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Principal Investigator

W. E. Spicer
Stanford University
Stanford, California

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I. PHOTOEMISSION STUDIES OF ELECTRON STATES IN SILVER CHLORIDE

Robert S. Bauer

A. Introduction

A good knowledge of the energy bands of silver chloride would be most valuable in understanding the physics of the photographic process. Using photoemission techniques, we are experimentally determining such information as the position of the Ag (4d) band, regions of high densities of states in the valence band, and details of the photoexcitation process. Both the yield and energy distribution of photoemitted electrons have been measured in a range of photon energies extending through 11.8 eV on epitaxial thin films of AgCl prepared by evaporation in ultrahigh vacuum. Our current understanding of the photoemission results is summarized below.

B. Energy Distributions

The energy distribution curves (EDCs) normalized to absolute quantum yield are presented in Fig. 1. The EDCs are characterized by four pieces of structure whose dependences on photon energy are summarized in Fig. 2. The peak which emerges from below the threshold in the curves between

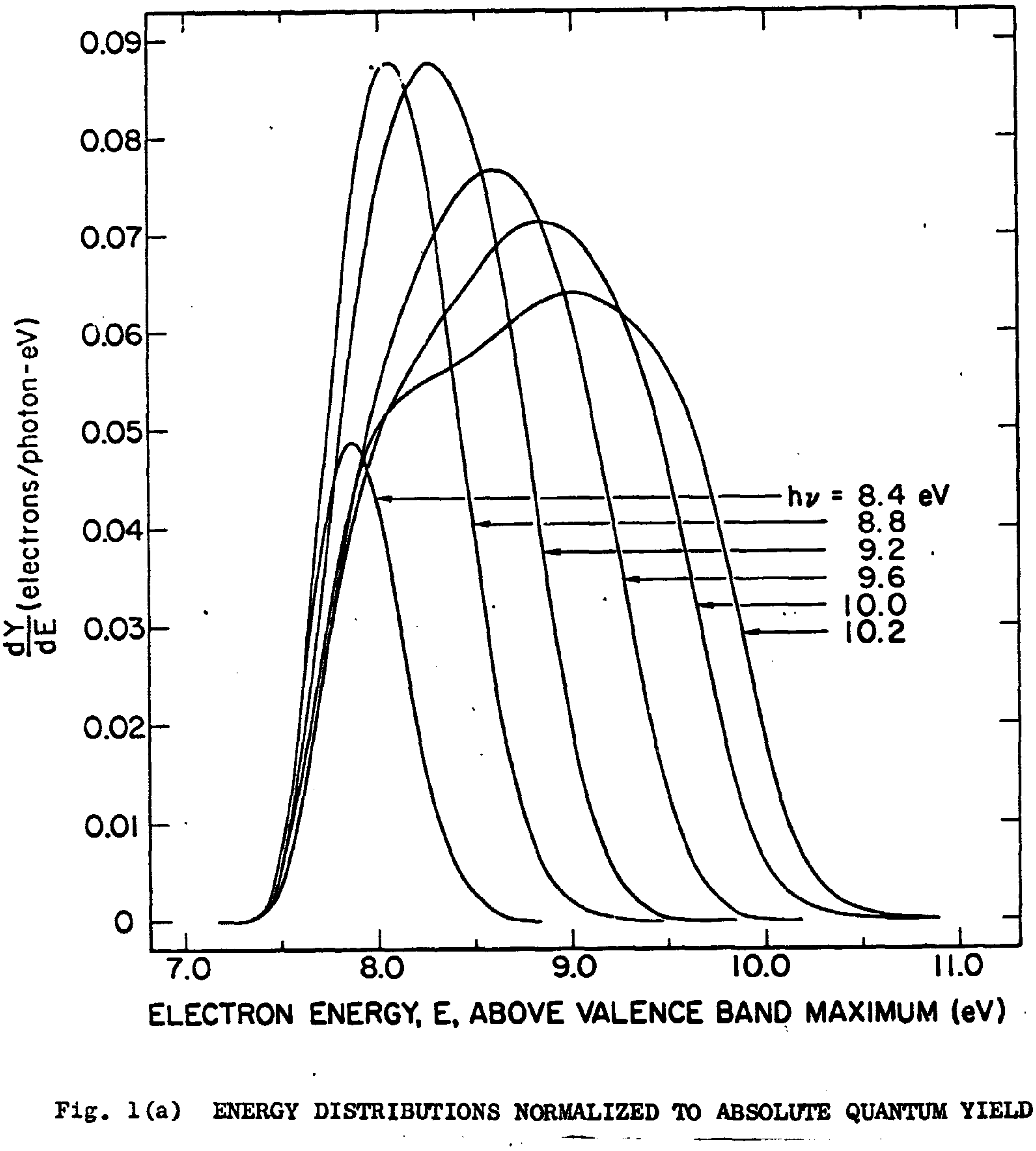

Fig. 1(a) ENERGY DISTRIBUTIONS NORMALIZED TO ABSOLUTE QUANTUM YIELD FOR ELECTRONS PHOTOEMITTED FROM AgCl FOR PHOTON ENERGIES BETWEEN 8.4 eV AND 10.2 eV.

