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Photoemission from CsI: Experiment*

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Photoemission spectra for $\hbar\omega \leq 11.7$ eV were measured from thin CsI films at 77 °K. The distribution of emitted electrons is interpreted in terms of optical excitation from a valence band comprising three branches of Bloch bands derived from the I^- $5p^6$ levels. A triplet in the energy distribution cannot be interpreted in terms of excitation from simple ionic states localized on the iodine ions. Measurements indicate a valence-band width of 2.5 ± 0.3 eV, somewhat larger than the 1.7-eV width calculated by Onodera. Flat regions in the conduction bands, about 0.8 and 2.1 eV above the band edge, cause a small enhancement of photoelectrons excited to these regions. Additional evidence for the flat conduction bands is seen in the distribution of scattered electrons and in the strong scattering of hot electrons photoinjected through CsI. Band parameters obtained by photoemission aid in an interpretation of optical-density measurements.

I. INTRODUCTION

The optical properties of the alkali halides have been exhaustively studied since the pioneering contributions of Hilsch and Pohl.[1] Most of the experimental work on uncolored crystals has been concerned with optical absorption and reflectivity which are dominated by sharp exciton lines near the band edge. The rich optical structure at energies above the band-edge exciton region has been interpreted in terms of various, somewhat inequivalent, models. Techniques which were very successful in increasing the understanding of semiconductors[2] have been applied to the alkali halides.[3-7] Structure in the optical spectra has been identified[7-10] as van Hove singularities assigned to transitions at critical points and as plasma resonances. Phillips has proposed that some structure is due to an enhanced transition at points with hyperbolic interband character.[8,11] Another interpretation given the optical data is that the structure above the band gap is identifiable in terms of the excitation of ionic states.[12] It seems that because of the ambiguity in the initial-state energy, simple optical measurements cannot uniquely determine which of the various proposed models is most nearly applicable. Photoemission techniques, which have been very successful in identifying optical transitions in semiconductors,[13] can be used to advantage in resolving the ambiguities in the optical spectra of the alkali halides.

Photoemission measurements on thin films of CsI have been reported by Philipp *et al.*,[3] for a few selected wavelengths. From these measurements, Philipp and Ehrenreich[4] identify a CsI valence band of width 3–4 eV which lies 6.4 eV below the vacuum level. The photoelectron spectrum has been attributed to transitions from Bloch valence states to a nearly-free-electron (NFE) conduction band.[4] Measurements of photoemission from CsI have been extended to a wider range of photon energies by Krolikowski and Spicer[14]; a tentative explanation of the data was made in terms of an excitation from the simple ionic levels of iodine.[15] In both of these previous studies, the measured energy distributions were broadened by sample charging, by thermal broadening effects, and by the experimental limits of the photoemission energy analyzer. As a result, a definitive identification of the valence-band character has not been made on the basis of these previous photoemission studies.

We present here the results of new photoemission measurements on CsI which were obtained with considerable care given to maximizing resolution of details in the spectra. The measurements were made on very thin films, at both 300 and 77 °K, by an improved photoemission apparatus. After the photoemission measurements were completed, the thin-film sample was checked *in situ* by reflectivity to verify that the sample was crystalline in the simple cubic structure. The photoemission data, obtained for photon energy less than 11.7 eV, are explained in terms of transitions from Bloch valence states. For CsI, the valence band is derived from the iodine $5p$ shell which is spin-orbit split by 0.94 eV in the free ion. In the CsI crystal, the iodine valence levels broaden into bands of total width 2.5 ± 0.3 eV. Near the edge of the conduction band, some evidence is seen for two flat band regions. In keeping with the band calculations of Onodera, these flat conduction bands are identified as the unfilled $5d$ levels of Cs^+. Further evidence for flat conduction bands is seen in the scattering of electrons photoinjected through the film.

II. EXPERIMENTAL TECHNIQUES

A. Apparatus

The measurements were made at an ultrahigh vacuum of better than 2×10^{-11} Torr in a stainless-

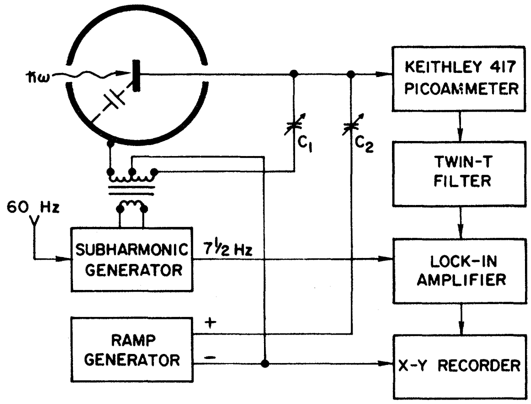

FIG. 1. Instrumentation for the photoemission measurements. The ramp generator determines the retarding potential on which is superposed an ac modulation at the eighth subharmonic of the 60-Hz power line. Capacitors C_1 and C_2 balance currents induced by the modulating potential and the retarding voltage, respectively.

steel vacuum chamber. Residual partial pressures of the deleterious gases H_2O and CO were less than 10^{-12} Torr. Light was admitted to the chamber through a LiF window which limited the measurements to $\hbar\omega \leq 11.7$ eV. Energy distributions of the photoelectrons were measured by a cylindrical retarding electrode which has a resolution limit[16] of about 0.3 eV at the highest kinetic energy measured. The ac technique was used to differentiate the *I-V* curves. An ac "tickling" voltage of 0.1 eV was found to introduce no significant experimental broadening onto peaks of more than 0.1-eV half-width. The spectral width of the light was negligible, less than 0.02 eV. In all, the experimental broadening is estimated to be 0.3 eV.

A few refinements shown in Fig. 1 were added to the ac differentiation circuitry in order to minimize effects of the considerable noise in the low-level signals being measured. The total photoemission currents had to be kept low, less than 10^{-10} A, in order to prevent sample charging. A technique was developed to reject the dominant noise caused by the pickup of power-line radiation. In essence, the tickler voltage was locked to an even subharmonic of the 60-Hz power-line frequency; at such frequencies, the phase-locked detector in the lock-in amplifier rejects the harmonic rich pickup at the 60-Hz repetition rate.

