

Electronic structure, photoemission spectra, and vacuum-ultraviolet optical spectra of CsPbCl_3 and CsPbBr_3

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Optical spectra of CsPbCl_3 and CsPbBr_3 have been measured in the range from 2 to 10 eV and have been combined with ultraviolet-photoemission-spectroscopy (UPS)—measurements at 21.1 and 40.8 eV. A quantitative band calculation is presented, which takes into account anion-anion interaction as well as electronic states of the Cs^+ ion. The prominent features of earlier band models and measurements are reestablished through our measurements and calculations, namely that the valence band consists of anionic p functions and $\text{Pb } 6s$ functions, the lowest conduction band being $\text{Pb } 6p$ type, and the lowest gap occurring at the R point of the Brillouin zone. Inclusion of a further ($\text{Cs } 6s -$ type) conduction band, however, is necessary to bring the calculated joint density of states into agreement with vacuum-ultraviolet optical spectra. The calculated densities of states of the valence bands are in quantitative agreement with those deduced from our UPS measurements.

I. INTRODUCTION

Optical and electronic properties of the complex, perovskite-type crystals CsPbCl_3 and CsPbBr_3 (hereafter called “plumbates”) have only recently been thoroughly investigated.^{1–3} Structural properties have been reported earlier, some structural phase transitions being of particular interest.^{4–7} In this paper optical properties are reported in the energy range up to 10-eV, as measured through thin-film absorption measurements and reflectivity measurements on bulk crystals. The valence-band density of states is measured through ultraviolet photoemission spectroscopy (UPS). All of these results are explained in a band calculation based on a quasicubic model and performed in an empirical linear combination of atomic orbitals (LCAO) scheme that goes beyond the earlier simple band model by Heidrich *et al.*,¹ which did not take into account anion-anion interaction nor electronic levels originating from the Cs^+ ion. The prominent features of the earlier model and of other measurements^{1,8} are reestablished through our calculations and measurements, namely that the valence band consists of $\text{Br } 4p$ ($\text{Cl } 3p$) and $\text{Pb } 6s$ functions, respectively, the lowest conduction bands being $\text{Pb } 6p$ type, and the lowest gap occurring at the R point of

the Brillouin zone (BZ). Inclusion of a $\text{Cs } 6s -$ type conduction band, however, is necessary to bring the calculated joint densities of states into agreement with vacuum-ultraviolet (vuv) optical spectra. The calculated densities of states of the valence bands are in quantitative agreement with those deduced from our UPS measurements.

II. EXPERIMENTAL SETUP

The ultraviolet excited photoemission spectra have been measured in a Vacuum-Generators ADES 400 spectrometer using a differentially pumped helium I resonance lamp ($\hbar\omega = 21.2$ eV). The resolution of the hemispherical analyzer was 250 meV, and 3° , respectively. We point out, however, that the spectra reported below were found to be independent of the take-off angle of the photoelectrons. *In situ* cleaved single crystals of CsPbCl_3 , CsPbBr_3 were investigated at 290 and at 90 K.

Optical investigations from the visible to the vacuum ultraviolet were performed by measuring the absorption of thin evaporated films of CsPbCl_3 and CsPbBr_3 and the reflectivity of bulk crystals of both plumbates. For measurements in the visible

and near ultraviolet (between 2 and 6 eV) we employed a Cary 17 spectrophotometer and in the vacuum ultraviolet a McPherson 218 monochromator at a spectral resolution better than 30 meV between about 5 and 10 eV. The signal was normalized to the incoming light by means of a double-beam setup. The reflected light was directed to the sample photomultiplier by a glass-fiber bundle the face of which had been coated with a sodium salicylate layer. The optical investigations were done at temperatures between 30 and 40 K.

All single crystals used in our experiments were grown following a method very similar to the one that has already been described in a previous paper.⁹ The reader is referred to this paper for further details. We should, however, make a remark concerning the preparation of thin films: If the plumbates are evaporated as a complex it appears in optical spectra that lines are rather broad due to a considerable degree of disorder. Evaporating on a heated surface or annealing will improve the situation only to a certain extent. Much better results were obtained by evaporating the components separately one after another, so that the lead salt is placed on top of the cesium salt. Within a few minutes after evaporation a solid state reaction occurs as evidenced by a gradual change in color of the film. In this way it was possible to achieve spectra which in their best form (on freshly cleaved alkali halides with a relatively thick CsCl or CsBr subcoating for CsPbCl₃ and CsPbBr₃, respectively) were very close to those obtained from Kramers-Kronig transformed reflection spectra of bulk crystals. For the absorption measurements we used mainly NaCl and KBr substrates for the visible

range. LiF substrates were used for samples that were also investigated in the vacuum ultraviolet.

