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Analysis of the electronic structure in Cs halides by reflectance and thermoreflectance studies

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Measurements of the reflectance and thermoreflectance of CsI, CsBr, and CsCl in the 5–9-eV region at several temperatures are reported. The spectra are compared and analyzed with particular reference to their dependence on temperature and chemical composition. The experimental results show that the principal features of the Onodera's energy-band system for CsI might be valid in the case of CsBr and CsCl, too, taking into account relativistic effects. Through an analysis of line shapes and temperature coefficients, the complex structure of the fundamental optical spectra of the three compounds can be explained by excitons associated with the s-like and d-like conduction bands at the Γ and M points of the Brillouin zone.

I. INTRODUCTION

This paper extends to cesium halides the systematic experimental study on optical properties and electronic structure previously carried out in the vacuum-ultraviolet region for diamond and zinc-blende semiconductors[1] and alkali halides.[2] In the case of NaCl-type alkali halides,[2] through an analysis of the thermoreflectance TR line shapes and temperature coefficients it has been possible to gain new information on the assignment of the principal optical structures in terms of transitions at points Γ, L, and X of the Brillouin zone (BZ).

The cesium halides have not been fully investigated as well. From the experimental point of view, absorption and reflectance measurements of thin films have been reported by several authors.[3-8] Only recently the reflectance of polished single crystals has been studied.[9-11] Fairly good agreement is found among the spectra, but more accurate measurements are still required for better assignment of the spectra features to the band structure. Theoretically, while the conduction-band structure of NaCl-type halides has been extensively studied, the cesium halides have not received so much attention.[13-15] It is shown that these crystals present more complex conduction-band structure then the face-centered cubic (fcc) crystals. Some uncertainty remains in the interpretation of the optical spectra.

On the basis of our studies on alkali halides,[2] this paper reports measurements of near-normal incidence reflectance and thermoreflectance spectra in the photon energy range 5 eV $<\hbar\omega<$ 9 eV for temperatures ranging from room temperature to 6 K. The results complete the study of important range of both energy and temperature for which the optical properties of these crystals are known. Moreover, in some cases the measurements presented here reveal much more detail than has previously been reported. The dependence of the observed structures on chemical composition and temperature is extensively used in the analysis of the electronic properties in order to try to find a general interpretation of the optical spectra of this compound series.

II. EXPERIMENTAL TECHNIQUE AND SAMPLE PREPARATION

The double-beam optical-reflectivity apparatus features a home-made hydrogen-discharge lamp, a McPherson vacuum monochromator model 218, and a gas-expansion Cryotipe cryostat. A thin crystal of LiF splits the incident radiation into the reference and sample reflected beams, which are collected by two photomultipliers. The reflectance is obtained electronically from the ratio of the two signals. The R spectrum is corrected by taking into account the wavelength dependence of both the reflectance of the beam splitter and the different responsivity of the two photomultipliers. The TR measurements have been performed with the usual technique of phase-sensitive detection. The experimental details were previously described.[1] All spectra have been measured at near-normal incidence with unpolarized light. A thermal modulation of no more than 0.5 K was observed. Generally, the modulation intensity $\Delta R/R$ in the first exciton peak was of the order of 5×10^{-3}.

The CsI and CsBr crystals were mechanically polished with alcohol only. They were then cleaned in alcohol by ultrasonic bath and annealed for several hours at 350 K in order to reduce the surface damage. The CsCl samples were prepared by vacuum evaporation onto freshly polished and cleaned CsI and LiF substrates. The films were annealed at 300 K for about 20 h. Different substrates induce insignificant differences in the optical spectra.