B. Samples

Past photoemission measurements on insulators have been hindered by sample charging, particularly in the case of large single crystals.[17] This charging of the sample surface affects the measured energy-distribution curves (EDC's) by broadening and lowering the significant structure. In the alkali halides, the sample is charged by immobile holes or V_k centers, which are left behind by the photoemitted electrons. For CsI, the surface of a 1000-Å sample film was typically found to charge to several volts during measurements at 77 °K. This charging problem was circumvented by the use of very thin samples so that prebreakdown currents limited the voltage buildup. With sample currents less than 10^{-10} A from a 110-Å sample, the surface charging was found to be less than 0.1 eV.

The CsI samples were evaporated onto a gold substrate in a 15-sec period at pressures below 10^{-8} Torr. Freshly evaporated gold was used as the substrate in order to minimize work-function variations which raise or lower the electronic bands of the insulating film.[3] Each thin-film sample was annealed for 15 min at 400 °K. The crystallinity of the samples was checked by reflectivity measurements performed *in situ* after the photoemission measurements were completed. Reflectivity of the alkali halides is somewhat sensitive to the crystalline structure of the sample. The sharp peaks due to band-edge excitons are severely broadened by any structural disorder of the films.[18] Further, the band-edge excitons of CsI are shifted in energy if a constraint forces the crystal from the usual simple cubic structure to the fcc structure.[19] Therefore, we have used reflectivity near the band edge as an indicator of film structure. Reflectivity of the photoemission samples was measured *in situ* with the apparatus shown in Fig. 2. The reflected light intensity was corrected for double transmission through the LiF window (3); the incident light intensity was obtained by rotating mirror (4) through 90°. The CsI reflectivity, measured at 300 °K from a 110-Å film, is shown in Fig. 3. Sharpness of the excitonic peaks near the band edge indicates that the film was nicely

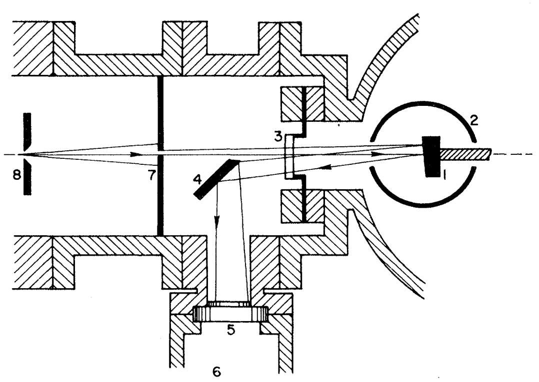

FIG. 2. Apparatus for the measurement of reflectivity *in situ*. Components include: (1) sample with surface 3° off axis, (2) photoelectron retarding electrode, (3) LiF window, (4) rotatable mirror, (5) sodium salicylate coated filter window, (6) electron multiplier, (7) diaphragm, and (8) monochromator exit slit.

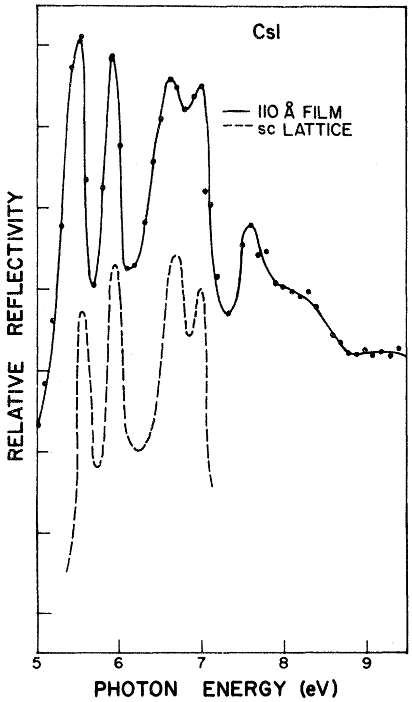

FIG. 3. Relative reflectivity of a 110-Å film of CsI (solid line) and the relative reflectivity of simple cubic CsI measured by Gavini and Cardona (dashed line).

crystalline. For comparison, the dashed curve in Fig. 3 shows the reflectivity measured from cubic CsI by Gavini and Cardona.[20] Films of CsI which contained an fcc phase were found[20] to have additional peaks in the reflectivity spectrum at 5.28 and 5.67 eV. Also, the excitonic peak found at 5.9 eV in the simple cubic lattice is absent in spectra from CsI films constrained to the fcc lattice.[18] From the reflectivity measurements, it is concluded that the 110-Å sample film was completely crystalline in the simple cubic structure.

III. PHOTOEMISSION DATA

A. Photoelectric Yield

The photoelectric yield[21] for films of CsI was found to vary with sample thickness and temperature, as is shown for the typical films represented in Fig. 4. For very thin films, about 100 Å thick, the yield saturates at 20–40%, which is consistent with the measurements of Philipp.[3] The yield for the thicker films increases slowly with photon energy to a value near unity as seen in Fig. 4. The enhanced yield in the thicker films is thought to be due to phonon scattering. In essence, an electron excited outside the escape cone may be scattered into the cone by subsequent phonon collisions. Duckett and Metzger[22] have used the random-walk model to show that quantum yield may exceed 50%, and even approach unity, if the electron suffers many phonon scattering events before recombination.

Since the yield curve does not terminate abruptly at low photon energies, it is difficult to obtain an exact value for the photoelectric threshold. Empirically, it was found that a half-power plot of the photoelectric yield in CsI is a straight line near threshold. As determined by the intercept on this half-power plot, the photoelectric threshold of CsI at 300 °K was 6.5 eV. However, it is recognized that there is no established theoretical justification for such a plot. The band gap of CsI at 10 °K has been placed[23] at 6.37 eV, which is the hydrogenic limit of the exciton lines at the step[3,24] in the optical data; after correction for temperature dependence, the band gap at 300 °K is 6.2 eV. Based on the threshold obtained by the half-power plot, the electron affinity is 0.3 ± 0.1 eV, which is somewhat larger than a previous estimate[3] of 0.1 eV.