III. EXPERIMENTAL RESULTS

A. Photoemission measurements

Photoemission spectra obtained from CsPbCl₃ and CsPbBr₃ for normal emission are presented in Fig. 1. The valence-band region extends from 0 to 5 eV binding energy, while the Cs 5*p* core levels show up around 9 eV below the top of the valence band. While it was no problem to obtain clean surfaces by cleaving the samples under ultrahigh vacuum conditions, no anisotropic photoemission from the valence bands as is characteristic for single crystal surfaces was observed. Except for some minor changes in relative peak intensities, spectra taken for different electron-escape angles are nearly identical. Most likely strong disorder was present at the cleaved surfaces. In fact, a microscopic investigation corroborated the assumption that the surfaces were far from being perfectly ordered. We have also tried to check the surface periodicity by means of low-energy electron diffraction. Since, however, much larger electron currents are involved in this technique than in photoemission, strong charging effects occurred and no meaningful results could be obtained.

Another effect that might be responsible for the lack of anisotropy of the photoemission from the surfaces of CsPbX₃ is differential charging. While the overall charging potential did not exceed 1 eV, as mentioned above, the local charging potential could very well be different at different locations of the surface. It is conceivable that the resulting local fields deflect the photoelectrons just after escaping from the surface in an irregular manner, the result being a practically isotropic photoemission pattern.

No matter what the true reason for the absence of angular effects is, we can take for granted that our measured "angular-resolved photoemission spectra" effectively resemble the joint density of states (JDOS), weighted by appropriate transition matrix elements.¹⁰

A quite pronounced sharpening of all valence-band features and core levels is observed at low temperatures. No attempt is made to interpret these thermal broadening effects; we just mention that electron-phonon deformation potentials and optical phonon frequencies can, in principle, be ob-

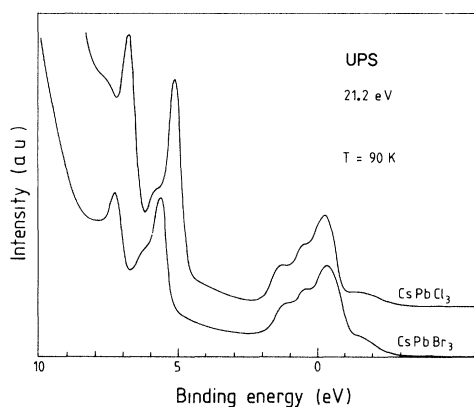


FIG. 1. UPS spectra of CsPbCl₃ and CsPbBr₃ at 90 K. Excitation energy was 21.2 eV. As reference energy we chose the valence-band center of mass. The photoelectron take-off angle was set to 0° (normal emission).

TABLE I. Core-level energies (in eV).

	CsPbCl ₃	CsPbBr ₃
Center of valence band	0	0
Cs 5 <i>p</i> (Main components)	-5.12/ -6.78 $\Delta_{so}=1.66$	-5.62/ -7.28 $\Delta_{so}=1.66$
Cs 5 <i>p</i> (Satellites)	-5.91/ -7.64 $\Delta_{so}=1.73$	-6.32/ -8.01 $\Delta_{so}=1.69$
Splitting between main components and satellites	0.81	0.71
Pb 5 <i>d</i> _{5/2}	-14.80	-15.17

tained from such an investigation.¹¹ We take, however, advantage of the fact that all peak energies are determined more easily from the low-temperature spectra. Thus all spectra shown and discussed subsequently have been taken at 90 K.

Several core levels of the constituents which form the trihalogenoplumbates are accessible by means of He I (21.2 eV) and He II (40.81 eV) radiation. These are the Cs 5*p* doublet and the Pb 5*d* doublet. Photoelectrons from the former can already be excited using He I photons, the corresponding peaks appearing around 8.5 and 10 eV binding energy (cf. Fig. 1). Due to the higher binding energy (20 eV) of the Pb 5*d* levels, these can only be studied with He II photons. Since, however, the uv lamp delivered only a mixture of He I and He II radiation, the Pb 5*d*_{3/2} core level coincides with the valence-band peak excited by He I photons. Thus only the Cs 5*p*_{1/2}, Cs 5*p*_{3/2} and Pb 5*d*_{5/2} levels can be identified unambiguously in the photoemission spectra.