In order to compare the *R* and *TR* spectra, we remark that *TR* spectra of insulators consist of a combination of the derivatives of the reflectance with respect to the transition energy (thermal shift) and to the broadening parameter (thermal broadening). When the shift term is dominant, thermal and wavelength-modulation spectra present similar line shapes; reflectance peaks correspond to the zero crossing points from positive to negative in the *TR* spectrum. Besides, inflection points in reflectance are indicated by nonzero, positive, or negative minima in the derivative spectrum. On the other hand, when the broadening term is dominant, the zero crossing from negative to positive could be assumed to give the transition energy. However, in order to determine the energy of the optical structures, we refer to the reflectance peaks as generally found in the literature. When many transitions occur in a small energy region, the resolving power of the thermoreflectance allows the resolution of weak structures and shoulders in reflectance spectra and a study of their temperature dependence.

III. BAND STRUCTURES

Cesium halides crystallize in a simple-cubic lattice (sc) with two ions per unit cell [X^- at position (0, 0, 0) and Cs^+ at position $(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a)$]. CsCl undergoes a phase transition from CsCl (sc) to NaCl (fcc) structure at about 400 °C.

An empirical band model for CsBr has been proposed by Phillips.[12] In this model the upper valence band is formed by Br *p* electrons and the conduction band is split into bands of *s* and *d* character. Evidence of the two conduction bands of different symmetry follows from the different temperature coefficients of the two low-energy peaks in optical spectra.[15] Deformation potentials for hydrostatic pressure for these peaks were found to have opposite sign.[7]

The energy bands of CsI have been calculated by Onodera[13] and Rössler,[14] both making use of relativistic Green's functions which are necessary because of the large atomic number of constituent ions. Onodera used free-ion potentials obtained by a self-consistent relativistic method. The band-gap ($\Gamma_8^- - \Gamma_6^+$) energy was fitted to the experimental value, 6.37 eV, derived from absorption measurements by Fischer and Hilsch.[15] It was found that this calculation produced the Γ_8^+ level (*d*-like conduction band) lower than the Γ_6^+ one (*s*-like conduction band) by 0.11 eV. However, the *s*-like Γ_6^+ level is expected to be the lowest because of isotropic magnetoconductivity[16] (in CsBr). Consequently, Onodera raised Γ_8^+ just above the Γ_6^+ level.

In order to interpret the results of Gavini and Cardona[6] on films grown on rock salt and which have a mixed sc and fcc structure, the energy bands of CsI in the two modifications have been calculated by Rössler.[14] Both atomic and ionic potentials for the sc structure have been used, with very little difference found between the calculated bands. Only atomic potentials for the fcc structure were considered. The Γ_6^+ and Γ_8^+ levels in the correct order are presented and separated by 0.3 eV (sc crystal with atomic potentials).

More recently, the conduction-band structures of RbCl and CsCl have been computed[17] by means of a model-potential approach.[18] To assess the influence of the crystal structure on the electronic energy levels of CsCl, calculations have been performed for fcc and sc CsCl.

In order to interpret our experimental results, we remark that it is reasonable to expect a regular trend in the energy positions of the optical structures going from CsI to CsBr and CsCl. Electronic-band calculations for the three compounds performed with the same assumptions for what concerns the crystal potential are lacking. We compare our results with the Onodera band calculations for CsI with the assumption that, at least in principle, the other cesium halides will present similar band features with different spin-orbit splittings and energy gaps. In Fig. 1 we report the energy-band system obtained by Onodera for CsI. Spin-orbit splitting is neglected in the conduction bands.

A quick look at the band structures reveals that the optical spectrum in the 5–9-eV energy range must be explained by interband and excitonic transitions from *p* valence bands to *s* and *d* conduction bands. Because the electron-hole interaction is strong, excitonic structures will be important in the optical spectrum.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Figures 2–7 show the *R* and *TR* spectra of CsI, CsBr, and CsCl, respectively at different temperatures. The absolute magnitude of the reflectance peaks reported by different researchers for ionic crystals in the vacuum ultraviolet differs by several percent on particular structures. These discrepancies are probably due to the differences in the conditions of the sample surfaces and to the particular optical techniques used.[9,11] Here we have not faced this question. In fact, for analyzing the electronic structure, the position

