

of Fig. 5, there exist periods that do not fit into the present analysis. These are probably due to the existence of a third carrier. It is, in fact, quite possible that the period  $\Delta(1/H) \cong 0.2 \times 10^{-6} G^{-1}$  for  $H \parallel x$  is due to this third carrier. The data is insufficient to give any clear picture about the Fermi surface of these carriers; however, they may be due to the rather isotropic light hole Fermi surface observed by Datars.

### V. CONCLUSIONS

Since interpretation II is in such strong disagreement with other experiments, we favor the first interpreta-

tion as being the correct one. Except for this point, there now exists a reasonably clear picture of two of the bands in antimony. Higher field measurements would aid in a more complete discussion of the other bands, and would eliminate the confusion resulting from the lack of accurate knowledge of the period of the principal electron ellipsoid for  $H \parallel x$ .

### ACKNOWLEDGMENTS

We would like to thank Dr. M. G. Priestley and Lee Windmiller for their pulsed-field measurements. We also wish to thank Edward Yasaitis for technical aid.

## Photoelectric Properties of Lead Sulfide in the Near and Vacuum Ultraviolet\*

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(Received 24 July 1963)

Measurements of photoelectric yield and electron energy distribution have been made on natural crystals of lead sulfide, Peruvian galena, in spherical photocells at pressures of  $10^{-8}$  mmHg. Under these conditions maximum yields are found to be of the order of 1% in contrast to the much higher yields previously reported for this material. Yield data for cesium-coated samples are also presented, as are values of the optical absorption coefficient in the range 4–12 eV. Observed effects are interpreted as indicating the existence of an additional valence band whose maximum is located approximately 4 eV below the top of the higher bands. Such an assignment is found to be in qualitative agreement with the computed band structure.

### INTRODUCTION

WHILE attempting to extend photoconductivity measurements on lead sulfide into the vacuum ultraviolet region, Smith and Dutton<sup>1</sup> discovered the onset, at approximately 5 eV, of an apparently very efficient external emission process. They measured yields which reached and exceeded 10% for incident energies above 10 eV and also observed unexpected changes in the energy distribution of the emitted electrons. Since such high yields are unprecedented for a material in which the electron affinity is considerably larger than the band gap<sup>2</sup> and there was some question as to the interpretation of the energy distribution data, it was thought worthwhile to conduct additional investigations.

Recent work has indicated that important band structure information may be obtained by analysis of reflectivity spectra<sup>3</sup> and investigation of emission from

cesium coated surfaces.<sup>4,5</sup> It was therefore felt that the application of such techniques to lead sulfide might provide additional information of assistance in understanding the previously observed phenomena.

### EXPERIMENTAL

The monochromator, radiation source, and associated measuring equipment used in this investigation have been described elsewhere.<sup>1</sup> The photocell, shown in Fig. 1, is basically similar to that described by Apker *et al.*<sup>6</sup> The lead sulfide emitting surface, in the form of a cleaved crystal approximately  $\frac{1}{2}$  in.  $\times$   $\frac{1}{2}$  in.  $\times$   $\frac{1}{8}$  in.,<sup>7</sup> is mounted rigidly at the center of the cell with the cesium source,<sup>8</sup> a mixture of cesium chromate and silicon contained in a metal foil, which upon heating releases metallic cesium, directly behind it. Radiation from the monochromator enters the cell through a LiF window cemented with epoxy resin<sup>9</sup> to a ground flat opposite the

\* Work supported by the U. S. National Aeronautics and Space Administration (Goddard Space Flight Center).

† This paper is composed of portions of a dissertation submitted to the Graduate Council of the University of Rochester in partial fulfillment of the requirements for the degree Doctor of Philosophy.

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<sup>1</sup> A. M. Smith and D. B. Dutton, *J. Phys. Chem. Solids* **22**, 351 (1961).

<sup>2</sup> E. Taft, H. Philipp, and L. Apker, *Phys. Rev.* **110**, 876 (1958).

<sup>3</sup> H. Ehrenreich, H. R. Philipp, and J. C. Phillips, *Phys. Rev. Letters* **8**, 385 (1962).

<sup>4</sup> W. E. Spicer and R. E. Simon, *Phys. Rev. Letters* **9**, 385 (1962).