The measured initial state energies of these levels are compiled in Table I. Since the top of the valence band is not well defined, we have taken the center of mass of the valence band as zero energy. The approximate positions of the top of the valence band are -3.0 and -2.8 eV for CsPbCl₃ and CsPbBr₃, respectively. The most striking result apparent from this table is the splitting of both Cs 5*p* levels into two components. The average amount of splitting varies from 0.8 eV for CsPbCl₃ to 0.7

eV for CsPbBr₃. We suggest that this splitting has to be interpreted in terms of different chemical shifts; thus it indicates the presence of cesium in two different chemical states. In view of the fact that all Cs atoms occupy chemically equivalent sites in the lattice of the trihalogenoplumbates, we conclude that the samples used in our experiments were chemical inhomogeneous. Since photoemission is a surface sensitive technique,¹² one possible explanation is a segregation of cesium atoms at the surface. We tried to confirm this assumption by studying the temporal development of the core-level spectra after cleaving. No unequivocal changes of the intensity ratio or of the splitting between main peaks and satellites with time or sample temperature could be found that would have indicated a thermally stimulated segregation effect.

Under the natural assumption that the main peaks represent the singly ionized cesium which is present in the trihalogenoplumbates, the satellites arise from atoms which carry a less positive charge (we note that the direction of the chemical shift for cesium atoms is opposite to what one usually would expect¹³), possibly from neutral atoms. We point out that this assumption is corroborated by the fact that the spin-orbit splittings are slightly different for the main components and the satellites. Comparing the values given in Table I with data given in the literature¹³ we again conclude that the main peaks represent Cs⁺, while the satellites prove the presence of Cs⁰ or Cs^{(1/2)+}. It is at

present not possible to give a straightforward explanation of the occurrence of cesium in two chemically different states in the trihalogenoplumbates. The attribution of the satellite peaks to shake-up structure can probably be excluded since no such evidence was found for the alkali metal suboxides¹³ nor for the case of a Cs covered GaAs surface.¹⁴

B. Optical measurements

Typical absorption spectra at 30 K are shown in Fig. 2 for CsPbCl₃ and for CsPbBr₃. Spectra obtained from layers that have been grown by a solid-state reaction are represented by a solid line, spectra of complex-evaporated films by a broken line. It becomes apparent that the first way of preparation produces sharper spectral lines and the corresponding spectra exhibit much more details. For both materials the situation looks much alike in many respects. Both absorption curves begin with two rather sharp excitonic lines 1 and 2 at 3.0 and 4.0 eV for CsPbCl₃ and at 2.33 and 3.44 eV for CsPbBr₃. These are followed by a group of lines denoted by 3 which is clearly resolved into three peaks 3, 3', and 3'' in the case of CsPbBr₃

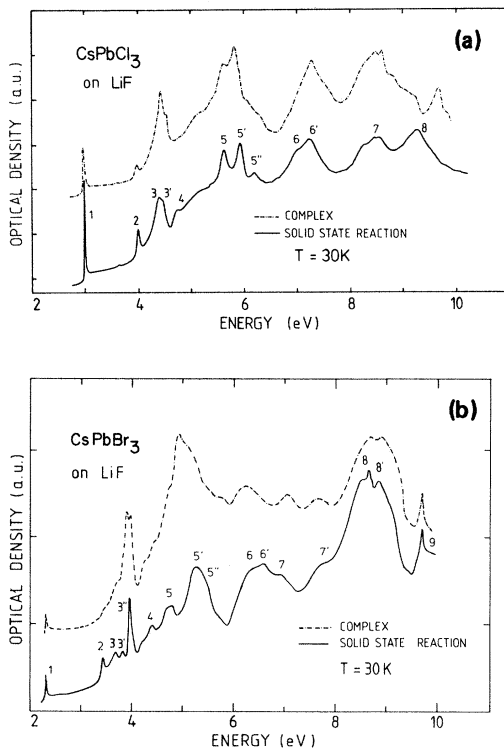


FIG. 2. Absorption spectra of thin films of (a) CsPbCl₃ and (b) CsPbBr₃ on LiF substrates. Spectra are shown for the two different methods of sample preparation mentioned in the text.

and into two peaks 3 and 3' in the case of CsPbCl₃. In the chlorine complex we find a strong triplet at 5.69, 5.94, and 6.2 eV which is followed by three rather broad absorption maxima at 7.2, 8.5, and 9.3 eV with a pronounced shoulder on its long-wavelength side, which can be seen especially in peaks 7 and 8.

In CsPbBr₃ there appear some smaller lines between 4 and 5 eV and a very large one at about 5.3 eV. Towards higher energies there are maxima of considerable oscillator strength at about 6.5 and 6.9 eV, a shoulder at 7.7 eV, and a very strong structure around 8.7 eV. One feature that is dominant in the lower energetic part of the CsPbBr₃ spectrum is the strong enhancement of the peak at 4 eV which was not found before in other absorption spectra or in normal reflectivity spectra of bulk crystals.¹⁻³ The reason for this behavior is not quite clear: As the first excitonic transition in lead bromide happens to occur around this energy one might suppose that the peak is due to a PbBr₂ surplus though we do not find a PbBr₂ character in the vuv range. We tried to examine this possibility by evaporating CsPbBr₃ as a complex but found a very similar structure with an additional splitting. It turned out that the peak could be reduced to normal size if there was a considerable excess of CsBr. This would correct the spectra in the visible