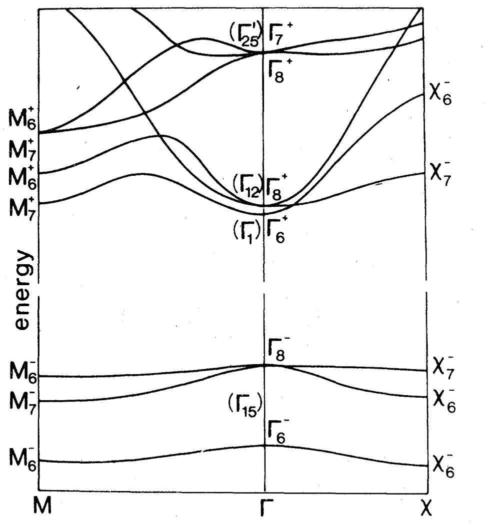

FIG. 1. Valence- and conduction-band structures of CsI (replot from Ref. 13).

and the shape of the features in reflectance spectra are more important than the actual reflectance magnitudes.

The characteristics of the *R* and *TR* spectra above the fundamental edge for all the crystals suggest a natural division of the structures (peaks in *R*) into three categories: (i) peaks which present a strongly-temperature-dependent energy position, (ii) weakly-temperature-dependent peaks, and (iii) weak structures. In the figures the same capital letter is used to indicate transitions arising from symmetry or spin-orbit and exchange split energy levels at the same point in the BZ. The *A* structures present a thermal-shift coefficient which ranges from -1×10^{-3} to -5×10^{-4} eV/K. In all crystals the *B* structures have a temperature coefficient of the order of a third or smaller than that of *A* peaks. C structures, generally weak in reflectance, are weakly temperature dependent.

We observe that in the 7–8-eV region in the CsI reflectivity different transitions with different temperature coefficients are superposed. It appears that by *TR* measurements (Fig. 3), it is possible to put in evidence the different contributions to the reflectance.

In order to compare the energies of the optical structures with the calculated interband gaps, let us first consider the multiplicity of the optically allowed excitons associated with the four M_0 band edges Γ_8^--Γ_6^+, Γ_6^--Γ_6^+, Γ_8^--Γ_8^+, and Γ_6^--Γ_8^+ (see Fig. 1). The excitonic states associated with Γ_6^+ (*s*-like conduction band) are responsible for the halogen doublet which characterizes the fundamental spectrum of the alkali

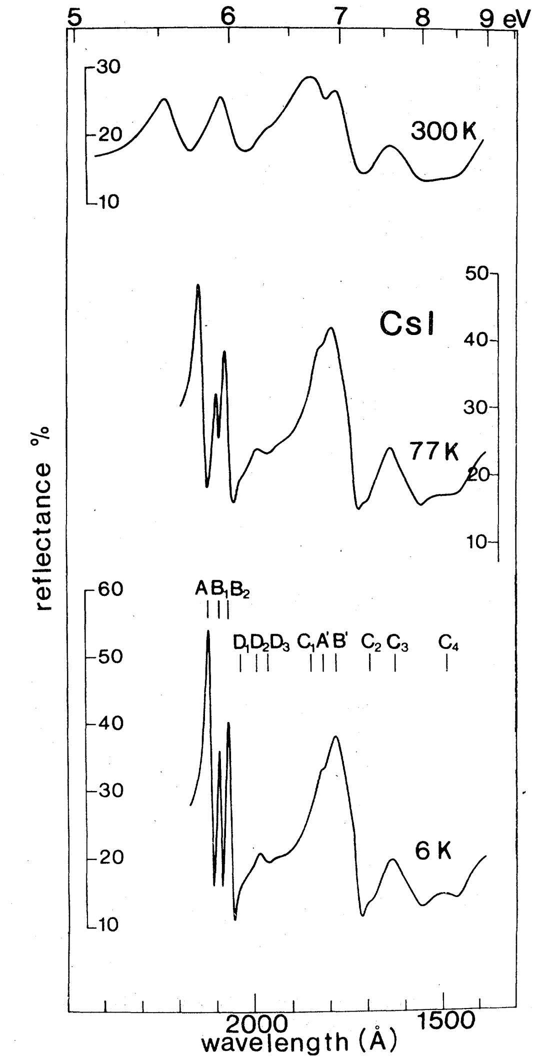

FIG. 2. Reflectance spectra of CsI at 300, 77, and 6 K.