<sup>5</sup> D. Brust, M. L. Cohen, and J. C. Phillips, *Phys. Rev. Letters* **9**, 389 (1962).

<sup>6</sup> L. Apker, E. Taft, and J. Dickey, *Phys. Rev.* **74**, 1462 (1948).

<sup>7</sup> Samples were obtained from Ward's Natural Science Establishment, Rochester, New York.

<sup>8</sup> Obtained through the courtesy of Dr. W. E. Spicer.

<sup>9</sup> Hysol "Epoxy-Patch" Kit No. 1-C obtained from the Hysol Company, Olean, New York.

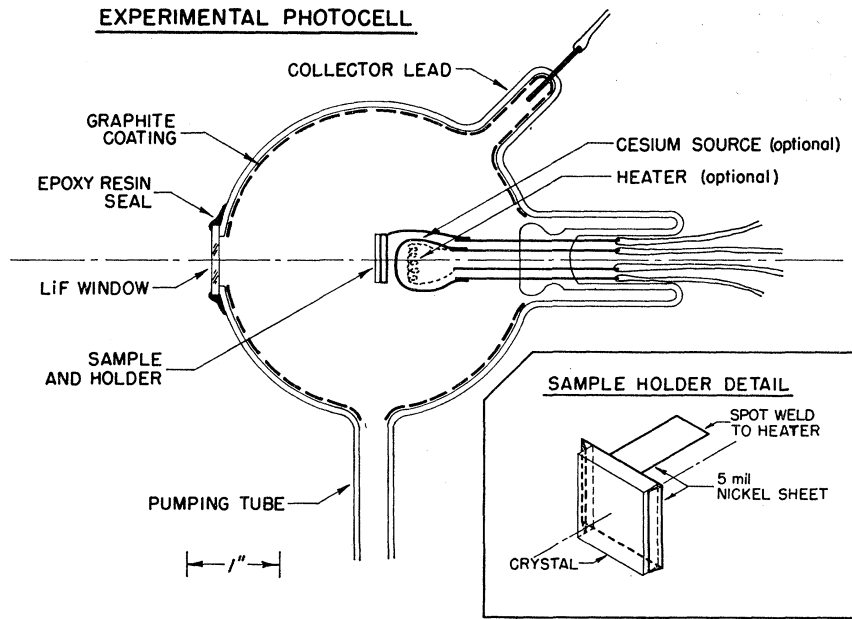


FIG. 1. Details of experimental photocell.