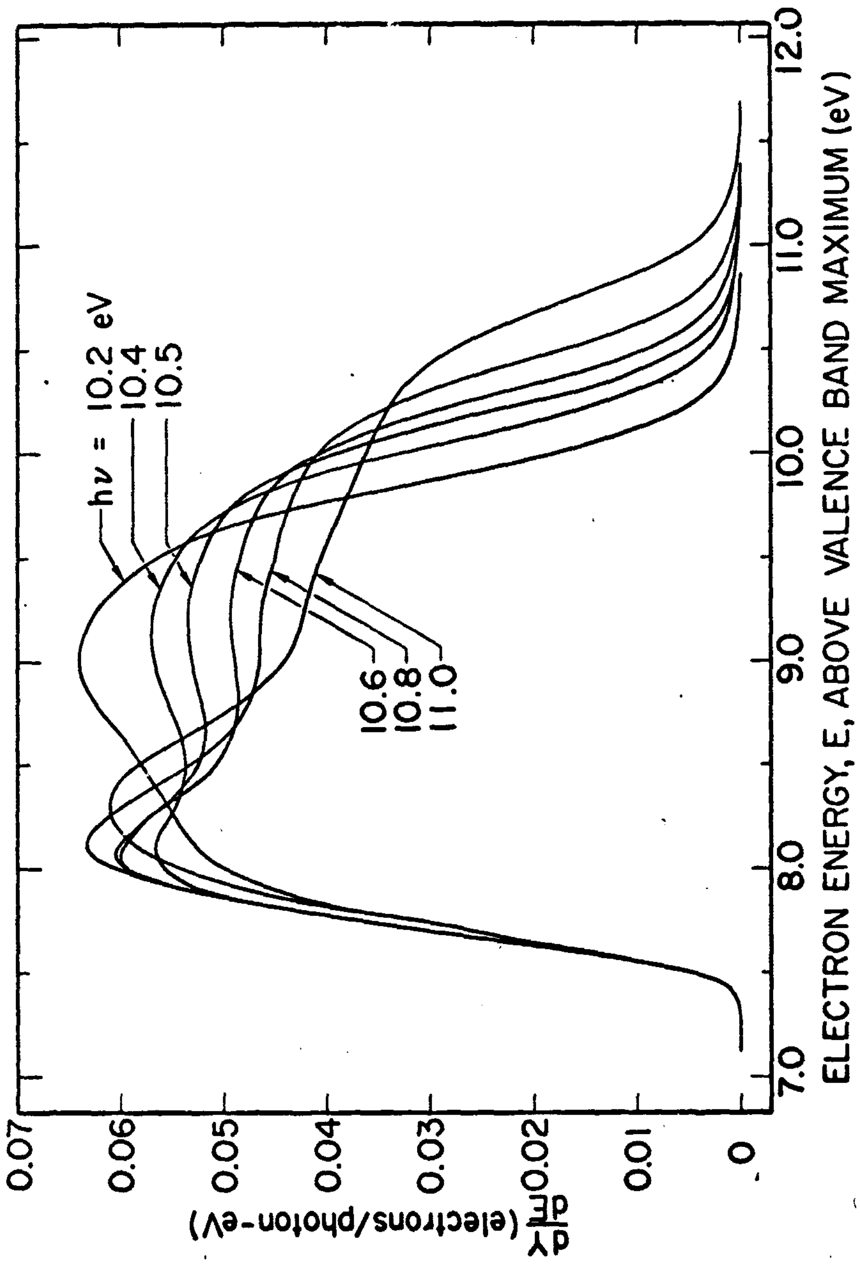

Fig. 1(b) ENERGY DISTRIBUTIONS NORMALIZED TO ABSOLUTE QUANTUM YIELD FOR ELECTRONS PHOTOEMITTED FROM AgCl FOR PHOTON ENERGIES BETWEEN 10.2 eV AND 11.0 eV.