B. Photoinjection

There is some interest in the scattering of hot electrons at energies near the band edge of a polar insulator. An electron of low group velocity may be captured by lattice polarization to produce a quasiparticle or polaron[25,26] of low mobility and high mass. Also, the flat *d* bands near the conduction-band edge of CsI should produce some enhanced scattering.[27] The question of hot-electron scattering was investigated in this work by photoinjection[28] of electrons from a metal substrate through a thin film of CsI. Those injected electrons which

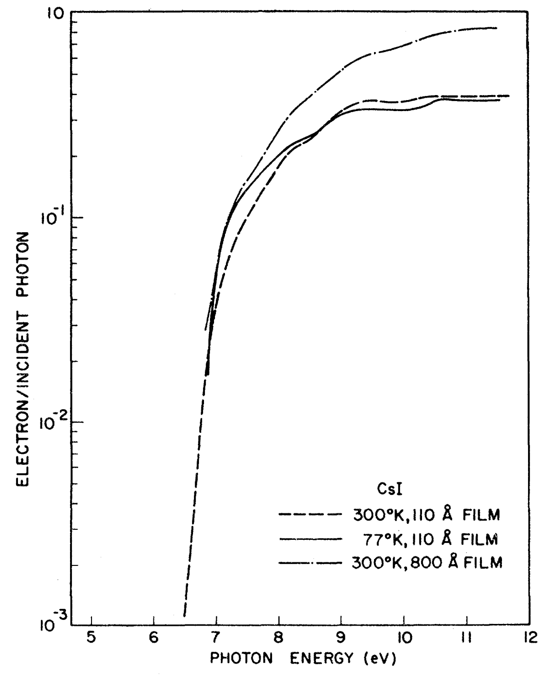

FIG. 4. Photoelectric yield from typical CsI thin films.

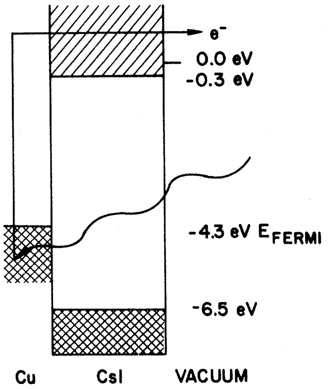

FIG. 5. A schematic representation of the photoinjection process. Light incident on substrate excites electrons which are injected through an insulating film and into vacuum.

are strongly scattered or trapped by the CsI may be recaptured by the substrate. Thus, we expect a paucity of electrons in the emitted distribution at energies where there is appreciable scattering.

We have measured the energy spectra of currents photoinjected through an 80-Å film of CsI at 300 °K. A schematic representation of the process is shown in Fig. 5. Monochromatic light, with energy less than the band gap of the CsI, passes through the film to excite photoelectrons from a copper substrate. The electrons escaping through the CsI and into vacuum were analyzed by standard photoemission techniques. The quantum yield for photoinjection is shown in Fig. 6 along with dashed curves representing typical yields from pure Cu and CsI. Below the 6.5-eV threshold of CsI, the yield is dominated by electrons which have been photoinjected through the CsI film and into vacuum. The photoinjection yield is higher than the yield for bulk copper, apparently because the CsI film has lowered the threshold for photoemission from the copper by 0.5 eV.

The EDC's of the injected electrons, shown in Fig. 7, display some depletion of electrons at about 1.8 eV and at the vacuum level. An arrow in Fig. 7 marks the energy at which we find strong electron scattering (at 1.8 or 2.1 eV above the band edge). This strong scattering region corresponds to a flat conduction band, derived from the 5*d* levels of the cesium ion, which calculations[29] place at about 2.2 eV above the band edge. Further evidence for a flat conduction band is presented in Sec. III C on the photoemission of electrons directly from CsI. At electron energies just above the vacuum level, there is an enhanced electron scattering which is manifested in the broad trailing edge of the EDC's in Fig. 7. The 0.65-eV width of the trailing edge is larger than the 0.3-eV resolution limit of the analyzer.[16] For comparison, an EDC of electrons excited by 6.6-eV light from the valence bands of CsI is also shown in Fig. 7; these electrons, which have not been greatly scattered, have a trailing edge that is sharp compared to that of the photoinjected electrons. Apparently, hot electrons in the first eV of the conduction band are strongly

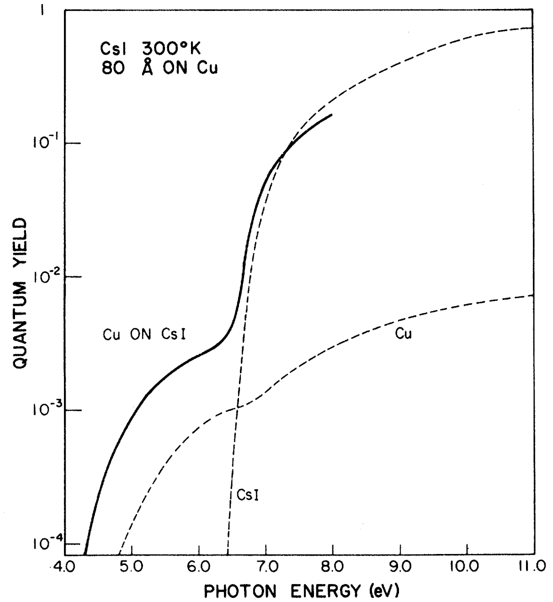

FIG. 6. Quantum yield for the photoinjection of electrons through a thin film of CsI. For comparison, the photoelectric yield for pure copper and for CsI are shown by the dashed lines.

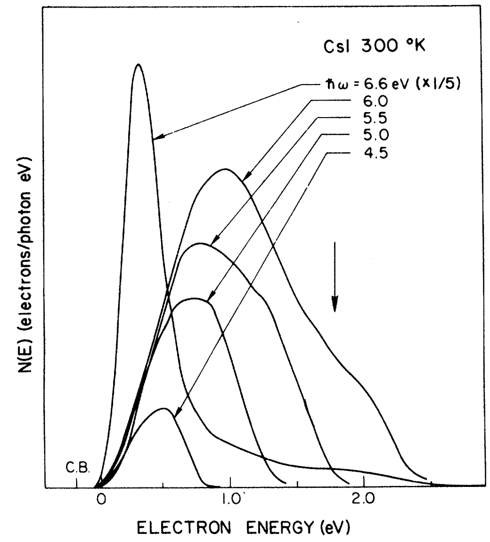

FIG. 7. Energy distributions of electrons photoinjected through CsI by photons of various energies. The arrow marks an energy at which electrons are strongly scattered. Photoemission from the valence band of CsI is apparent in the distribution measured at $\hbar\omega = 6.6$ eV.