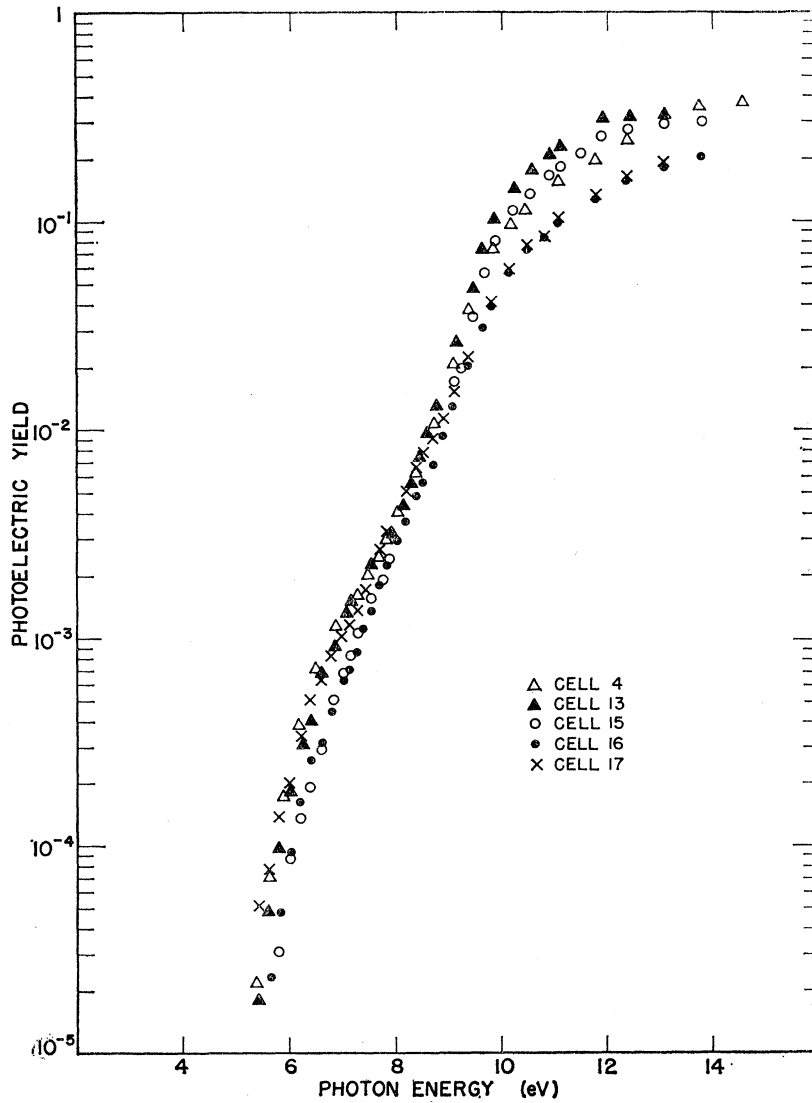
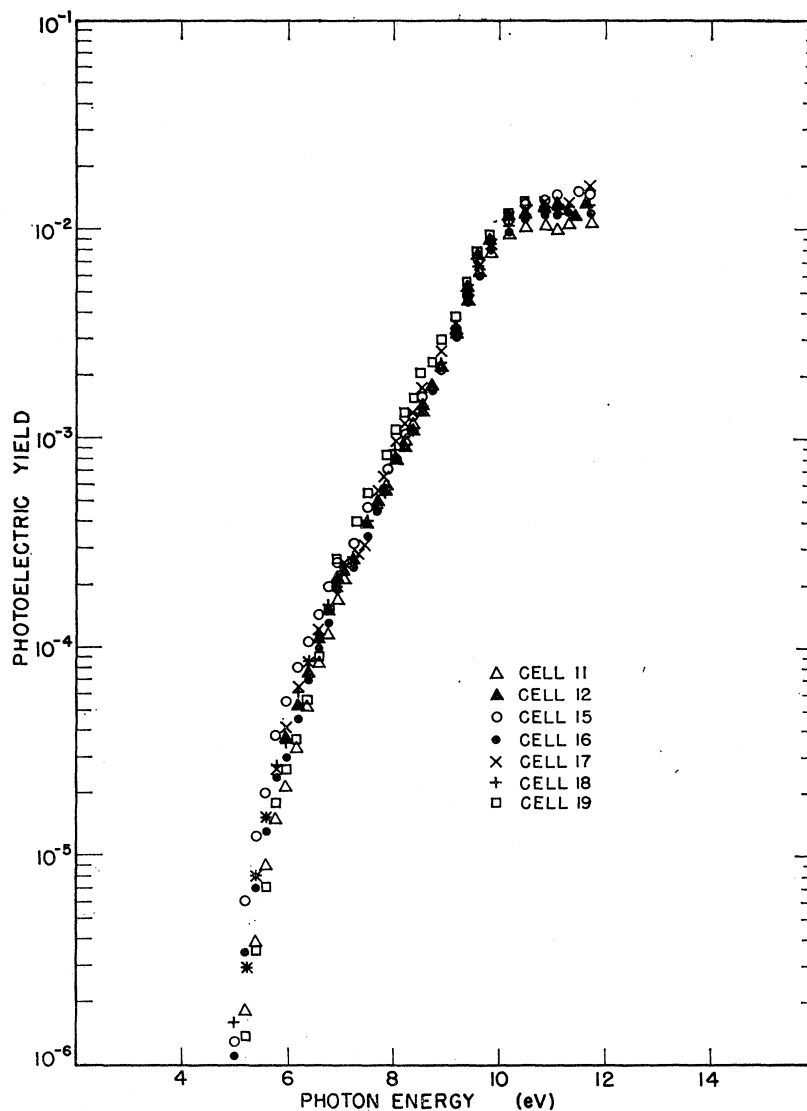


FIG. 2. Photoelectric yield of 5 galena samples measured with the photocell evacuated by the pumping system of the monochromator and no window installed. Pressure  $\sim 10^{-3}$  mmHg.