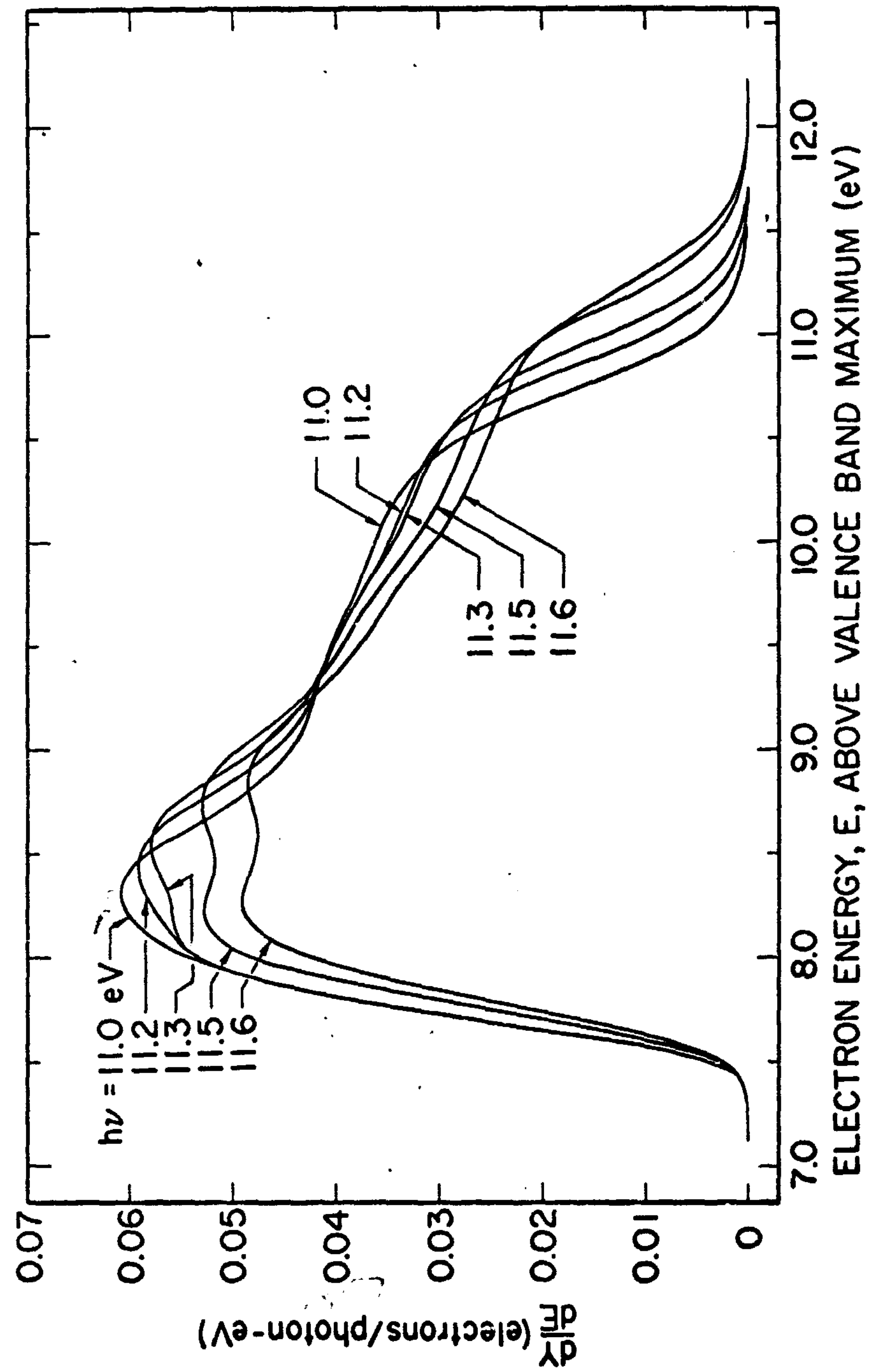

Fig. 1(c) ENERGY DISTRIBUTIONS NORMALIZED TO ABSOLUTE QUANTUM YIELD FOR ELECTRONS PHOTOEMITTED FROM AgCl FOR PHOTON ENERGIES BETWEEN 11.0 eV AND 11.6 eV.