halides. When we consider the excitons associated with the *d*-like conduction bands, we remark that two Γ_{15} states occur from the Γ_8^--Γ_8^+, transition. Because the point group for CsI is O_h, the excitons of symmetry Γ_{15} are the only excitons which can be created in the dipole approximation.[13,19] In the effective-mass approximation including the electron-hole exchange interaction,[20] if fluting in the valence and conduction bands is neglected about the Γ_8^- and Γ_8^+ edges, one of the two states turns out to be an optically forbidden pure spin triplet, while the other contains a spin-singlet component. However, when the fluting in the energy bands (very large about the conduction-band state Γ_8^+ in CsI)[13] is considered, the pure triplet state is coupled to the other Γ_{15} state containing singlet character. So, the band fluting at Γ_8^+

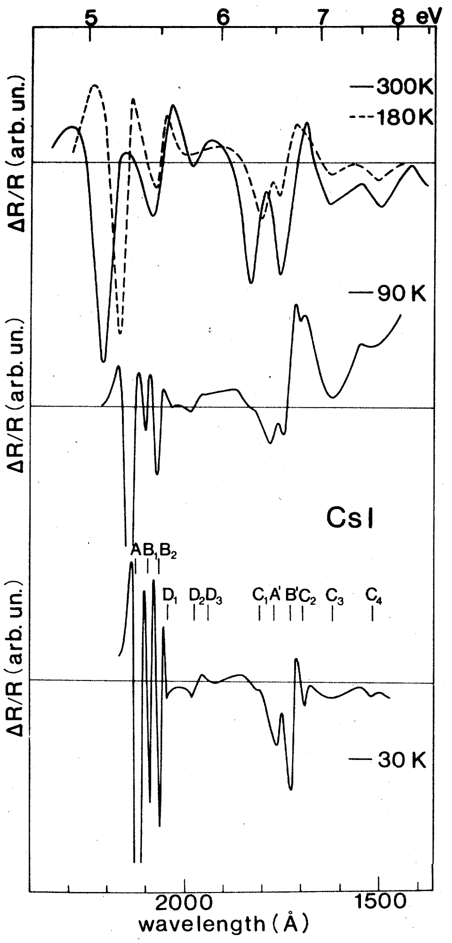

FIG. 3. Thermoreflectance spectra (arbitrary units) of CsI at 300, 180, 90, and 30 K.

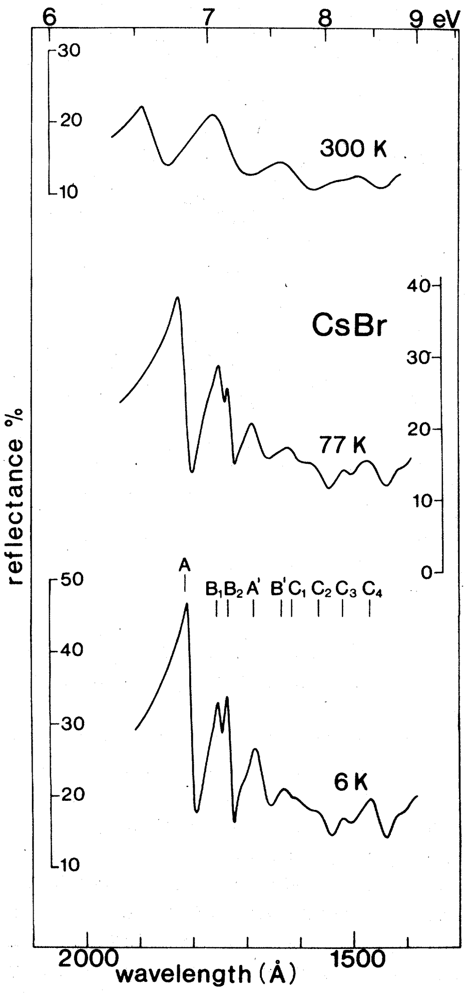

FIG. 4. Reflectance spectra of CsBr at 300, 77, and 6 K.