FIG. 3. Photoelectric yield of 7 galena samples measured with window installed. Pressure  $\sim 10^{-8}$  mmHg.



emitter. Although the use of this epoxy limits baking temperatures to less than  $100^{\circ}\text{C}$ , higher temperatures would no doubt result in lower ultimate pressures; the fact that irreversible composition changes occur in lead sulfide in the neighborhood of  $200^{\circ}\text{C}$ <sup>10</sup> makes the use of more elevated temperatures somewhat questionable.

Continuous evacuation is accomplished with an Ultek 5 liter/sec gettering pump connected to the cell through a length of glass tubing, a copper to glass tubulation and a "Swagelok" compression fitting. With this arrangement pressures in an outgassed cell average  $1-2 \times 10^{-8}$  with occasional readings of  $7-9 \times 10^{-9}$  being observed.

Measurements of reflectivity have been made on cleaved samples contained in a specially designed reflectometer<sup>11</sup> which is attached directly to the exit slit assembly of the monochromator.

<sup>10</sup> W. W. Scanlon, Phys. Rev. **92**, 1573 (1953).

<sup>11</sup> A. M. Smith, J. Opt. Soc. Am. **50**, 862 (1960).

## RESULTS

The experimental results of yield measurements for unsealed and sealed samples are summarized in Fig. 2 and Fig. 3. "Unsealed" refers to measurements made with the LiF window removed and the cell evacuated by the pumping system of the monochromator. Vacuum conditions obtained in this way are comparable to those in the work of Smith and Dutton.<sup>1</sup> The high yields observed under these conditions have been found to be due to contamination of the emitting surface by vapors of diffusion pump oil.<sup>12</sup>

The data for the sealed cells show maximum yields of approximately 1% and indicates a threshold in the neighborhood of 5 eV. Using a value of 0.4 eV for the band gap of lead sulfide,<sup>13</sup> the electron affinity is found

<sup>12</sup> R. A. Knapp (unpublished).

<sup>13</sup> W. W. Scanlon, J. Phys. Chem. Solids **8**, 423 (1959).

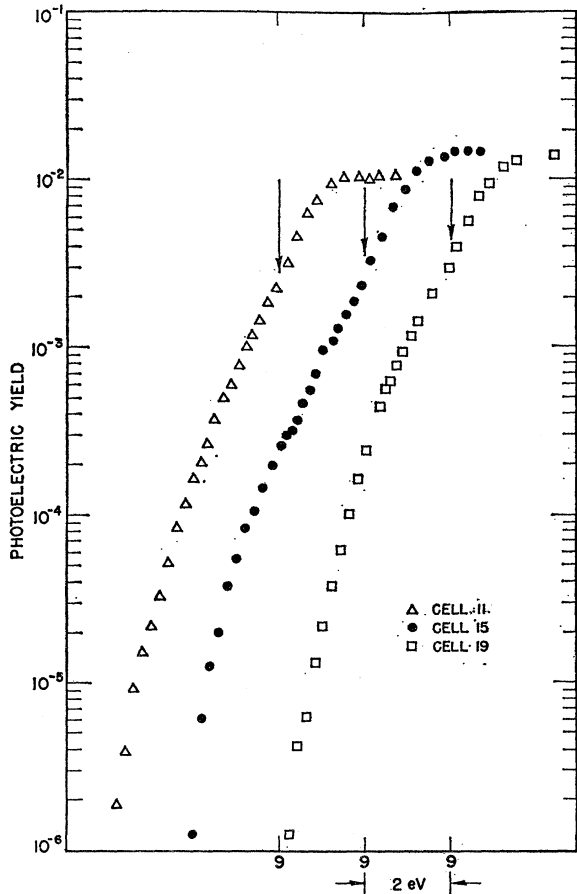


FIG. 4. Photoelectric yield of three samples showing inflection point near 9 eV.