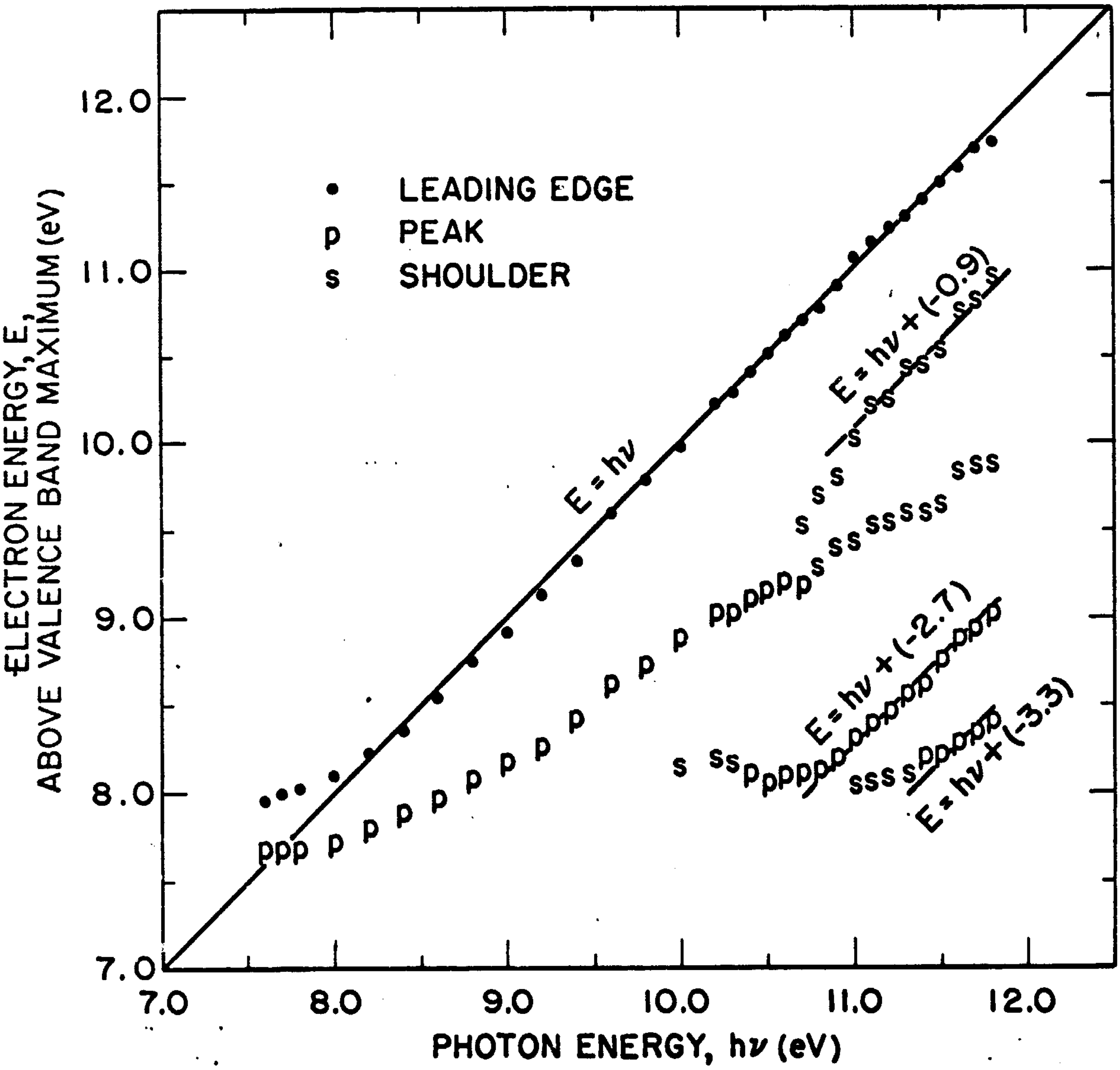

Fig. 2 STRUCTURE PLOT FOR THE AgCl ENERGY DISTRIBUTION CURVES OF FIG. 1

10.0 eV and 10.8 eV (Figs. 1(a) and (b)) has a behavior which can be described by the nondirect constant matrix element model for photoemission.[1] Beyond 10.8 eV, this peak changes position by the same amount as the change in photon energy ($\Delta E = \Delta h\nu$) as can be seen in the structure plot (Fig. 2). A straight line fit to these points intersects the E-axis at about -2.7 eV. Thus, this peak is due to a high density of states region 2.7 eV below the top of the valence band. High resolution measurements of the optical absorption edge of AgCl at low temperatures by F. C. Brown and his coworkers[2,3] agree quite well with the theory of phonon-assisted indirect transitions with excitonic effects.[2] It has been proposed for quite some time that this indirect behavior is due to the Cl (3p) band being the highest occupied band and having its maximum at a point other than the center of the Brillouin zone, Γ.[4] Published tight-binding[5] and APW[6] energy band calculations and recent piezo-optical measurements[7] have further supported this interpretation. If we assume that the halogen p band is the highest valence band and that the approximately 3 eV width calculated by Bassani, Knox, and Fowler[5] (BKF) for this band is a reasonable value, the density of states region 2.7 eV below the valence band maximum is associated with the Cl (3p) band. It should be noted that the location of the p band at the L point by BKF[5] agrees quite well with this energy.

