

Ultraviolet photoelectron spectra of cesium halides*

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Energy distributions of photoelectrons from evaporated films of cesium halides were measured at photon energies of 11–23 eV. The photoelectron spectra show structures that can be identified as relatively high densities of states in the Cs^+ 5*p* core as well as in the valence and conduction bands. Doublet core states due to spin-orbit splitting are observed for all the cesium halides. The bandwidths of these states are 3.1 ± 0.3 eV for CsCl, CsBr, CsI, and 4.0 ± 0.3 eV for CsF. The valence-band widths for CsCl, CsBr, CsI, and CsF are found to be 1.8 ± 0.3 , 2.1 ± 0.3 , 2.4 ± 0.3 , and 1.7 ± 0.3 eV, respectively. The energy distribution curves of CsBr indicate a valence-band splitting of 0.5 ± 0.2 eV, which is consistent with the spin-orbit splitting of the Br (4*p*) atomic state. The photoelectron spectra also show the triplet structure associated with the excitation from the I^- 5*p* band of CsI as reported recently by DiStefano and Spicer. Some evidence of core-exciton decay can be seen in the spectra of CsCl. The photoemission results are used to estimate the binding energies of the Γ core excitons of cesium halides.

I. INTRODUCTION

The ultraviolet absorption spectra of cesium halides have been studied extensively in recent years.^{1–10} The multiplet structure observed at the fundamental absorption edge is attributed to exciton transitions from the valence band which is formed by the outermost electrons of the halogen ions.⁶ Structure at higher energies is associated with interband transitions and core excitons. Excitation of the Cs^+ 5*p* core level in cesium halides starts at about 13 eV. As shown in recent measurements using synchrotron radiation, the absorption spectra above 13 eV are complex.⁸ At certain energies, it is difficult to determine whether the absorption is due to interband transitions or core-exciton formation. Consequently, the interpretation of the high-energy spectra is not completely unambiguous.

In order to provide a more reliable interpretation of the spectra, it is necessary to locate the density-of-states structures of the energy bands and determine the band thresholds. Such information would be of considerable value in identifying the transitions from the core levels and in finding the binding energies of the core excitons.^{11–13} The results would also be useful in checking the various band calculations.

In this paper we report some new photoelectron spectra of cesium halides in the photon energy region 11–23 eV. The energy distribution curves show features that can be associated with the Cs^+ 5*p* core as well as valence and conduction bands.

II. EXPERIMENTAL METHOD

The photoemission measurements at 300 °K were made with the equipment described in our earlier work.¹⁴ Radiation of photon energies in the range

12–23 eV was produced by a helium continuum source. For experiments involving photon energies less than 12 eV, a hydrogen discharge source was used. The radiation was dispersed with a windowless 1-m normal incidence monochromator of approximately 8-Å bandwidth.

In order to resolve the density-of-states structure of the valence bands, some measurements were made on thin-film samples at 195 °K. The sample was evaporated on a conductive substrate that was electrically insulated from the cold substrate holder by a thin sheet of mica. The substrate and cylindrical baffle were kept at 195 °K with dry ice in a methanol solution. The photoelectron energy distributions were measured by the ac method using a cylindrical collector.¹⁵ The total instrumental broadening was estimated to be 0.3 eV. All measurements were made *in situ* immediately after evaporation at base pressures 10^{-7} – 10^{-8} Torr. Measurements were also performed on samples annealed at 400 °K. No significant differences were observed in the results.

III. RESULTS AND INTERPRETATION

A. Valence-band and core-states structures

The energy-distribution curves indicating the density-of-states structure of the valence band and the Cs^+ 5*p* core states of CsCl are shown in Fig. 1. The curves are plotted with respect to initial-state energies relative to the vacuum level (zero energy). These curves represent energy distributions in which the peaks associated with the photoelectrons from the filled band states move in energy by an amount equal to the increase in photon energy. The spectra appear to be consistent with the model of nondirect transitions¹⁶ between the bands. The