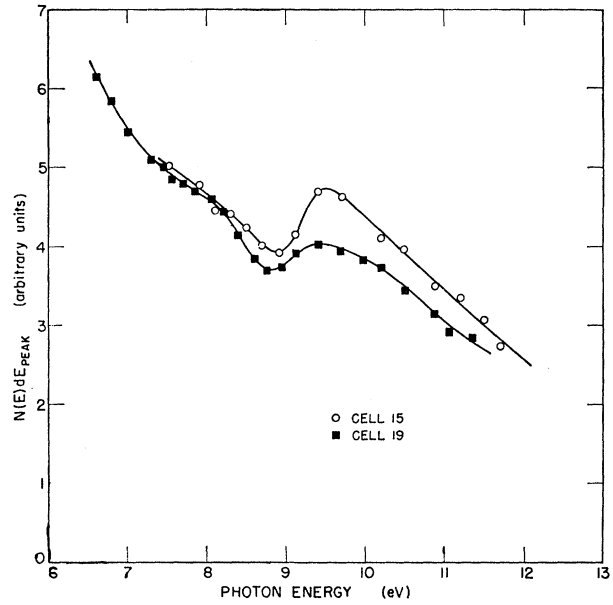


FIG. 6. Plot of the height of the peak of electron energy distribution curves versus photon energy; note behavior near 9 eV.

in Fig. 4 for three samples is an inflection point at approximately 9 eV whose interpretation will be discussed in a later section. Near threshold the yield dependence on photon energy can be represented by either of the equations below

$$y \propto (h\nu - 4.94)^2,$$

$$y \propto (h\nu - 4.85)^{5/2},$$

so that no definite conclusions as to the type of excitation, direct or indirect, can be reached.<sup>14</sup> The known

to be 4.6 eV. Not evident in Fig. 3 but seen more clearly

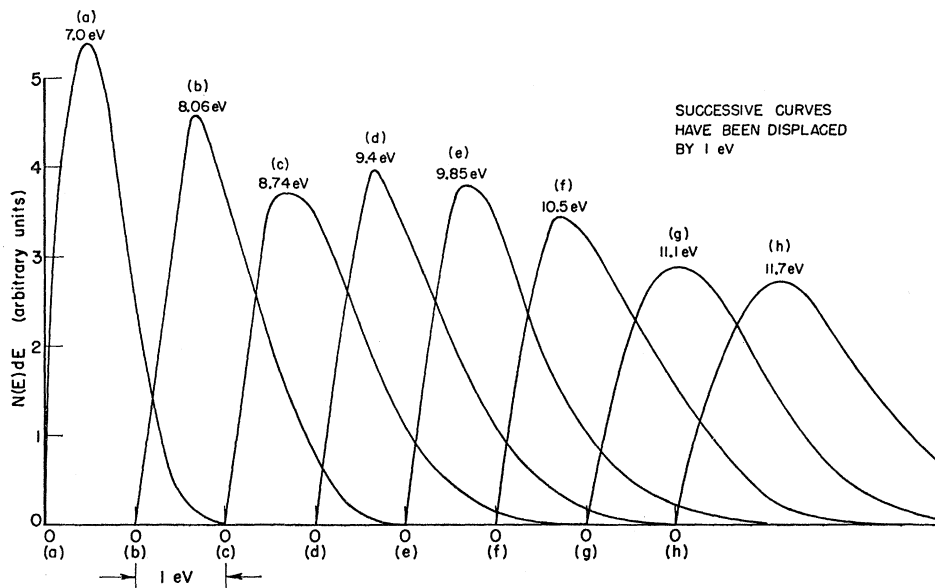


FIG. 5. Electron energy distribution curves for a representative sealed cell. Successive curves have been displaced by 1 eV for clarity.

<sup>14</sup> E. O. Kane, Phys. Rev. **127**, 131 (1962).