makes the triplet state optically allowed. Summarizing, regarding the optically allowed excitons associated to transitions from spin-orbit split p-valence bands to s and d conduction bands at the Γ point of the BZ, we expect five excitonic structures differently spaced owing to the spin-orbit splitting of the halogen p-valence states, the electron-hole exchange, and the Coulombic interaction.

Yet, from theoretical results[13] (Fig. 1) it seems that the transitions at the M point could produce additional structures in the fundamental spectrum. In this case, symmetry splitting of p and d bands must be considered also. Transitions at X and R points are parity forbidden.

We remember that in comparing the optical-structure energies with the calculated interband gaps, it must be considered that the former should be smaller than the latter by an amount equal to the exciton binding energy (in principle, different for different edges). However, our first purpose is only to assign the structures to transitions at specific points in the Brillouin zone.

With the remarks made above in mind, we now proceed to interpret the R and TR spectra. Let us first consider CsI (Figs. 2 and 3). If one takes into account the band calculations pictured in Fig. 1, the interpretation of the A structures is straightforward: it is related to a transition from the unexcited crystal to an exciton state formed by a hole in the top of the valence band at Γ_8^- and by an electron in the bottom of the s-type conduction band at Γ_6^+. Observing that the energy difference of the A and A' structures does not depend on temperature, it is possible to identify the A' structure as the spin-orbit partner of $A(\Gamma_8^- - \Gamma_6^+)$. According to Onodera's assignment,[13] the B_1 and

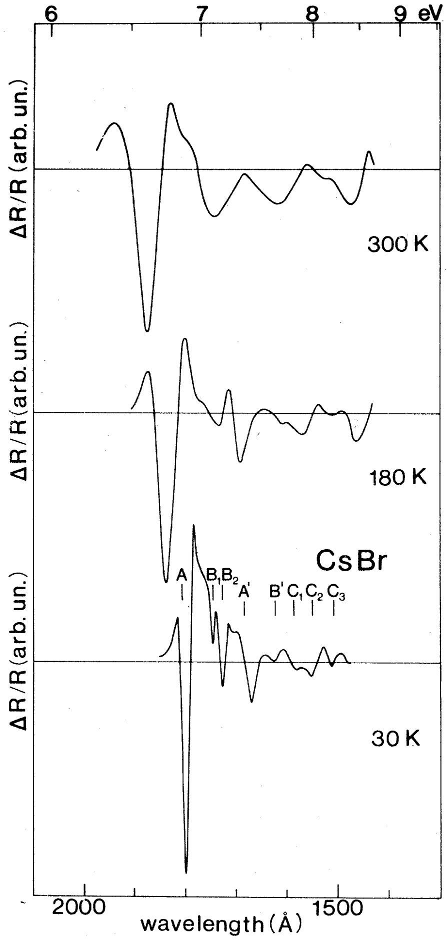

FIG. 5. Thermoreflectance spectra (arbitrary units) of CsBr at 300, 180, and 30 K.

B_2 doublet can be due to the exciton states related to the $\Gamma_8^- - \Gamma_8^+$ interband edge. Because of the positive exchange energy, the B_1 structure corresponds to the triplet state which becomes optically allowed owing to the fluting of the conduction band about Γ_8^+. The structure B', which presents a very similar temperature dependence to B_1 and B_2, is interpreted as the spin-orbit partner ($\Gamma_6^- - \Gamma_8^+$) of this doublet. As regards the A and B structures, the above assignment is compatible with the results obtained on the shift of the peak position of these transitions as a function of hydrostatic pressure.[7]

