# Photoemission and Band Structure of the Semiconducting Compound CsAu

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(Received October 5, 1961)

The energy distribution of the photoelectrons and the quantum efficiency of the photoemission from CsAu were measured in the spectral range from 1.6 to 6.2 ev. From the measurements the following conclusions were drawn: For $h\nu > 4.0$ ev, photoelectrons are excited principally from the valence band; for $h\nu < 4.0$ ev, photoelectrons are excited from states near the bottom of the conduction band. A bandgap of $2.6(\pm0.2)$ ev and an electron affinity of $1.5(\pm0.2)$ ev are deduced.

## I. INTRODUCTION

IN a previous paper,[1] it had been suggested that the semiconductor[2] CsAu has an electron affinity of $1.5(\pm0.2)$ ev and a direct bandgap of between 2.6 and 3.3 ev. There also appeared to be some possibility of an indirect band transition at energies much less than 2.6 ev. The experimental evidence also indicated that the samples studied were $n$-type and degenerate with a carrier density of between $10^{19}$ and $10^{20}$ electrons/cm$^3$. More recently, Wood and Reitz have made a band structure calculation for CsAu and found the minimum band-to-band transition to be direct with an energy difference of 2.3 ev.[3] It is the purpose of this paper to report on measurements of the energy distribution of photoelectrons and the spectral distribution of the quantum yield in the ultraviolet and to draw from these results conclusions concerning the band model of CsAu.

## II. EXPERIMENTAL METHODS

The tubes used to measure the energy distributions of photoemission by the retarding potential method were of the simple cylindrical type described by Apker, Taft, and Dickey[4] and by Taft and Philipp.[5] The tubes had quartz windows. The formation of the CsAu films has been described previously.[1,2]

For measurement of the spectral distribution of the photoemissive yield between 3.7 and 5.6 ev (the upper limit was set by the quartz window) a Bausch & Lomb Model No. 33–86–45 grating monochromator was employed in conjunction with a sodium salicylate phosphor[6] which was used to measure the light intensity. The system used from 1.0 to 4.2 ev has been described previously.[1]

In making the retarding potential measurements, a small (at most 0.05 v) 24-cps ac voltage was superimposed on the retarding potential voltage. By this means the photocurrent was modulated and a 24-cps

output signal was generated which was proportional to the number of photoelectrons with energy corresponding to the retarding potential. The retarding potential was varied continually at a rate of about 1 v/min, so that a complete energy-distribution curve could be obtained in 5 min.[7]

## III. RESULTS AND DISCUSSION

Curves of the spectral distribution of the photoemissive yield are presented in Fig. 1. The curve labeled "S-1050" was taken from the tube from which the energy distributions give in Figs. 2, 3, and 4, were obtained. For the spectral range 1.6 to 3.9 ev, the spectral-distribution curves are similar to those published previously.[1,8] As in the previous work,[1] a variation
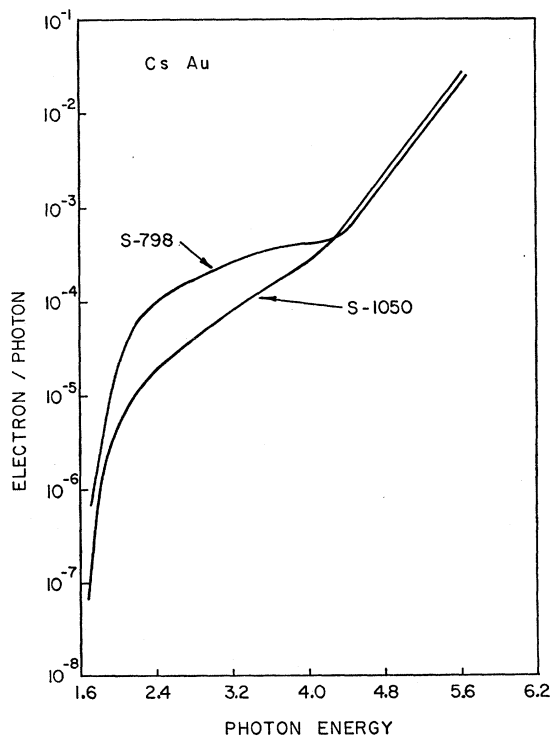


FIG. 1. Spectral distribution of the photoemission from CsAu.

[1] W. E. Spicer, A. H. Sommer, and J. G. White, Phys. Rev. **115**, 57 (1959).

[2] A. H. Sommer, Nature **152**, 215 (1943).

[3] V. E. Wood and J. R. Reitz, Bull. Am. Phys. Soc. **6**, 108 (1961).

[4] L. Apker, E. Taft, and J. Dickey, J. Opt. Soc. Am. **43**, 78 (1953).

[5] E. Taft and H. R. Philipp (to be published).