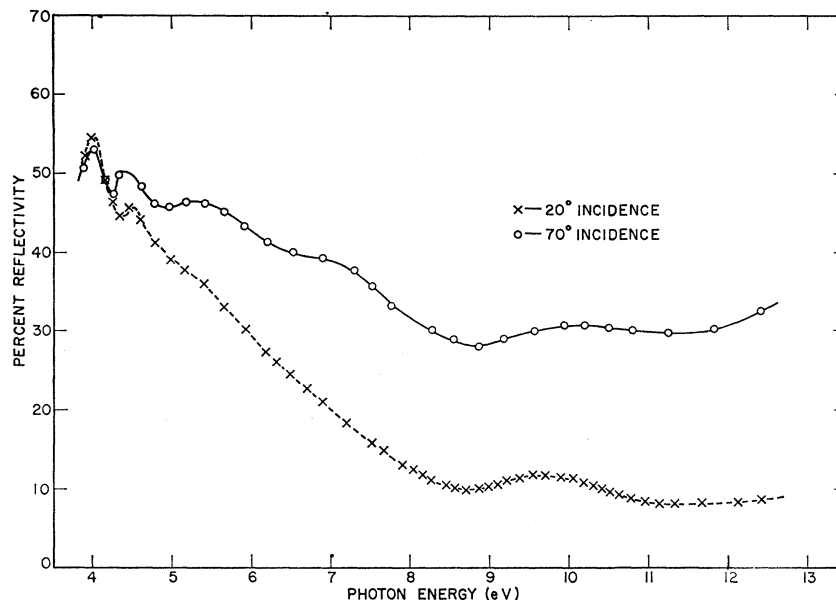


FIG. 7. Measured reflectivity of a cleaved sample of Peruvian galena.

existence of electron multiplication<sup>15</sup> and the rather large penetration depth for the incident radiation, discussed below, however, indicate that the emission is a volume effect with scattering.

Representative electron energy distributions for a sealed sample are shown in Fig. 5. These are obtained by graphical differentiation of the current-voltage characteristics:  $d/dV(I/I_s)$ . For energies below approximately 9 eV, the relative number of low-energy electrons is decreasing, as evidenced by a decrease in peak height and an increase in width, as photon energy is in-

creased. In the neighborhood of 9 eV, the distributions become higher and narrower, a behavior which is interpreted as an increase in the fractional number of low energy electrons. For higher energies the distributions again show a decreasing number of low energy electrons. This behavior is illustrated more clearly in Fig. 6 in which the height of the peak of the distributions is plotted against  $h\nu$  for two samples.

The measured reflectivity of a cleaved lead sulfide sample is shown in Fig. 7. The double peak in the data for 20-deg incidence at approximately 4 eV is repro-

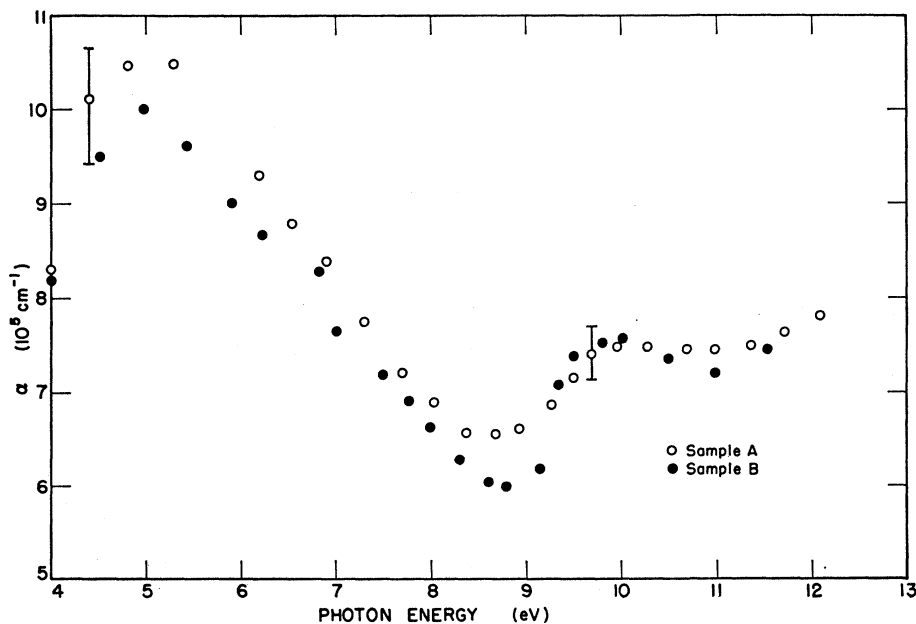


FIG. 8. Optical absorption coefficient of Peruvian galena. Values were obtained by analysis of reflectivity data using methods discussed in Ref. 16.

<sup>15</sup> A. M. Smith and D. B. Dutton, J. Opt. Soc. Am. 48, 1007 (1958).