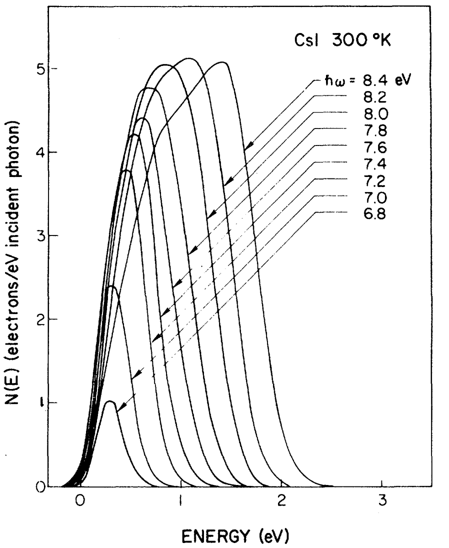

FIG. 8. Photoelectron distributions measured from CsI at 300 °K at low photon energies.

scattered as they traverse the film. However, there is no direct evidence for self-trapping of electrons with energy greater than 0.3 above the band minimum.

C. Energy-Distribution Curves

A series of EDC's for photon energies extending from 6.5 to 11.7 eV was measured from CsI at 77 °K. Structure in the EDC's measured at 77 °K is considerably sharpened in comparison to that measured at 300 °K. Total broadening of the EDC's measured at 77 °K, as judged by the width of the leading edge, is less than 0.5 eV. Of this broadening, 0.3 eV or less is due to experimental resolution of the photoemission analyzer.[16] Although thermal broadening is large in data taken at room temperature, the general characteristics of the EDC's remain unchanged. The EDC's measured at photon energies below 8.6 eV are roughly Gaussian in shape, with no sharp structure that can be correlated with the excitonic peaks found in the reflectivity over this range. However, at energies above 8.6 eV the EDC's exhibit very distinct structures which are correlated with theoretical predictions for band-to-band transitions. This division of the data into a band-to-band regime above 8.6 eV and an exciton-dominated regime below 8.6-eV is similar to the findings of Haensel *et al.*[30] in x-ray photoemission from NaCl.

Energy distributions of electrons photoemitted by light of energy 8.4 eV and below are shown in Fig. 8. The distributions are not greatly affected by sample temperature, so that the curves measured at 300 °K differ only slightly from those at 77 °K. All of the EDC's are structureless, except for the beginnings of a peak at high energy in the 8.4-eV curve. Although the curves are roughly Gaussian in shape, the leading edge increases approximately linearly with photon energy. Significantly, there is no sharp structure in the curves which can be related to excitonic transitions although excitons dominate the oscillator strength in this range. Any excitons which autoionize before interacting with the lattice should contribute a narrow peak to the photoelectron EDC; the width of the narrow peak is a measure of the extent of the Wannier exciton in the Brillouin zone (BZ). The absence of any such narrow peak in the EDC's might indicate that there is considerable lattice relaxation before an autoionization takes place.

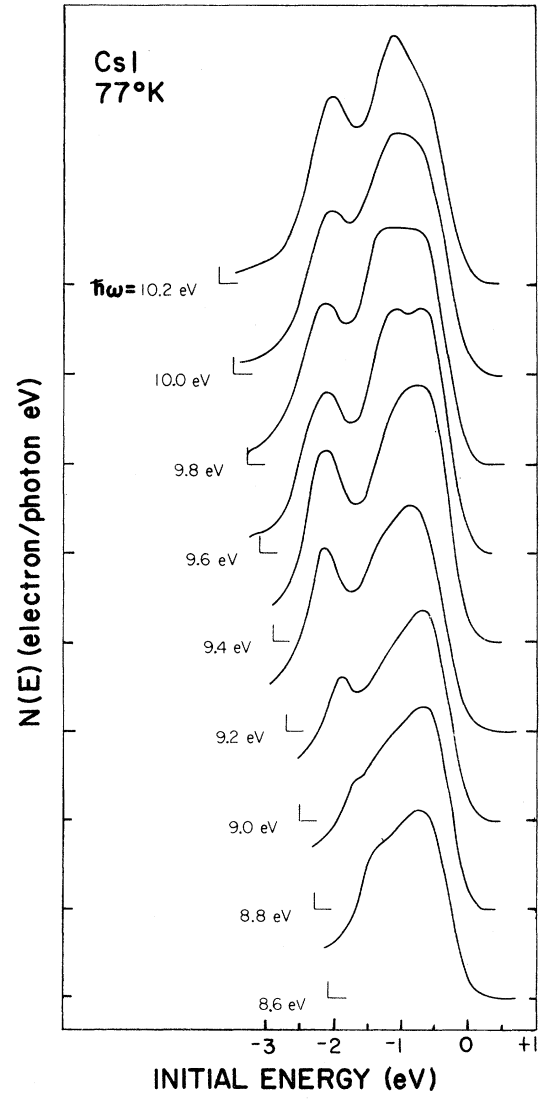

FIG. 9. Photoelectron distributions measured from CsI at 77 °K. The vacuum level of each curve is marked by an angle.