The structure which emerges beyond 11.0 eV (see Fig. 1(c)) is unaffected by the threshold function in only the last few EDCs. From these few structure positions, a high valence band density of states would be predicted at -3.3 eV. Based on the assumptions enumerated above, this density of states is associated with the Ag(4d) electron states. The location of the d band in the BKF calculation[5] is in good agreement with this energy.

At low photon energies (see Fig. 1(a)) there is a single peak whose position does not change by amounts equal to the increment in photon energy ($\Delta E \neq \Delta h\nu$). Since part of the final state energy region over which this occurs is identical with the region over which the previously discussed Cl (3p) peak moves with $\Delta E = \Delta h\nu$, the behavior of the low-energy peak must be due to reasons other than structure in the final density of states or threshold function modulation. The behavior may be due to the importance of conservation of crystal momentum k as a selection rule for this transition. This peak is not prominent beyond 10.6 eV; however, two shoulders are present in the EDCs (Figs. 1 (b) and (c)). The higher energy shoulder moves as $\Delta E = \Delta h\nu$ while the lower energy one moves in the same manner as the peak seen for photon energies below 10 eV. As noted in Fig. 2, the higher energy shoulder electrons appear to originate at a region of high density of states about 0.9 eV below the valence band maximum. Work is continuing to understand the physical origin of these pieces of structure in the energy distributions.

