. 13. Resistance-pressure isotherms for a PbSe film heated in chlorine.

Since the long wavelength limit is independent of sensitizer we conclude that we are dealing with an intrinsic electron transition. This is in agreement with the situation in PbS.[16]

The conversion of a film from *n* to *p* type and the raising of its resistance to a maximum value is not sufficient to produce room temperature sensitivity, except when oxygen is used. Oxygen must thus play some additional role in sensitization. The 5-msec time constant found at −195°C in films sensitized with oxygen

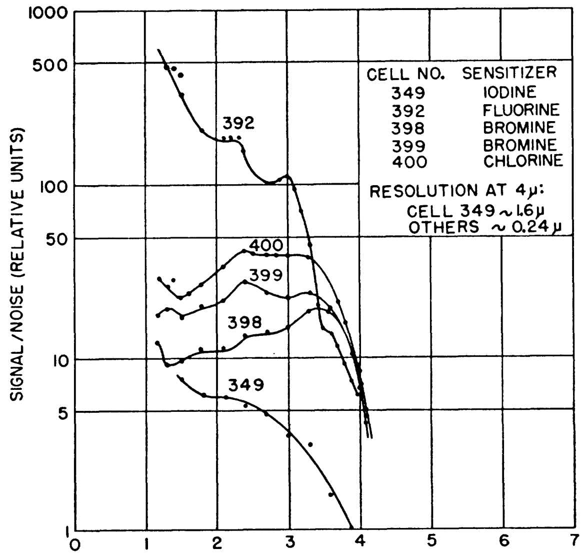


FIG. 14. Spectral response at 25°C for PbSe films sensitized with halogens following air pretreatment.

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[15] J. N. Humphrey and R. L. Petritz (to be published).

[16] W. W. Scanlon, Phys. Rev. **92**, 1573 (1953).

suggests the presence of trapping levels. Such traps could increase the majority carrier lifetime and thereby increase the photoconductive sensitivity according to Eq. (5). Further details of a model based on this mechanism will be discussed in a following paper.[17]

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the help of the Naval Ordnance Laboratory Glass Shop under the supervision of Wellman L. Clark, in developing and constructing the equipment and cell blanks used in this work.

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[17] J. N. Humphrey and R. L. Petritz (to be published).

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Modified Deformable Potential for Thermal Scattering of Electrons*

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In order to study thermal scattering of moderately bound electrons in a metal, corrections are considered to a deformable scattering potential. A constant multiple of the dilatation is derived that must be added to account for the correct zero of potential in a homogeneously deformed crystal. In an inhomogeneously deformed crystal (a crystal undergoing thermal vibrations), a function of the strain must be added to take care of charge redistribution. The deformable potential must also be modified to treat umklapp processes consistently. The modification provides that as the phonon wave vector increases in magnitude, some umklapp character must gradually be added to the scattering amplitude.

1. INTRODUCTION

IN calculating the thermal scattering of electrons in a metal, one considers each electron to be approximately describable by a Bloch wave function. The thermal distortions of the crystal alter the potential felt by the electrons, and thus scatter the electrons from one Bloch state to another. A central problem in the theory of thermal scattering is to estimate the scattering potential V_{sc}, which is the difference between the actual potential V_d in a thermally deformed crystal and the potential V of an undeformed crystal.

$$V_{\mathrm{sc}}(\mathbf{r})=V_d(\mathbf{r})-V(\mathbf{r}). \tag{1.1}$$

In a vibrating crystal, the displacement $\mathbf{S}_n$ of the ionic core, whose equilibrium position is at $\mathbf{r}_n$, can be expanded in normal modes of the lattice (phonons), as

$$\mathbf{S}_n(\mathbf{r}_n)=N^{-\frac{1}{2}}\sum_{qj}\boldsymbol{\varepsilon}_{qj}[a_{qj}\exp(i\mathbf{q}\cdot\mathbf{r}_n)+a_{qj}^*\exp(-i\mathbf{q}\cdot\mathbf{r}_n)]. \tag{1.2}$$

Here a_{qj} and a_{qj}^* are respectively proportional to the destruction and creation operators for the phonon with wave vector $\mathbf{q}$ and polarization vector $\boldsymbol{\varepsilon}_{qj}$; N is the number of unit cells in the crystal. (Discussion is limited to the case of a single atom per unit cell.) One can also consider Eq. (1.2) as defining a general displacement function $\mathbf{S}(\mathbf{r})$ by replacing $\mathbf{r}_n$ in that equation by the continuous variable $\mathbf{r}$.

Bloch,[1] in his early work on the conductivity of metals, assumed that the potential deforms along with the crystal. That is,

$$V_d(\mathbf{r}+\mathbf{S}(\mathbf{r}))=V(\mathbf{r}). \tag{1.3}$$

The potential in the deformed crystal at the displaced point is equal to the potential of the undeformed crystal at the corresponding equilibrium point. Nordheim[2] used an alternative assumption that the potential in a deformed crystal is the sum of the contributions from the several ion cores, and that each contribution to the potential moves rigidly with the corresponding core. Probably the most satisfactory calculation of the scattering potential to date is Bardeen's self-consistent formulation,[3] but Bardeen's method seems limited to metals whose conduction electrons are nearly free.

The object of the present paper is to find a scattering potential that would also be applicable to moderately tightly bound electrons, such as the d electrons of transition metals. We base our work on the deformable potential, but we suggest three important modifications. (1) In a crystal with a small homogeneous strain, it is necessary to add a constant to the deformable potential in order to maintain the energy of the crystal independent of the strain (to terms linear in the strain). (2) In a crystal with locally varying strain, such as the sinusoidal deformation corresponding to a phonon of finite wavelength, some redistribution of charge takes place to keep the Fermi level constant throughout the crystal. The calculation of this second effect follows closely the work of Hunter and Nabarro.[4] (Bardeen's

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* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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[1] F. Bloch, Z. Physik **52**, 555 (1928); **59**, 208 (1930).

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