When the spectrum details at 6.3 eV are investigated, the identification of the D_1, D_2, and D_3 structures is questionable. The D_1 structure occurs in the *TR* spectra at low temperature only; in absorption[4,15] and reflectance[11] measurements it might be hidden in the strong signal at lower energy. Previously, the D_2 and D_3 peaks were assigned[13] to the $n = 2$ Wannier exciton states associated with the $\Gamma_8^- - \Gamma_6^+$ and $\Gamma_8^- - \Gamma_8^+$ interband transitions. The doublet structure of $\Gamma_8^- - \Gamma_8^+$ excitons, seen in the case of $n = 1$, was not resolved in the case of $n = 2$. However, this assignment of D_2 and D_3 structures is not compatible with their temperature dependence. In fact, (a) the energy differences of D_2 and D_3 structures do not depend

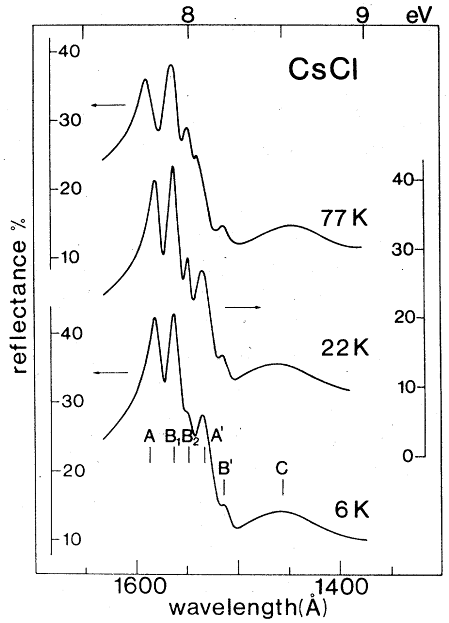

FIG. 6. Reflectance spectra of CsCl at 77, 22, and 6 K.

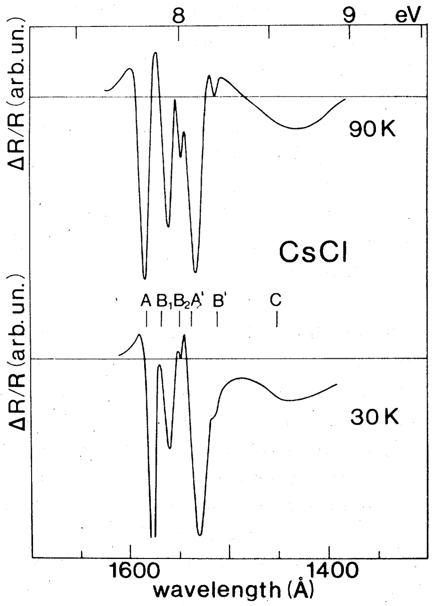

FIG. 7. Thermoreflectance spectra (arbitrary units) of CsCl at 90 and 30 K.

on temperature, in contrast to A and B structures, (b) D_2 and D_3 structures present temperature coefficients very similar to those for B_1 and B_2. We suggest that the D_2 and D_3 structures belong to the B_1 and B_2 excitonic series, respectively. The D_1 structure would be the $n=2$ companion of the A exciton.

From theoretical results,[13] at 0.2 eV above the Γ_8^--Γ_8^+ interband edge there should be another interband edge M_6^--M_7^+ with possibly M_0 singularity. However, such an M structure has not been well observed in its details as yet. It has been suggested[13] that one may speculate that the oscillator strength of the M exciton is taken away by the Γ exciton (configuration interaction) or its absorption might be hidden by excitonic transitions. Now we observe that the main structures in the spectrum can be explained by excitons formed at Γ, and at this point in the discussion we have already assigned the transitions to Γ_6^+ and Γ_8^+. From calculated energy-band systems, the transitions from Γ_8^- and Γ_6^- to the next higher point (Γ'_{25}) occur at about 9 eV. So, in order to interpret the C structures in our spectra, the remaining alternatives are the sets of M transitions. On the other hand, experimental evidence based on photoemission[21] indicates that the group of bands associated with Γ_8^+ and Γ_7^+ (d-character conduction bands) lies at a lower energy than from theoretical results, with a center about 8.4 eV above the valence-band edge. Consequently, as regards the C-structure identification, Γ'_{25} excitons must be taken into account. However, a discrimination between the contributions of the Γ and M transitions to the observed optical structures is difficult. In Table I a tentative assignment is proposed.