C. Yield

A typical plot of the absolute yield of photoemitted electrons is presented in Fig. 3 for a film that was about 130 Å thick. The quantum yield is seen to rise sharply with $h\nu \lesssim 8.8$ eV from a threshold of approximately 7.4 eV. The yield at photon energies below this threshold is due to photons which are not absorbed by the AgCl film and excite electrons in the Ag substrate. The resulting electrons which escape through the AgCl thin film cause the observed low-energy structure seen in Fig. 3. This is similar to the subthreshold yield measured for thin alkali halide films on Cu substrates.[8]

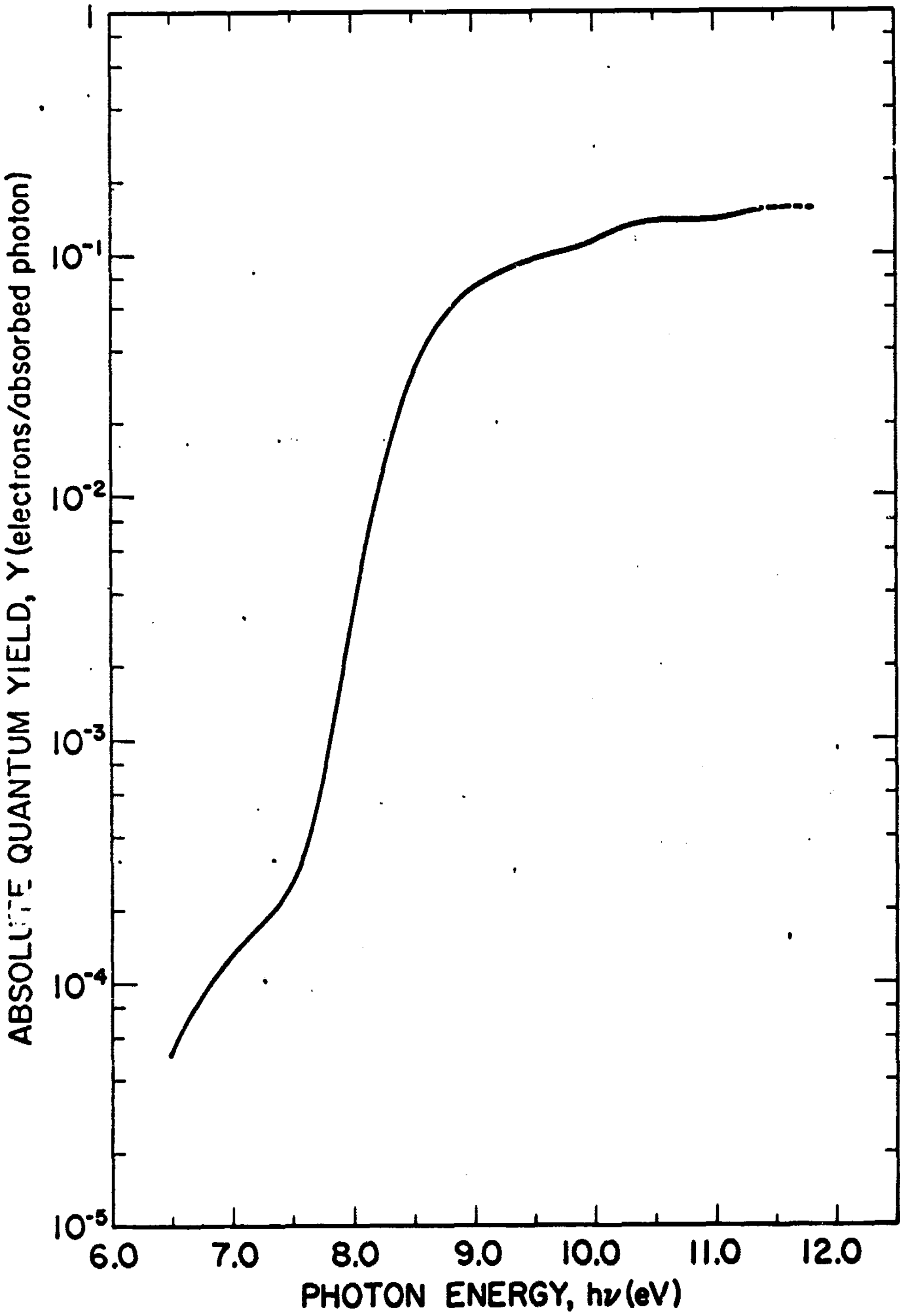

Fig. 3 SPECTRAL DISTRIBUTION OF ABSOLUTE YIELD OF ELECTRONS PHOTOEMITTED FROM AN EPITAXIAL FILM OF AgCl ON A Ag SUBSTRATE (FILM THICKNESS ≈ 130 Å). The yield for photon energies below about 7.5 eV is due to photoemission from the Ag substrate.