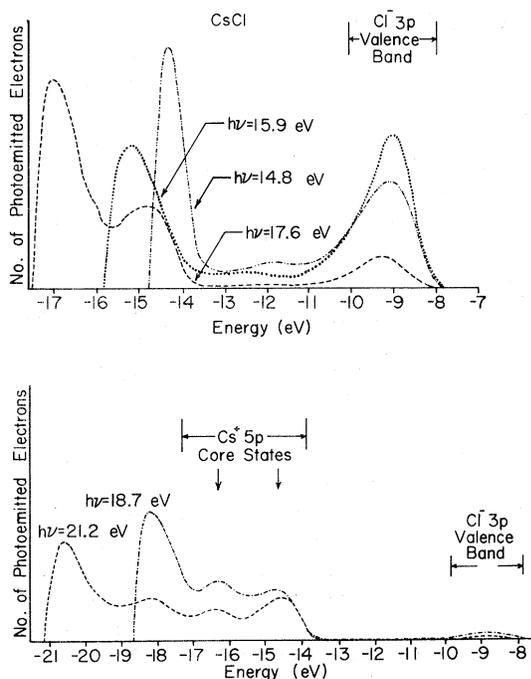


FIG. 1. Normalized energy distributions of photoemitted electrons from CsCl at 300°K. The spectra show the width of the valence band and the splitting of the Cs^+ 5*p* core states.

slight shift in the valence-band peak to lower energy for photon energies above 15.9 eV can be attributed to the onset of electron-electron scattering across the band gap. The effect of this type of inelastic scattering can be seen for photon energies exceeding approximately twice the band-gap energy.¹⁷ The spectra show no splitting of the valence band. The spin-orbit splitting of the valence band of CsCl is probably too small for our measurements to resolve. On the other hand, the

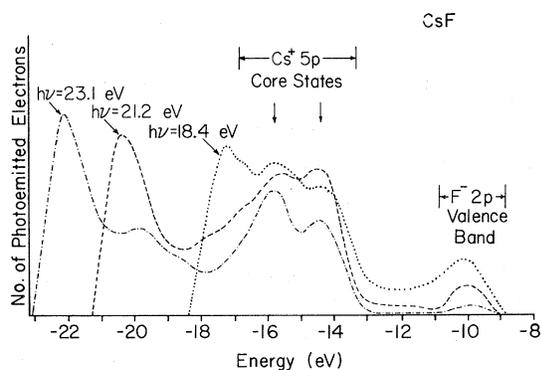


FIG. 2. Normalized energy distributions of photoemitted electrons from CsF at 300°K. The spectra show the width of the valence band and the splitting of the Cs^+ 5*p* core states.

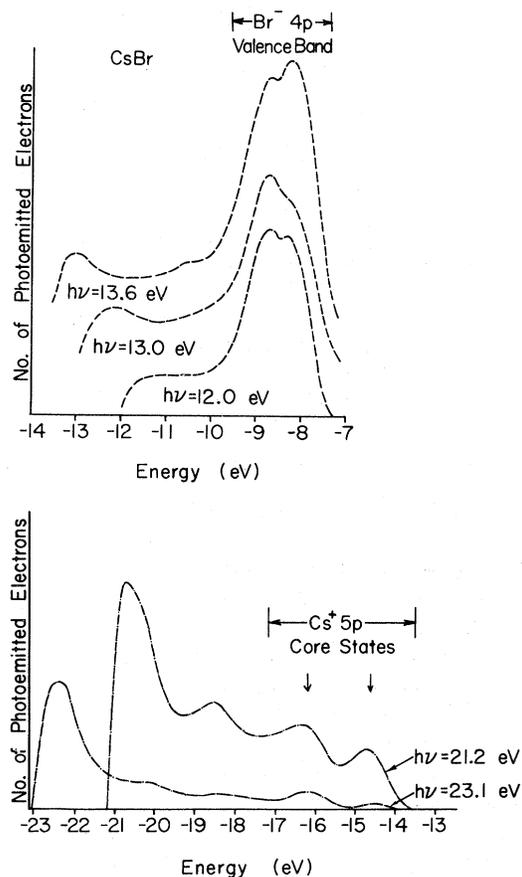


FIG. 3. Normalized energy distributions of photoemitted electrons from CsBr. The valence-band spectra were obtained at 195°K; Cs^+ 5*p* core spectra, at 300°K.

spectra show splitting of the Cs^+ 5*p* core states. The separation of the doublet core structure is about the same as the spin-orbit splitting of the Cs (5*p*) atomic state, which is approximately 1.7 eV.¹⁸ Similar structures in the Cs^+ 5*p* core states of other cesium halides can be seen in Figs. 2, 3, and 4. The splitting is dominated by the spin-orbit interaction. This is in agreement with the interpretation of the optical data on Cs^+ 5*p* core level in cesium halides.⁷