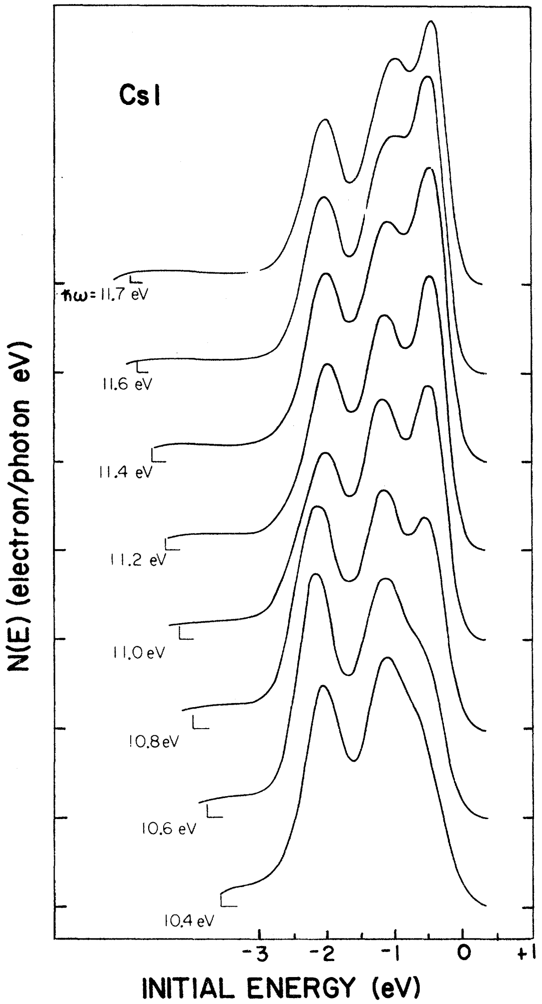

FIG. 10. Photoelectron distributions measured from CsI at 77 °K. The vacuum level of each curve is marked by an angle. The small number of slow electrons indicates that scattering is not an important factor.

Band-to-band transitions do occur at photon energies below 8.6 eV, but the oscillator strength is dominated by excitonic transitions.

At photon energies above 8.6 eV, band-to-band transitions dominate the photoemission spectra. The EDC's in Figs. 9 and 10 were measured at 77 °K from CsI samples which were 110 Å thick. A particularly striking feature of these electron distributions is the paucity of low-energy electrons. Apparently, an excited electron loses little energy by inelastic scattering before being emitted from such thin samples. The total width of the valence bands, which stands out clearly in the EDC's, is seen to be less than 2.8 eV. After correction for experimental broadening, the estimated valence-band width is 2.5 ± 0.3 eV.

The general nature of the photoelectron distributions is similar in each curve measured at photon energies of 9.6 eV and above. There is a broad, high-energy peak and a smaller, low-energy peak. The two peaks correspond to excitation out of states derived from the iodine ${}^2P_{3/2}$ and ${}^2P_{1/2}$ levels, respectively. Splitting between the centroids of the two peaks is about 1.2 eV, which compares with the 0.94-eV spin-oribt splitting of the valence levels in free iodine. The position and width of peaks measured from CsI are displayed in the structure plot of Fig. 11. The peak positions in the low-temperature data are similar to those measured at room temperature as well as to those measured from thick films. The sharp and structureless low-energy peak in the EDC's results from excitation from the ${}^2P_{1/2}$ derived branch of the iodine valence band. On the other hand, the high-energy peak is broad and split, at some photon energies, into two sharp subpeaks. This broad leading peak, which is due to excitation from the two branches of the valence band derived from the iodine ${}^2P_{3/2}$ level, has a total width of about 1.2 eV after corrections for experimental broadening.

Quite significantly, the splitting of the broad leading peak into two subpeaks suggests that the electrons were excited from valence states which comprise Bloch states.[31] A comparison of predictions based on Bloch valence states and simple ionic valence states is given in Sec. IV, and a detailed calculation for CsI based on transitions between

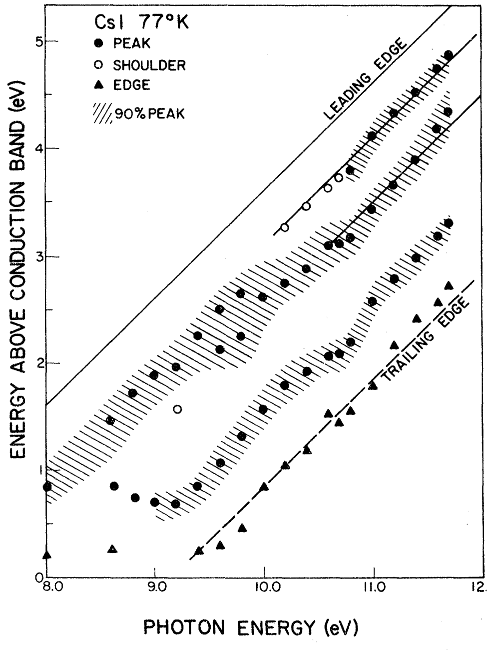

FIG. 11. Structure plot for CsI at 77 °K. The energy of each peak, shoulder, and edge is displayed for distributions measured at photon energies between 8 and 11.8 eV. The valence-band width, uncorrected for broadening, is seen to be 2.7 eV.

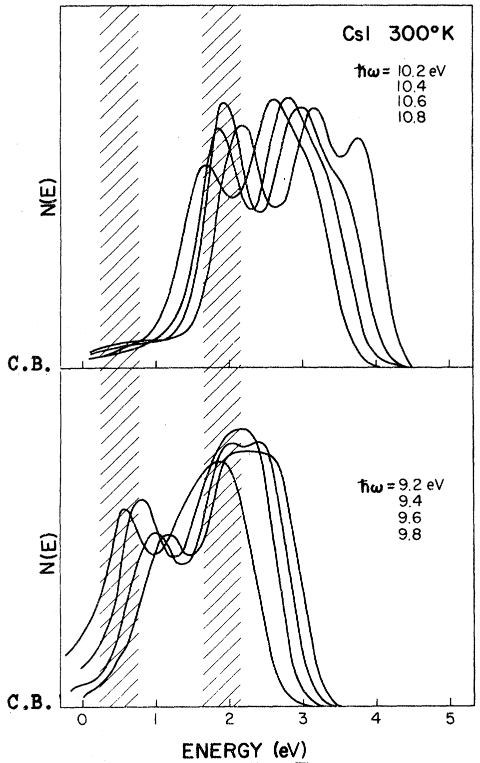

FIG. 12. Photoelectron distributions from CsI showing enhancement of optical transitions to two regions of energy in the conduction bands. These two regions, centered around 0.8 and 2.1 eV above the conduction-band bottom, are shaded in the figure.