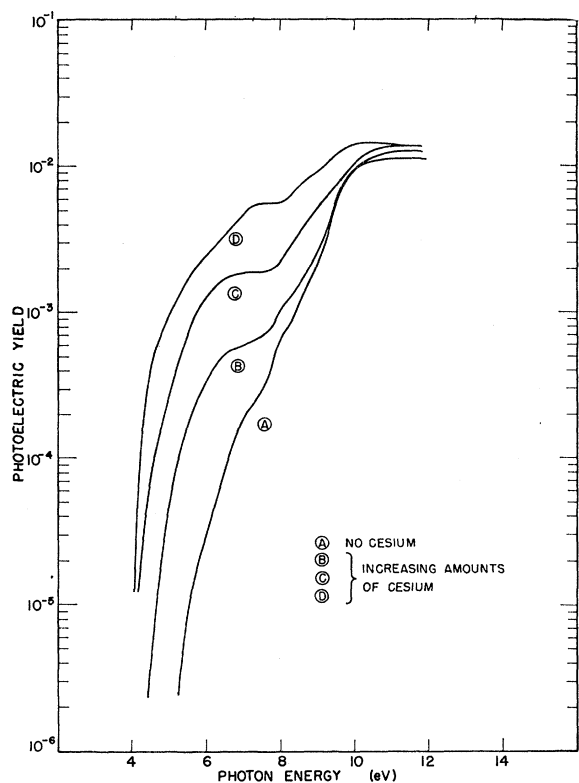


FIG. 9. Photoelectric yield of several cesium coated lead sulfide samples. Curves A, B, and C are in order of increasing amounts of cesium.

ducible from sample as is the smaller broader peak at 10 eV. The absorption coefficient derived from the above reflectivity data<sup>16</sup> is shown in Fig. 8. Although absolute values may be uncertain, due to the necessary graphical interpolation, by as much as 20%, penetration depths of 100 to 200 Å are nevertheless indicated in the region of interest. From the point of view of the discussion to be presented in the following section, the increase in absorption starting at slightly less than 9 eV is significant.

Figure 9 shows the observed photoelectric yield for several cesium covered samples. The change in threshold, to approximately 4 eV, is quite constant from sample to sample, but the change in yield appears to depend on the amount of cesium deposited. This is attributed to incomplete coverage of the surface by the cesium; a "patch" effect whereby the threshold is determined by small areas of lower work function while the yield is determined by the fraction of the total emitting area covered by such patches. A strong inflection point is evident in these curves at slightly less than 8 eV, a change of 1 eV from the position in the samples without cesium, and in general no inflection point is

apparent at 9 eV. The yield at energies above 10 eV is not appreciably effected by the cesium treatment.

Energy distribution curves for the cesium coated samples suffer from serious distortion at low energies due to the failure of the current-voltage characteristics to show a clear saturation. Although there is some indication of a behavior, displaced by 1 eV, similar to that for the untreated samples, it is felt that additional data are required before definite conclusions can be drawn from this information.

## DISCUSSION

The results previously described for the samples without cesium coverage could be explained in part by assuming appropriate changes in the scattering cross section, the approach taken by Smith and Dutton,<sup>1</sup> and the observed variation of the penetration depth of the incident radiation. However, since the energy at which the effects of such mechanisms would be seen should be independent of the work function of the material, it is felt that such arguments cannot account for the data for the cesium coated samples and other possible explanations must be investigated.

The band structure of lead sulfide has been computed by Bell *et al.*<sup>17</sup> Although their results, shown in Fig. 10, are incomplete and suffer to some extent from inaccuracies inherent in the methods used,<sup>18</sup> it is felt that the phenomena observed here can best be explained on the basis of band structure arguments supported, qualitatively, by this calculation.

The occurrence of an inflection point in the yield curve for the samples without cesium and a corresponding increase in the number of low-energy electrons can be accounted for by assuming the existence of an additional valence band whose maximum is located approximately 4 eV below the top of the higher bands. At energies near the threshold for transitions from this band the yield would be expected to rise due to the larger density of possible initial states and once such transitions were taking place a larger fraction of lower energy electrons would be observed since most of the photon energy is expended in bringing the electrons to the vacuum level. In addition, since the position of this lower band is fixed relative to the top of the higher bands and not the vacuum level, the energy at which phenomena associated with it appear would depend on the value of the work function as is observed in the cesium treated samples. The optical data add some support to this argument since the increased density of states in this assumed band would be expected to add to the absorption and this is observed.