The widths of the valence band and core states of CsCl are found to be 1.8 ± 0.3 and 3.1 ± 0.3 eV, respectively. A correction of 0.3 eV for the estimated instrumental broadening was applied in finding the bandwidths. It should be noted that the 3.1-eV width of the core states includes the splittings due to the spin-orbit interaction and the crystal potential. It may be useful to describe the Cs^+ 5*p* core as two bands with corresponding widths to indicate the crystal-field effects. However, there is another factor that we must consider. The lattice-relaxation effects in a highly ionic insulator such

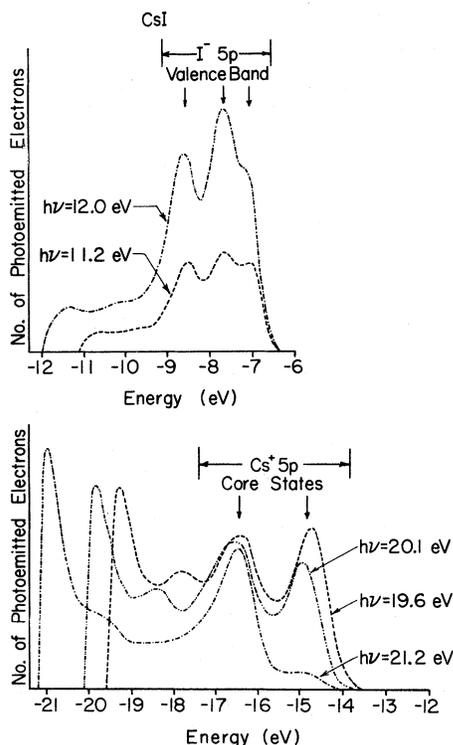


FIG. 4. Normalized energy distributions of photoemitted electrons from CsI. The valence-band spectra were obtained at 195 °K; Cs^+ 5p core spectra, at 300 °K.

as CsCl could introduce appreciable widths into the photoemission energy distribution. This problem has been discussed by Spicer.¹⁹ The relaxation after optical excitation which involves a core hole with a large local distortion of the lattice may cause broadening to be as large as 1 eV. More recently, the lattice effect on photoemission linewidths in polar materials was investigated by Citrin *et al.*²⁰ They used a simple theoretical expression to account for the phonon broadening to the K (2p) linewidths in potassium halides. Apply-

ing their model of phonon broadening to CsCl at 300 °K, we estimate a linewidth (full width at half-maximum) of 0.5 eV. Since the lattice effect appears to be significant, the bandwidth of the core states as seen in our photoemission spectra should be regarded as an upper limit on the actual bandwidth.

In Fig. 2 the spectra of CsF exhibit a width of about 4 eV for the core states, which is somewhat wider than those of other cesium halides. One may expect a greater width for CsF because the interionic distance is smaller, which means that greater phonon broadening and crystal-field splitting may arise.

The structure associated with the excitation from the valence band of CsBr is shown in Fig. 3. The spectra were obtained at 195 °K on thin films of estimated thickness 100–200 Å. The separation of the peaks of the doublet structure is 0.5 ± 0.2 eV, which is about the same as the spin-orbit splitting of the Br (4p) atomic state. The variation in relative heights of the peaks for different photon energies suggests that k -conserving transitions between the bands may be present.²¹

In the low-temperature measurements on thin films of CsI, we were able to obtain photoemission spectra showing the triplet structure due to the excitation from the I^- 5p valence band. These curves are shown in Fig. 4. The doublet structure near the leading edge of the curve is attributed to the excitation from two relatively flat branches of the iodine $^2P_{3/2}$ level near the boundaries of the Brillouin zone.²² The separation of the iodine $^2P_{3/2}$ and $^2P_{1/2}$ levels is about 1.2 eV. Our photoemission spectra of CsI are in good agreement with those reported by DiStefano and Spicer.²¹

The bandwidths, band thresholds, and splittings of the valence and Cs^+ 5p core bands of cesium halides are summarized in Table I. It is interesting to note that the valence-band threshold increases in going from CsI to CsF, whereas the Cs^+ 5p core threshold shows a decreasing trend.