Beyond the threshold region, the yield rises slowly to about 10.0 eV where there is a change in slope. Since the energy distributions of electrons photoemitted at low photon energies (Fig. 1(a)) show that the low-energy electron peak has fully emerged from below the vacuum level by $h\nu$ = 9.0 eV, the quantum yield could be expected to have reached nearly a constant value at this photon energy as is the case for the yield for 10.4 eV $\lesssim h\nu \lesssim$ 11.0 eV and $h\nu \gtrsim$ 11.4 eV. The observed reduction in the yield from this constant level could be due to the reduced absorption in the region around the dip in α at 9.4 eV (see Fig. 4).* The relatively low absorption in this region means that on the average the electrons are excited deeper in the film thus increasing the probability for an electron to be scattered before reaching the surface and being unable to escape. As is observed in other solids,[11] this reduced electron transport probability could lead to the reduced yield. The increases in yield from 10.0 eV through 10.4 eV and 11.0 eV through 11.4 eV could be due to the "uncovering" of new regions of high densities of states in the valence band. As seen in the EDCs (Fig. 1) in these photon energy regions, the structure associated with the halogen p band begins to emerge at 10.0 eV; similarly, the structure associated with the Ag (4d) band emerges starting at 11.0 eV. This behavior could produce the changes in slopes of the yield curve at these photon energies.

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* The absorption coefficient presented in Fig. 4 is the result of a Kramers-Kronig analysis of the reflectivity of White and Straley[9] which was smoothed over a 1 eV range in accordance with earlier measurements. The reflectivity data values were generously supplied by J. J. White, III. Some details of the calculation were presented in an earlier report.[10]