Bloch states is given in the following paper. The change in shape of the broad leading peak with increasing photon energy is ascribed to optical transitions from different parts of the BZ. In particular, the abrupt rise of a high-energy portion of the leading peak beginning at a photon energy of 10.6 eV results from an onset of transitions to a higher conduction band near X in the BZ. Such abrupt changes in shape of the EDC with photon energy are characteristic of k-conserving transitions between Bloch bands.[32]

We have observed several indications of flat conduction bands which lie close to the conduction-band bottom. Previously, low-lying conduction bands derived from Cs^+ $5d$ states were suggested[28] in order to explain a portion of the optical spectra of CsI. In the photoemission data, transitions to these flat bands are seen as an enhancement of transition strength to a particular final-state energy. Peaks in the EDC's shown in Fig. 12 are increased in amplitude and distorted as they move through the energy of the flat conduction bands. The estimated positions of the flat bands lie in the shaded regions of Fig. 12, where the position of the conduction-band bottom is labeled C.B. Along with the change in peak shape, there is a modulation of the peak energy which is best shown in the structure plot of Fig. 11. The energies of peaks in the EDC's do not increase linearly with photon energy as they move through conduction band 2.0–2.2 eV above the band bottom. Instead, peaks from this region of the conduction band fall at an energy somewhat lower than would be expected. This modulation of peak energies may be explained, in part, by a mechanism which involves scattering of electrons by a flat conduction band. Electrons excited to such a flat band will lose energy in a short distance and emerge near the bottom of the flat band. The short scattering length in the flat band region is produced by the low group velocity and high density of final scattering states for such electrons.[27] On the basis of peak enhancement and of peak energy modulation, we find a flat conduction band centered at about 2.1 eV above the conduction-band bottom.

Further evidence of flat conduction bands is found in the distribution of scattered electrons photoemitted from thick films of CsI. Scattering in these films is much more pronounced than it is in thin films where excited electrons have little chance to scatter before emission. Because electrons tend to be scattered to energies at which there is a high density of available states, the distribution of scattered electrons reflects, to some degree, the density of states in the conduction band. Typical peaks of scattered electrons are evident in the dashed EDC shown in Fig. 13. Electrons photoemitted without appreciable energy loss lie well above the two scattering peaks labeled 1 and 2. For comparison, Fig. 13 also displays

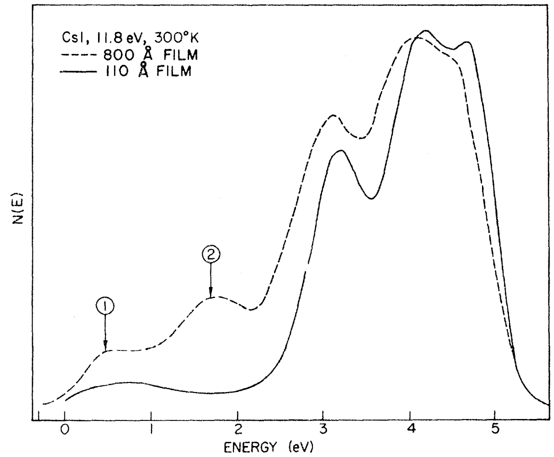

FIG. 13. Comparison of electron distributions from CsI films of two different thicknesses. The distribution from the 800-Å film displays two pronounced scattering peaks, labeled 1 and 2, while that from the 110-Å films shows few scattered electrons.

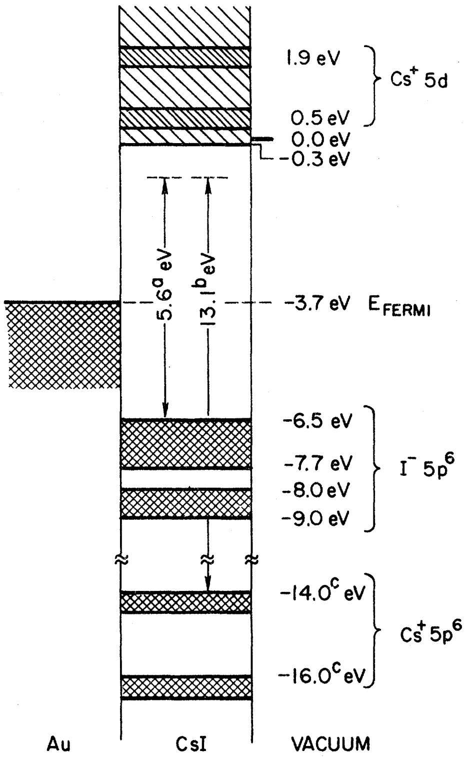

FIG. 14. Energy levels of CsI at 300 °K. Two flat band regions of the conduction bands are marked by double hatching. Information is included from (a) Knox and Teegarden (Ref. 41), (b) Roessler (Ref. 35), and (c) Helmer (Ref. 34).

photoemission from a very thin film in which electron scattering is not appreciable. Notice that structure and the leading edge are much sharper for the thin film because of the smaller scattering effects. The peaks of scattered electrons indicate two flat conduction bands at about 0.8 and 2.0 eV above the band edge. Peak 2 corresponds quite well with the flat band which was identified on the basis of peak enhancement and on the basis of the scattering of photoinjected electrons.