TABLE I. Band thresholds, splittings, and bandwidths of the valence and Cs^+ 5p core bands of cesium halides. The energy values are in eV.

| Cesium halide | CsF | CsCl | CsBr | CsI |
|---|----------------|----------------|----------------|----------------|
| Valence-band threshold ^a | 9.0 ± 0.2 | 7.9 ± 0.2 | 7.3 ± 0.2 | 6.5 ± 0.2 |
| Valence-band width | 1.7 ± 0.3 | 1.8 ± 0.3 | 2.1 ± 0.3 | 2.4 ± 0.3 |
| Splitting of valence band | | | 0.5 ± 0.2 | $\sim 1.2^b$ |
| Cs^+ 5p core-states threshold ^a | 13.3 ± 0.2 | 13.7 ± 0.2 | 13.9 ± 0.2 | 14.1 ± 0.2 |
| Total width of Cs^+ 5p core | 4.0 ± 0.3 | 3.1 ± 0.3 | 3.1 ± 0.2 | 3.1 ± 0.3 |
| Splitting of Cs^+ 5p core | 1.5 ± 0.2 | 1.7 ± 0.2 | 1.6 ± 0.2 | 1.5 ± 0.2 |

^a Relative to the vacuum level.

^b Splitting between the low-energy structure and the centroid of the doublet near the upper band edge.

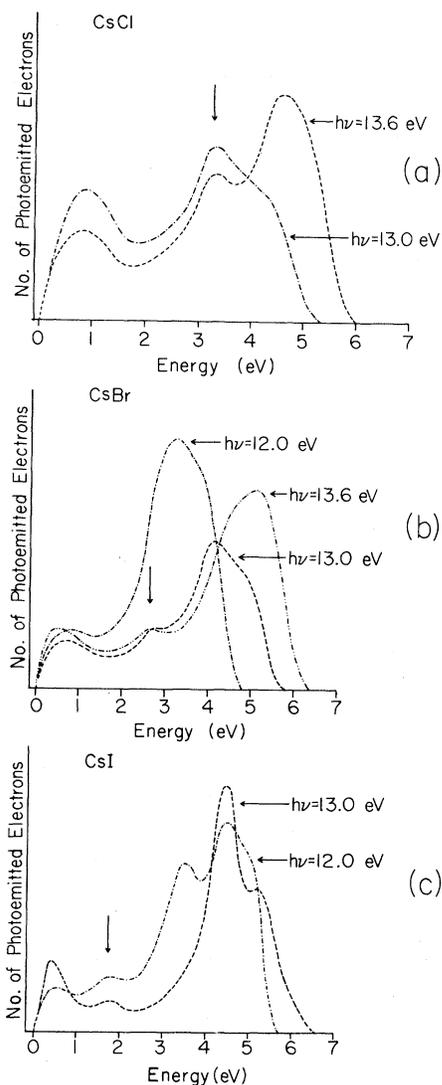


FIG. 5. Normalized energy distributions of photoemitted electrons from cesium halides at 300°K. Vertical arrows indicate positions of conduction-band structures above the vacuum level (zero energy). In (a) the structure is found at 3.1 eV; in (b), at 2.6 eV; in (c), at 1.7 eV.

B. Conduction-band structures

The photoelectron energy distribution curves in Figs. 5 and 6 reveal the conduction-band structures of cesium halides. Structures which occur at given final-state energies remain stationary with respect to the vacuum level for all photon energies. We assume that the high-energy photoexcited electrons would more likely be scattered into conduction-band regions having high densities of states.²³ Accordingly, a stationary structure in the spectra corresponds to a relatively high density of states above the vacuum level.

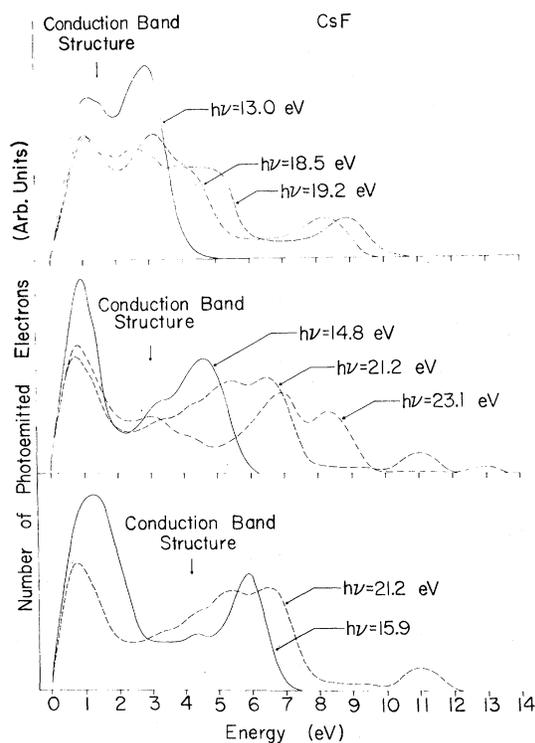


FIG. 6. Normalized energy distributions of photoemitted electrons from CsF at 300°K. Conduction-band structures are found at 1.5, 2.9, and 4.2 eV above the vacuum level.