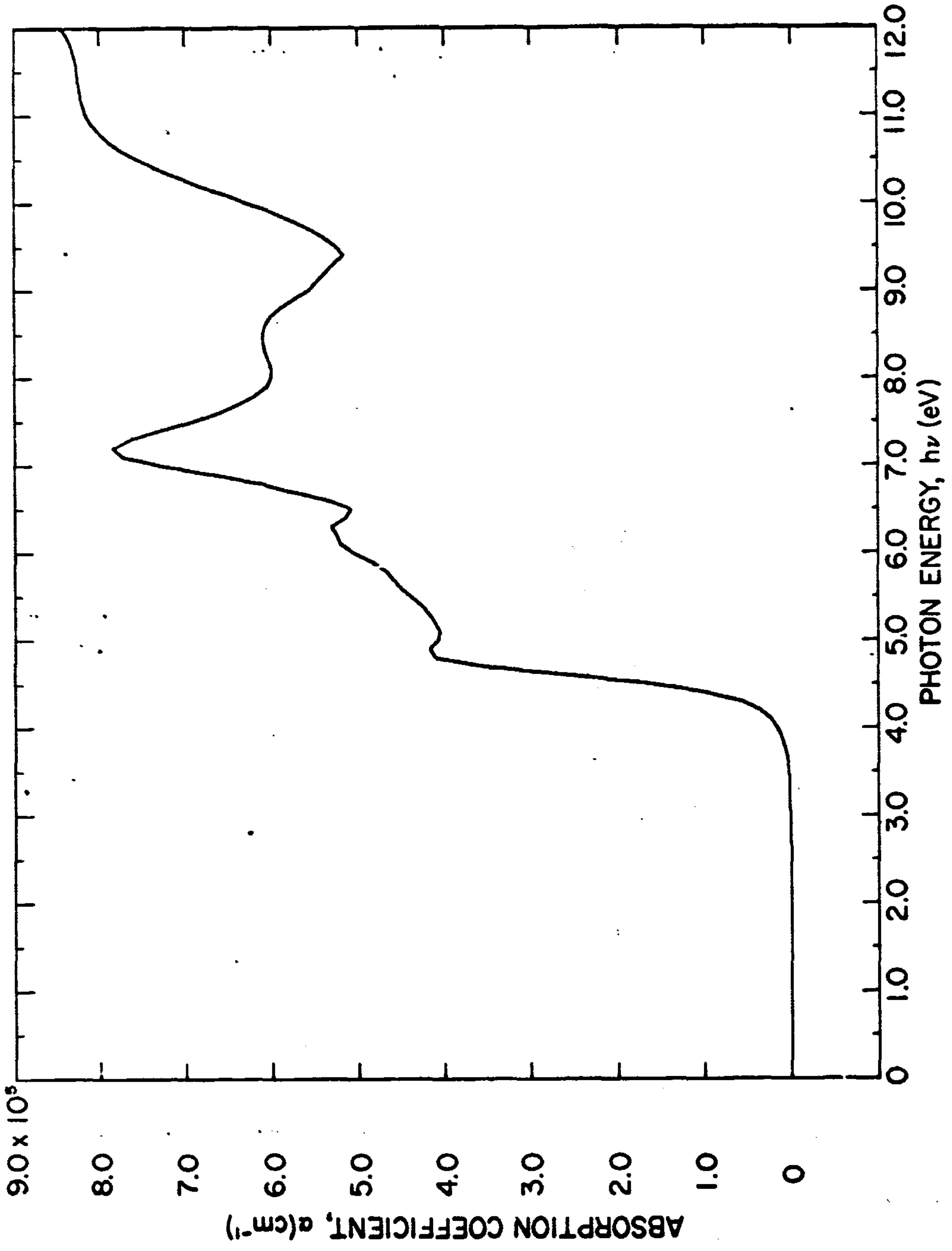

Fig. 4 ABSORPTION COEFFICIENT FOR AgCl (See footnote on p. 9).

D. Conclusion

Some of the significant differences between the results of this study and previously reported measurements have been discussed in an earlier report.[10] It should be added that the structure seen in the yield (Fig. 3) beyond the threshold was seen for the first time due to the higher resolution of the experiments and better sample surface conditions. It should be kept in mind that the association of regions in the density of states seen in the photoemission data with the electronic energy band structure are based on the widely accepted[2-7,12] view that the highest occupied band is the Cl (3p) band. The foundations of this assignment are being reviewed in light of the results of this photoemission investigation and new "first-principles" band calculations by Herman.[13] Future studies will be directed toward elucidating characteristics of electron states of the silver halides AgBr and AgI.

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II. ALKALI HALIDES

T. DiStefano and W. E. Spicer

Studies have been made of the alkali iodides (LiI, NaI, KI, RbI, and CsI). Energy distribution curves (EDCs) as well as quantum yield has been measured. Particular attention was paid to the doublet structure observed in the valence states of these materials. This structure has been associated with the halogen spin orbit splitting. A splitting of 1.1 eV is observed for CsI in good agreement with the atomic splitting. However, the splitting is found to increase as one goes to the lighter alkali compounds. It is approximately 1.6 eV for LiI. The data is now being analyzed and will be reported on more completely in the next quarterly report.

Apparatus has been built so that optical reflectivity measurements can be taken from the photoemissive surfaces without breaking vacuum. This has been successfully used for CsI. The results have strong similarity with the absorption spectrum of Eby and Teegarden,* except that a strong reflection peak was observed above 10 eV which would not have been anticipated from any of the earlier optical studies. A strong piece of structure also appears in the EDCs near the maximum energy in this photon energy range. These effects will be examined more closely.

Preliminary work has been done on the coevaporation of two alkali halides to form mixed crystallites. Experimental difficulties have been encountered in the coevaporation. However, it is felt that these are understood and that they will be eliminated shortly.

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* J. E. Eby and K. J. Teegarden, Phys. Rev. <u>116</u>, 1099 (1959).