IV. DISCUSSION

As a point of convenience we have summarized the experimentally determined energy levels for CsI in Fig. 14. The relevant energies are given with respect to the Fermi level for thin films at 300 °K. Uncertainty in the energy levels is ± 0.1 eV. The bands are flat throughout the sample. As is typical of the ionic insulators,[33] CsI shows no evidence of surface states or the resulting band bending near the surface. The photoemission measured from uncolored CsI at $\hbar\omega \leq 11.8$ eV originates entirely from the band derived from I^- $5p^6$ states. No photoemission was observed from the Cs^+ $5p^6$ levels, which are placed at 14 and 16 eV below the conduction band by the x-ray photoemission measurements of Helmer[34] and by the reflectivity measurements of Roessler.[35] Interpretation of the photoelectric spectra is facilitated by the absence of other electronic energy levels near the iodine valence bands. As is discussed below, the width of the valence band is somewhat larger than expectations based on previous calculations.[29,36] The conduction bands contain two regions of high state density marked by the double hatching of Fig. 14. Evidence for these flat bands includes the distribution of scattered electrons, an enhancement in measured EDC's at the corresponding energies, a modulation of peak energy in the EDC's, and the scattering of photoinjected electrons. These regions are identified as the flat *d*-symmetry bands proposed by Knox and Inchauspe[37] and by Phillips.[5]

An important aspect of the findings presented here concerns the triplet of peaks found in the photoemission spectrum from CsI. The three well-resolved peaks in the EDC's at photon energies above 10.6 eV can be interpreted in terms of optical excitation from the three branches of the valence-band dispersion curve. In the double group notation of Elliott,[38] Table I displays the degeneracies of the valence band at various symmetry points of the zone. The doublet of energy levels associated with simple, localized ionic states of I^- are shown as Γ_6- and Γ_8- in the table. Photoemission from CsI cannot be explained in terms optical excitation from simple localized valence states because the photoemission spectra from such ionic states could yield only a doublet of peaks. On the other hand, the triplet of observed peaks in the EDC's can be explained as an excitation from the three separate branches of the valence-band dispersion curves away from Γ and R in the zone. A comparison is made in a following article between EDC's calculated from transitions between Bloch states and those found experimentally; it is concluded that the Bloch-wave basis is the most appropriate for describing optical excitation from the narrow valence bands of CsI.

Historically, there has been some question as to the applicability of Bloch states to the narrow

TABLE I. Energy levels of the iodine ion. Group theoretically allowed levels are given for the ion in free space, in the crystal field of CsI, and for Bloch states in the CsI lattice.

I^- $5p^6$ Free space	I^- $5p^6$ O_h^1 Crystal field	Bloch levels in CsI lattice
$^2P_{3/2}$	Γ_8^-	Γ_8^- X_7^- M_6^- R_8^- X_6^- M_7^-
$^2P_{1/2}$	Γ_6^-	Γ_6^- X_6^- M_6^- R_6^-

valence levels of the alkali halides.[39–42] Within the Hartree–Fock scheme, the Wannier basis and the Bloch basis are equivalent representations for the closed-shell valence levels of ionic insulators. When correlation energy is included in the problem, the two bases are no longer equivalent, but rather one of the two becomes a more appropriate description of the many-body state. Correlation energy, which is large compared to the bandwidth in the alkali halides,[43] can break the periodicity of the total Hamiltonian; the corresponding eigenfunction then need not be of the periodic Bloch form. For a sufficiently narrow closed-shell valence band, Wannier states may be more appropriate as a basis than Bloch states. For the case of CsI, in which the largest width of any single valence band is about 1.2 eV, we have found evidence that Bloch-wave states are the most appropriate basis for describing optical excitations. Such evidence for Bloch states has not been observed to date in the other alkali iodides, in which the iodine valence levels are so narrow that it is difficult to resolve differences in the predictions of the two bases. Of course, in any of the alkali halides, a hole created by an optical process is subsequently localized by a Jahn–Teller lattice relaxation[42] to produce a localized, lattice-trapped V_k center. Because all free holes are eventually trapped by the lattice, they have not been seen to participate in the conduction process.

Some points of comparison can be made between the photoemission results and band calculations for CsI.[29,36,44] The Wigner–Seitz type of calculation by Flower and March[44] is of a preliminary nature and does not include relativistic corrections; the resulting valence band is 4.35 eV wide, which is clearly too large. More refined calculations were made by Onodera, and later Rössler, with the method of a fully relativistic Green's-function technique described by Onodera and Okazaka.[45] In both cases, the intermuffin potential was adjusted so that the direct band gap agreed with experiment. The total widths of the top two valence bands found by Onodera and by Rössler were 0.77 and 0.8 eV, respectively. The photoemission data we have presented indicate that the total width of these bands is about 1.2 eV, or $\frac{3}{2}$ of the calculated width. The small calculated bandwidths may be too small due to the large intermuffin potentials which were used to adjust the band gap to observed values. The structure that we have observed in the conduction band of CsI, at about 0.8 and 2.1 eV above the band bottom, can be related to two regions of energy at which flat bands occur. The higher of these two bands corresponds to the d bands of the type $\Gamma_{25'}$ which Onodera's calculations place in a narrow energy range around 2.2 eV, in excellent agreement with experiment. The enhanced transitions we find near 0.8 eV are identified as d bands of the type Γ_{12} which are pulled down and broadened by the CsCl crystal structure.[36,46] The center of the experimentally determined band (about 0.8 eV) is somewhat approximate because of the large width of the band.

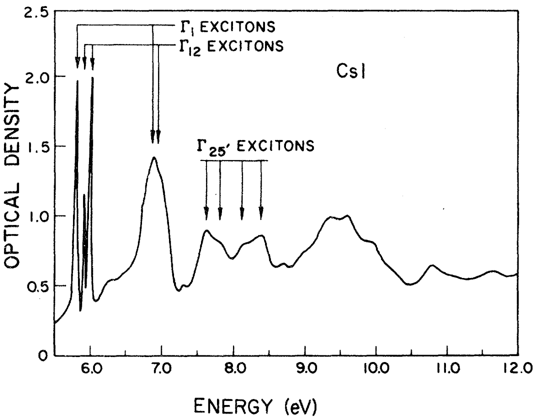

FIG. 15. Optical density of CsI at 10 °K by Teegarden and Baldini (Ref. 12).

Although the calculated conduction bands are quite complex, we shall consider the NFE bands which are strongly coupled to the valence band. These are the only states in the first 5 eV of the conduction band that have a strong band-to-band matrix element coupling to the p-like valence band. The other bands in this energy range are weakly coupled to the valence band either because they do not have s or d symmetry at Γ or because they are strongly localized on the Cs^+-ion sphere. With increasing photon energy, transitions from the valence band occur on a surface in the zone which moves away from Γ. In the photoemission spectra, we associate the sharp rise of the leading peak, which begins at a photon energy of about 10.6 eV, with the onset of transitions to the second NFE band. From Onodera's calculations the direct gap to the second NFE band occurs at 10.8 eV, near X in the zone, in agreement with experiment.