The structures that we have attributed to the conduction band could not be due to Auger processes²⁴ which refill the Cs^+ 5*p* core levels. In Fig. 5 the threshold for transitions from the core levels has not been reached. In Fig. 6 we note that the photon energies are sufficiently high, but the difference between the top of the valence band and the lowest Cs^+ 5*p* core states is less than the threshold for emission from CsF. Hence Auger emission should not occur in either case.

Caution should be exercised in identifying the peak near the vacuum level as shown in Fig. 5. This peak could be an artifact caused by the emission cutoff and the large secondary background. Any attempt to associate the peak near the vacuum level with a maximum in the density of states must be made with careful consideration. Referring to the low-energy peaks in Fig. 5, we should note that the spectra were obtained at photon energies for which electron-electron scattering across the band gap is negligible. These peaks appear as a result of inelastic scattering by defects and phonons. This explanation is compatible with the observation that the structures are more noticeable for thicker films. A small scattering peak appear-

ing in this manner near the vacuum level may be attributed to a conduction-band structure.²¹ Nevertheless, the actual position of the structure is difficult to determine because it is obscured by the escape function.

C. Core-exciton decay

In the recent optical studies of cesium halides,^{8,10,25} the multiplet bands at photon energies of 13–16 eV were explained in terms of core-exciton formation. For example, a strong peak in the absorption spectrum of CsCl at 14.7 eV is interpreted as an exciton transition from a Cs^+ 5*p* core level to states above the conduction-band bottom.²⁵ In this case, the exciton can dissociate into continuum states which are at the same energy.²⁶ If the exciton states are above the vacuum level, the excitons can be autoionized and produce a narrow low-energy peak in the photoelectron energy distribution. We have found evidence of this exciton effect in the photoemission spectra of CsCl. As shown in Fig. 7, the peak of the energy distribution near the vacuum level, corresponding to initial-state energies at the top of the core, passes through a strong maximum as the photon energy passes through 14.7 eV. It should be noted that the photon energy 14.7 eV is not sufficiently high to cause electron-exciton scattering or pair production. Exciton transitions from the valence band of CsCl start at approximately 7.8 eV.² To have inelastic scattering across the band gap would require photon energies greater than 16 eV. Thus the appearance of the narrow low-energy peak is not caused by inelastic scattering.

Core-exciton effects in photoemission from KI have been reported recently by Lapeyre *et al.*²⁷ and Blechschmidt *et al.*²⁸ They explained their spectra in terms of the Auger and nonradiative direct-recombination decay processes. In CsCl, however, these processes are either negligible or absent in the core-exciton decay at 14.7 eV. The Auger process cannot occur because the difference in energy between the Cl^- 3*p* band and Cs^+ 5*p* core states is less than the threshold for emission from the valence band. If the direct-recombination process is dominant, the valence-band peak should show an increase in height at 14.7 eV. We see no evidence of this enhancement. The spectra show that it is slightly reduced at this photon energy.

IV. DISCUSSION

The observed bandwidths, band thresholds, and structures of the Cs^+ 5*p* core states and valence bands should be useful in the evaluation of the various computational methods which have been applied to cesium halides.^{6,29,30} The valence-band