[6] J. F. Hamman, Z. angew. Phys. **10**, 187 (1958); A. M. Smith and D. Dutton (to be published).

[7] The ac method was suggested by L. Leder and is similar to a system developed for other purposes. [L. Leder and J. A. Simpson, Rev. Sci. Instr. **29**, 571 (1958)].

[8] P. G. Borzyak, Trudy Inst. Fiz. Akad. Nauk Ukr. S.S.R. **2**, 1924 (1952).
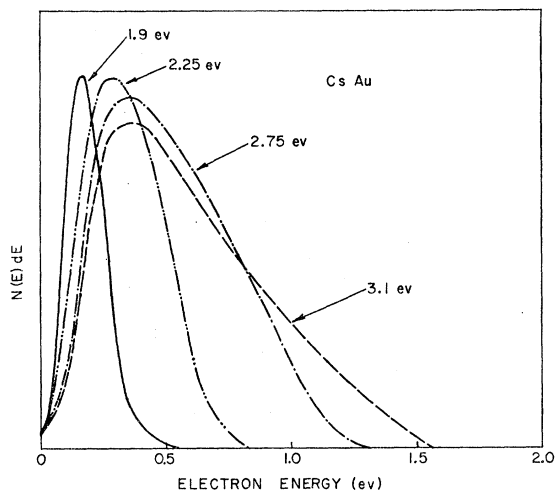
FIG. 2. The energy distribution of the photoelectrons from CsAu for photon energies between 1.9 and 3.1 ev.

of as much as a factor of 5 is found in the absolute magnitude of the yield for photon energies of about 2.2 ev, in agreement with the assumption that the photoemission in this spectral range is due to the presence of defect states. The yield rises sharply above 4.0 ev, increasing by about two orders of magnitude between 4.0 and 5.6 ev. At 5.6 ev, it has a value of about 0.03 electron/photon and is still rising.

Figures 2, 3, and 4 show the energy distributions of the photoelectrons from CsAu for various values of the exciting radiation. For photons with energies below 4.0 ev, the energy of the emitted electrons increases monotonically with increasing photon energy as would be expected for electrons excited from one band. This group of electrons will be referred to as the fast group. For photon energies greater than 4.0 ev, a group of slower electrons appears.[9] This indicates that for $h\nu > 4.0$ electrons are being excited from a second band which lies about 4.0 ev below the vacuum level.[10] The percentage of the photoelectrons in the slow group increases swiftly with the photon energy. For photons of 4.28 ev, the number of electrons in the slow and fast groups are about equal; for photons of 4.52 ev, there are about 4 times as many electrons in the slow group as there are in the fast group and, for photons of 4.97 ev, there are about 20 times as many electrons in the slow group as there are in the fast group. Above 5.5 ev the

slow group of electrons dominates the energy distribution so completely that the fast group of electrons can no longer be detected.

The increase with photon energy of the number of electrons in the slow group relative to the number in the fast group is approximately equal to the rise in the quantum yield. This indicates that the rise in quantum yield above 4.0 ev is due principally to the excitation of electrons from the band lying about 4.0 ev below the vacuum level. It seems plausible to identify this band with the valence band, since the high quantum yield associated with this excitation (0.03 electron/photon at 5.6 ev) is only to be expected for transitions from the valence band.[11,12] Since excitation from the valence band occurs only for $h\nu > 4.0$, the photoelectrons which are excited by photons with energy less than this must be due to $n$-type defect levels. Based on the argument given in reference 1,[13] it is clear that these electrons come from states quite close to the bottom of the conduction band. From the threshold of photoemission as well as from the difference between the energy of the photons and the maximum energy of the resulting photoelectrons, it can be seen that the electron affinity lies within the limits suggested previously (1.3–1.7 ev). Either from the difference between the threshold for photoemission from the
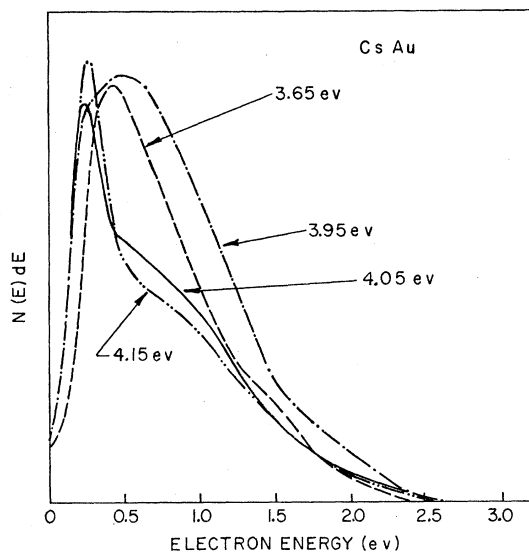


FIG. 3. The energy distribution of the photoelectrons from CsAu for photon energies between 3.65 and 4.15 ev (note the change in electron energy scale between Fig. 2 and Fig. 3). The group of slow electrons which appear for $h\nu = 4.05$ ev are due to excitation from the valence band.