On the basis of Bell's calculation this assumed lower

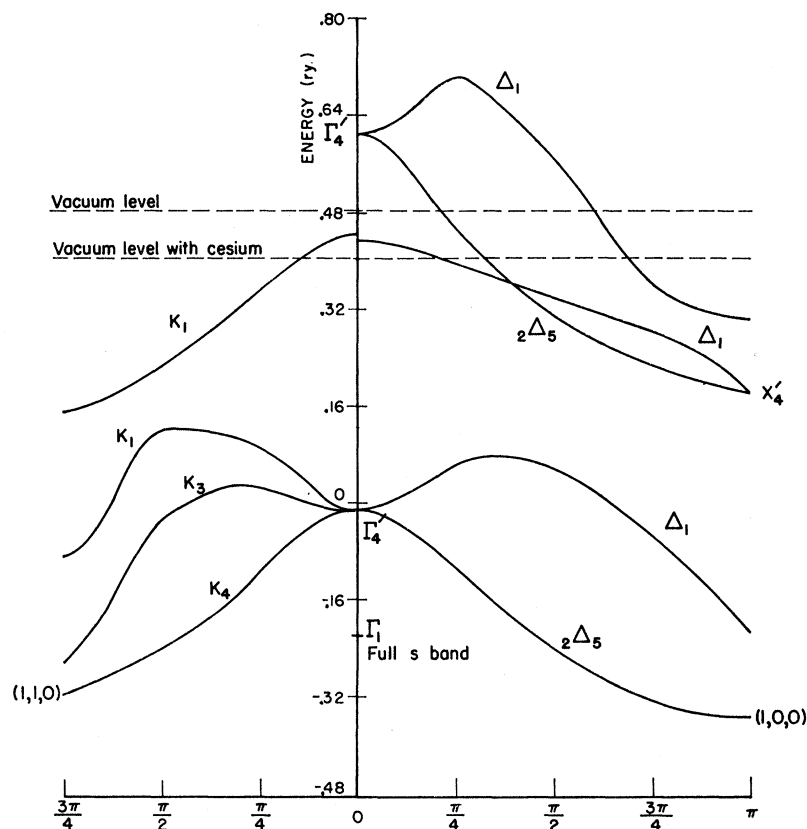
<sup>16</sup> Values of absorption coefficient were obtained from reflectivity data using graphical information found in the work of S. P. F. Humphreys-Owen, Proc. Phys. Soc. (London) **77**, 949 (1961).

<sup>17</sup> D. B. Bell, D. M. Hum, L. Pincherle, D. W. Sciamia, and P. M. Woodward, Proc. Roy. Soc. (London) **A217**, 71 (1953).

<sup>18</sup> R. A. Smith, *Semiconductors* (Cambridge University Press, London, 1959), p. 425.

<sup>19</sup> D. Redfield, Phys. Rev. **124**, 1809 (1961).

FIG. 10. Band structure of lead sulfide after Bell *et al.* (Ref. 17).



band is identified as the band arising from the 6s electrons of lead. At  $k=0$ , this band is located approximately 4.5 eV below the top of the higher bands and since this value may be in error, as mentioned previously, or the band maximum may lie at some other  $k$  value, it is felt that this assignment is the only reasonable one allowed by both the experimental data and the computed band structure.

The double peak observed near 4 eV in the reflectivity data cannot at present be identified using the computed band structure. The splitting of this peak is of the same order of magnitude as that observed in other materials for a spin-orbit interaction<sup>3</sup> and may therefore prove useful if additional band structure calculations are undertaken for lead sulfide.

The assumption that the electrons seen near threshold are those from states at the top of the valence band cannot be immediately confirmed. This is due to both

the low band gap of lead sulfide, which allows the existence of electrons near the bottom of the conduction band at room temperature, and possible band bending due to impurity states. Both of these effects would cause the observed threshold to be somewhat smaller than the true threshold for valence band emission. It has been pointed out<sup>19</sup> that such effects tend to cause a pronounced tail in the yield at low energies and since such a behavior is not observed here it is felt that our results are not significantly affected by these mechanisms.

#### ACKNOWLEDGMENTS

It is a pleasure to acknowledge the advice and encouragement extended by Dr. David B. Dutton and Dr. Kenneth J. Teegarden during the course of this work. Thanks are also due Dr. Robert S. Knox for many helpful suggestions and a critical reading of this manuscript.