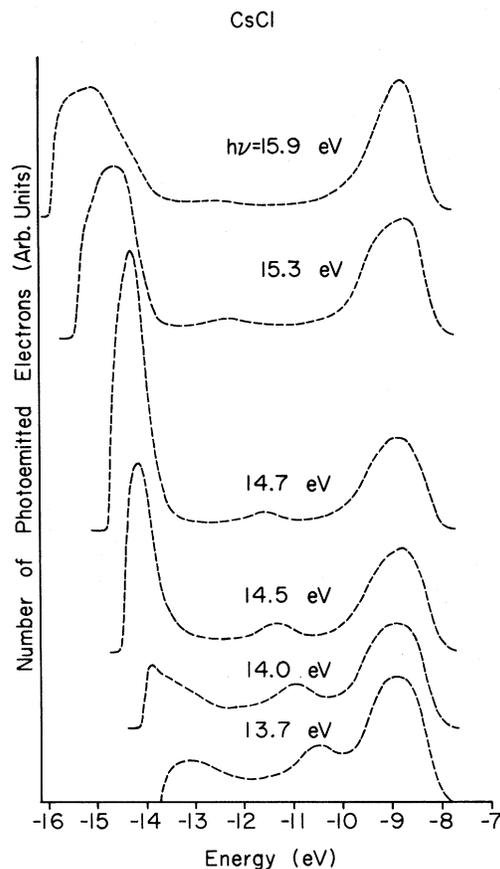


FIG. 7. Normalized energy distributions of photoemitted electrons from CsCl at 300 °K. The spectra show a strong narrow peak at approximately $\frac{1}{2}$ eV above the vacuum level for photon energies near 14.7 eV. The onset of this peak coincides with that of strong optical absorption at 14.7 eV, which has been interpreted as a core-exciton transition in CsCl.

width calculated by Rössler²⁹ and Onodera⁶ for CsI, using relativistic Green's-function methods, is in reasonable agreement with the observed value. For CsF, the calculations by Fowler and Kunz³⁰ indicate that the point X_3 of the conduction band is about 4.5 eV above Γ_1 . This point may correspond to the observed structure located at 4.2 eV above the vacuum level; however, we also see two additional structures at lower energies. It is apparent that more detailed calculations are necessary to identify all the observed features.

Interest has recently been shown in determining the binding energies for excitons generated by transitions from the core states of the alkali halides.^{11–13} The results of the present work enable us to calculate these energies for the lowest-energy excitons from each of the cesium halide Cs^+ 5*p* cores. In these calculations, we assume that the

TABLE II. Binding energies of Cs⁺ 5*p* core and halide excitons at Γ in cesium halides. The energy values listed in this table are in eV.

| | E_{vc} | E_g | E_{xc} | E_{xv} | E_{cb} | E_{vb} |
|------|----------|--------------------|-------------------|------------------|----------|----------|
| CsF | 4.3 | 9.8 ^a | 13.0 ^b | 9.2 ^c | 1.1 | 0.6 |
| CsCl | 5.8 | 8.3 ^a | 13.3 ^b | 7.8 ^c | 0.8 | 0.5 |
| CsBr | 6.6 | 7.3 ^a | 13.2 ^b | 6.9 ^c | 0.7 | 0.5 |
| CsI | 7.6 | 6.4 ^{c,d} | 13.1 ^b | 5.8 ^c | 0.9 | 0.6 |

^a Reference 5.

^b Reference 25.

^c Reference 2.

^d Reference 31.

first strong peak shown in the optical spectra near 13 eV corresponds to an exciton transition from the top of the Cs⁺ 5*p* band. Furthermore, it is assumed that the highest occupied Cs⁺ 5*p* states and the bottom of the conduction band are located at Γ_3^- and Γ_1^- , respectively. The latter assumption is consistent with the recent band structure calculations for cesium halides.^{6,29,30} Accordingly, the binding energy E_{cb} of the core exciton at Γ can be calculated from

$$E_{cb} = E_{vc} + E_g - E_{xc}, \quad (1)$$

where E_{vc} is the difference in energy between the top of the Cs⁺ 5*p* band and that of the valence band; E_g , the optical band gap between the valence and conduction bands; E_{xc} , the lowest-energy core exciton observed in the optical spectra. E_{vc} is obtained from the observed band thresholds. Similarly, the binding energy E_{vb} of the lowest-energy valence-band Γ exciton can be computed from

$$E_{vb} = E_g - E_{xv}, \quad (2)$$

where E_{xv} is the energy of the exciton peak observed in the optical spectra. The values of E_{cb} and E_{vb} for cesium halides are listed in Table II along with the optical energies used in the calculations. Phillips¹¹ has suggested that the Cs⁺ 5*p* core excitons should be more strongly bound than the corresponding halide excitons because of the lack of dielectric screening near the Cs⁺ core. This is in agreement with the values of the binding energies shown in Table II.

The present results for CsCl and CsF can be compared with those reported by Poole *et al.*^{32,33} for photon energy 40.8 eV. Their spectra are in reasonable agreement with the present work; however, their resolution is not as good.

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