Let us consider CsBr and CsCl spectra, keeping in mind that a regular trend in the energy positions of the structures could be expected.[2] In the past, different identifications have been proposed for the main structures of the reflectance[9] and absorption[4,6] spectra, but all contrasting with the picture generally accepted for CsI and with the temperature dependence of the structures reported here.

If we suppose that, also taking into account the differences in the exchange, Coulomb, and spin-orbit interaction, the principal features of the energy-band systems calculated for CsI are present as well in the CsBr and CsCl case, we can extend the same procedure used for CsI to the other halides. Consequently, the reflectance peaks A and A' at 6.85 and 7.37 eV in CsBr and 7.85 and 8.08 eV in CsCl, respectively, which present a similar temperature dependence (Table I), are associated with the transitions Γ_8^--Γ_6^+ and Γ_6^--Γ_6^+. The B_1 and B_2 structures at 7.07 and 7.15 eV in CsBr and at 7.93 and 8.01 eV in CsCl are identified as due to the triplet and singlet excitons related to the Γ_8^--Γ_8^+ gap. Their spin-orbit-split companion Γ_6^--Γ_8^+ corresponds to the B' structure at 7.70 eV in CsBr and at 8.19 eV in CsCl. From Table I it is possible to see that the B_1, B_2, and B' peaks are weakly temperature dependent as in the case of CsI. C structures in the spectra could be associated to transitions at the M or Γ points in the BZ.

TABLE I. Energies of the optical structures from 22-K reflectance data. All energies are in eV. The temperature coefficients of the structures are also given in eV/K.

Optical structure and temp. coefficients	CsI	CsBr	CsCl
A (Γ_8^--Γ_6^+)	5.82	6.85	7.85
$-dE/dT$	9.5×10^{-4}	1.0×10^{-3}	6.7×10^{-4}
A' (Γ_6^--Γ_6^+)	6.85	7.37	8.08
$-dE/dT$	8.7×10^{-4}	7.3×10^{-4}	4.7×10^{-4}
B_1 (Γ_8^--Γ_8^+)	5.91	7.07	7.93
$-dE/dT$	3.2×10^{-4}	10^{-4}	1.5×10^{-4}
B_2 (Γ_8^--Γ_8^+)	5.98	7.15	8.01
$-dE/dT$	3.2×10^{-4}	10^{-4}	10^{-4}
B' (Γ_6^--Γ_8^+)	6.98	7.70	8.19
$-dE/dT$	3.5×10^{-4}	10^{-4}	10^{-4}
C_1 (M or Γ trans.)	6.76	7.58	8.60
C_2 (M or Γ trans.)	7.30	7.85	
$-dE/dT$	10^{-4}	10^{-4}	
C_3 (M or Γ trans.)	7.58	8.15	
$-dE/dT$	10^{-4}	10^{-4}	
C_4 (M or Γ trans.)	8.30	8.40	
$-dE/dT$	10^{-4}	10^{-4}	
D_1 ($\Gamma_8^- - \Gamma_6^+$, $n=2$)	6.06		
D_2 ($\Gamma_8^- - \Gamma_8^+$, $n=2$)	6.23		
D_3 ($\Gamma_8^- - \Gamma_8^+$, $n=2$)	6.34		

In conclusion, by R and TR measurements at different temperatures, it has been possible to identify some features of the fundamental optical properties of Cs halides in the 5–9-eV range. If our proposal is correct, the energy-band systems of Cs halides in the simple-cubic phase are similar.

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