A few connections are made between our photoemission results and the optical properties of CsI. The optical density of CsI, measured at 10 °K by Teegarden and Baldini,[12] is displayed in Fig. 15. The "halogen doublet" which is labeled "Γ_1 excitons" has been identified as an excitonic transition to the s-like conduction-band bottom. The spin-orbit splitting of the halogen doublet is somewhat less than the valence-band splitting at Γ because of a strong exchange interaction between the electron and hole.[37,47] The next set of peaks, labeled Γ_{12} excitons, has been identified by large pressure[23] and temperature[48] dependences as being excitonic transitions to Γ_{12} derived bands largely concentrated near the Cs^+ ions. Another group of excitonic lines found at higher energy can be identified as being due to excitonic transitions to the very flat Cs^+ $5d$ bands of the type associated with $\Gamma_{25'}$. The four excitonic peaks which we have labeled are consistent with the fourfold theoretical multiplicity of excitonic lines due to transitions to the $\Gamma_{25'}$ derived bands.[37] For this identification of excitonic structure, the quite large binding energy for the d exciton is due to the large number of electronic states in the flat conduction bands which are available for the binding of an excitonic wave function. We discern no definite excitonic structure in the optical density above 8.6 eV.

V. CONCLUSIONS

The principal features of the photoemission spectra from CsI cannot be explained on the basis of simple transitions from localized ionic states because such a model would predict a doublet instead of the triplet observed in the photoemission data. A better explanation of the data can be given by optical transitions between Bloch states, for photon energies greater than 8.6 eV.

Band parameters deduced from experiment are in fair agreement with the calculations of Onodera and Rössler. The total width of the valence band was found to be 2.5 ± 0.3 eV. The width of each valence band is about $\frac{3}{2}$ of the calculated value. The onset of transitions to the second NFE band occurs at 10.6 eV, in good agreement with the calculated value of 10.8 eV. Some enhancement of photoemission occurs for transitions to flat bands at 0.8 and 2.1 eV above the conduction-band bottom; these bands are identified as the d states concentrated near the cesium ions, as predicted by Knox and Inchauspe and by Phillips. Further evidence for such flat conduction bands occurs in the photoinjection data in the distribution of scattered electrons.

An enhanced scattering of low-energy electrons was found by the technique of photoinjection. However, there was no conclusive evidence for the self-trapping of electrons of energy above the electron affinity of 0.3 eV.

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Photoemission from CsI: Calculation*

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Photoemission spectra were calculated for CsI based on crystal-momentum-conserving transitions between Bloch electron states. The energy bands of CsI were interpolated between levels at Γ and *X* obtained from calculations by Onodera. A fully relativistic tight-binding approximation and a pseudopotential fit were used for the valence and conduction bands, respectively. Weakly coupled Cs^+ 5*d* conduction bands were not included in the calculation. Photoelectron distributions, generated by a computer sampling of the bands at 2600 points in the zone, agree reasonably well with experiment. The agreement confirms the interpretation of photoemission from CsI in terms of optical excitation between Bloch-wave states.

I. INTRODUCTION

Recent experimental evidence from photoemission[1] and from two-photon spectroscopy[2] indicates that transitions between Bloch states are of some importance in describing the optical properties of the alkali halides, particularly those which are less ionic. We report calculations of optical and photoemission spectra for CsI based on first-order allowed transitions between Bloch-wave states. The calculations, utilizing published energy bands[3] for CsI, were performed by computer sampling of regions in the Brillouin zone (BZ). A constant dipole matrix element was assumed to connect the valence bands to the nearly-free-electron (NFE) conduction bands. Those conduction bands derived from states of *f* symmetry or from wave functions concentrated near the Cs^+ ion were not included in this calculation because they are only weakly coupled to the valence bands. In this way, the calculation of transitions to the conduction band is considerably simplified.

Calculation of photoelectric energy distribution curves (EDC's) and of the optical constant ϵ_2 was carried out with the aid of convenient interpolation schemes for regions of the BZ between the symmetry points. Energies at Γ and *X* were set to the eigenvalues determined by Onodera.[3] The valence bands were interpolated by a relativistic tight-binding approximation while an empirical pseudopotential model was used for the first two zones of the NFE conduction band. Photoelectric and optical spectra were calculated by summing all possible transitions occurring at approximately 2600 points throughout the primitive $\frac{1}{48}$th of the BZ. The computational techniques used were similar to those described by Smith.[4] Because of their value in determining the initial band states of the photoelectron current, the *k*-space surfaces on which transitions occur were determined and plotted for several photon energies. A comparison is made between the photoemission data measured from CsI and the EDC's calculated here. We find that a better fit to the experimental data may be obtained by using a valence-band width and a spin-orbit splitting which are somewhat larger than those found by Onodera.

II. BAND STRUCTURE OF CsI

A. Existing Theoretical Calculations

The interpolated bands were fixed to symmetry-point energies found from calculations[3] utilizing a Green's-function technique.[5,6] Onodera's bands, which are shown in Fig. 1, were chosen as the basis for the interpolation. There is reasonably good agreement between valence bands calculated by Onodera and those found by Rössler, although Rössler finds a slightly larger spin-orbit splitting at Γ. As a crystal potential, Onodera used Madelung-shifted ionic potentials,[7] with full Slater exchange, in the spherical muffin region around each ion. The constant potential of the intermuffin region was adjusted to produce a band gap to match the experimental value of 6.37 eV. In order to obtain the correct band gap, it was found necessary to use the quite large intermuffin potential of 6.94 eV.[3] This results in a calculated conduction-band edge of the type Γ_{12} instead of the type Γ_1, which is thought to be the case. As is reviewed in Sec. III, such a large intermuffin potential leads to valence bands which are somewhat narrower than those observed experimentally.

In our calculations, it was necessary to make some arrangement for the various matrix-element strengths coupling the valence and conduction bands.