[9] Although the average energy of this group of electrons increases with increasing $h\nu$, it will be called, for convenience, the slow group.

[10] There is a superficial similarity between the appearance of the slow group of electrons here and that which accompanies pair production by electrons in certain materials [see references 4 and 5 and W. E. Spicer, Proceedings of the 1961 International Conference on Photoconductivity (to be published)]. However, one can not associate an increase of two orders of magnitude in yield between photon energies of 4.0 and 5.6 ev with pair production, since in CsAu each electron excited by a photon of 5.6 ev has sufficient energy to produce at the most only two or three secondaries.

[11] The data presented here is quite similar to that reported by Sorokin for HgI [O. M. Sorokin, Soviet Phys.—Tech. Phys. 3, 1331 (1958)].

[12] W. E. Spicer, RCA Rev. 19, 55 (1958); J. Appl. Phys. 31, 2077 (1960).

[13] These arguments were based on the low (0.01 ohm-cm) temperature-independent (from 4° to 410°K) resistivity of CsAu and on the fact that the photoemission threshold at 1.6 ev must be due to the same electrons which produce the high conductivity.
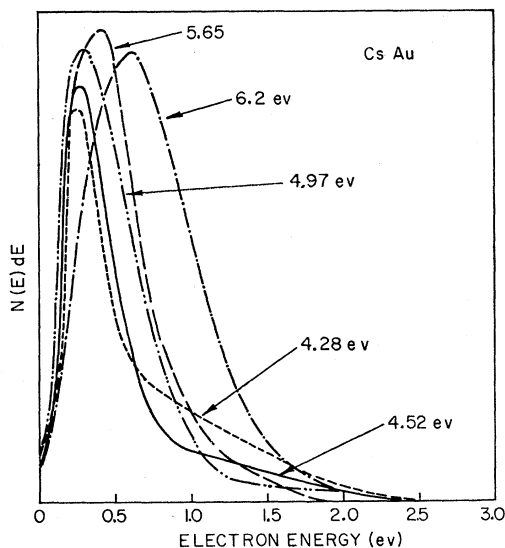
FIG. 4. The energy distribution of the photoelectrons for photon energies between 4.28 and 6.2 ev. The number of electrons in the slow group increases very rapidly with increasing $h\nu$. For $h\nu \geq 5.65$ ev, the slow group of electrons completely dominates the distribution.

valence band and the threshold for photoemission from the conduction band (about 2.4 ev) or from the maximum energy (2.6 ev) of the fast group of electrons at 4.0 ev (4.0 ev is the threshold energy for the slow group), a band gap of about 2.6 ev is found. Since this is within the range of the direct band-to-band transition determined from the optical absorption data (2.6–3.3 ev), it is clear that there are no indirect band-to-band transitions lying appreciably below the direct transition. The accuracy with which the bandgap is known is probably no better than $\pm 0.2$ ev.

It should be noted that the photoemission above 4.0 ev is greater for the sample which has less photo-emission below 4.0 ev. This suggests that the escape probability of the excited electrons is reduced by the high density of defects and conduction-band electrons present in these samples.

## IV. CONCLUSIONS

The photoemissive studies reported here indicate that the conduction and valence bands of CsAu are separated by a minimum energy of 2.6($\pm 0.2$) ev. Since this is within the range of the direct band-to-band transition determined previously from the optical absorption data,[1] it is clear that the 2.6-ev bandgap is associated with a direct transition and that there are no indirect transitions lying appreciably below the direct transition.

The value of 2.6($\pm 0.2$) ev lies at the lower limit of the bandgap values suggested previously (2.6–3.3 ev) and is close to the value of 2.3 ev obtained by Wood and Reitz[3] from their calculation. Wood and Reitz found the minimum band-to-band transition to be direct in agreement with the results reported here. It is interesting to note that the three exciton-like optical absorption peaks[1] occur at photon energies equal to or greater than the bandgap energy. By contrast, in the alkali halides the bandgap seems to lie between either the first and second or second and third exciton peaks.[14]

The data presented here also support the previous conclusion that the photoemission for $h\nu < 4.0$ ev is due to the excitation of electrons from states close to the bottom of the conduction band and confirm the value of 1.5($\pm 0.2$) ev for the electron affinity.

## ACKNOWLEDGMENT

It is a pleasure for the author to acknowledge his indebtedness to A. H. Sommer for both the synthesis of the samples studies and many useful discussions.

[14] E. A. Taft and H. P. Philipp, J. Phys. Chem. Solids 3, 1 (1957).