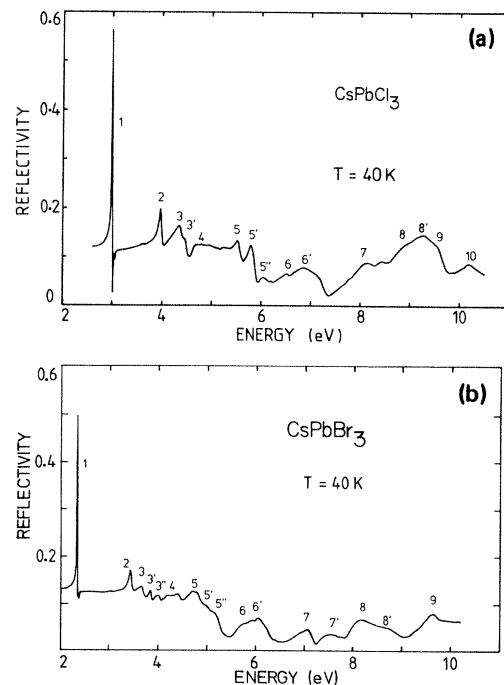


FIG. 3. Reflectivity spectra of (a) CsPbCl₃ and (b) CsPbBr₃ taken at $T=40$ K.

range but caused marked CsBr absorption lines in the vuv. For this reason we feel that the influence of the specific substrate might contribute more strongly to the shape of line 3'' than an accidental nonstoichiometry. From Fig. 2 some differences in the energetic position of lines 6, 7, and 8 can be observed for both methods of preparation. Compared to the solid-state reaction spectrum in the complex-evaporated layers line 6 seems to have shifted to lower energies to unite with line 5 whereas 7 and 8 appear to have moved apart, a situation which is also found in reflectivity spectra of CsPbBr₃ (Fig. 3) where line 6 only appears as a wide shoulder around 5 eV and 6 and 7 are separated from each other by almost 1 eV.

Figure 3 shows reflection spectra of bulk crystals of CsClBr₃ and CsPbBr₃. Both spectra start with a very intensive and sharp exciton line with a 2s exciton on its short-wavelength side. This is followed by another strong excitonic line 2 which is relatively sensitive to crystal preparation. We found it missing in some cases but could always restore it by careful annealing of the sample. The overall correspondence between absorption and reflection spectra is rather obvious. This holds in particular for the sharp excitonic lines 1 and 2, if one compares the reflectivity spectrum with the absorption spectrum of the layers grown by solid-state reaction. From this we conclude that the latter are indeed representative for the ideal, undisturbed compounds. Whereas a critical point assignment of the first spectral lines is possible, an interpreta-

tion of the higher transitions is more difficult and spectra have to be compared with band-structure and joint density of states calculations.

IV. BAND STRUCTURE

The experimental data presented give information about the density of states of valence and conduction bands. We fit a band structure to explain these data by using the empirical tight-binding method. Thus, in contrast to common applications of this scheme which determine the Hamiltonian matrix elements from energy separations at high-symmetry points of the Brillouin zone taken from first-principles calculations or from experimental data, we use the whole information contained in the spectra.

The tight-binding method rests on the existence of a set of localized wave functions which can be used to set up the Hamiltonian matrix for a band complex disconnected from all others. The symmetry properties of these so-called generalized Wannier functions are determined by the transformation properties of the respective atomic or ionic functions, which are approached by the Wannier functions in the limit of large lattice separation.

In general, the behavior of the Wannier functions will be much more complicated than that of the ionic functions due to orthogonalization effects on all (core, valence, conduction) functions of the neighboring atoms, and the admixture of higher states with the same angular momentum (see, e.g.,

TABLE II. LCAO matrix elements (in eV).

	CsPbCl ₃	CsPbBr ₃
E_{6s}^{Pb}	-1.2	-0.8
E_p^{halogen}	0	0
E_{6p}^{Pb}	5.8	5.4
E_{6s}^{Cs}	8.7	8.2
$V_{sp}^1(\text{Pb-halogen})$	-0.45	-0.55
$V_{pp}^{2\delta}(\text{halogen-halogen})$	0.3	0.35
$V_{pp}^{1\sigma}(\text{Pb-halogen})$	1.5	1.5
$V_{pp}^{1\pi}(\text{Pb-halogen})$	-0.25	-0.25
$V_{sp}^3(\text{Pb-Cs})$	0.8	0.7

Ref. 15). Except the symmetry, detailed information about the functions, however, is not necessary in the empirical tight-binding scheme, in which the Hamiltonian matrix elements are considered as fitting parameters. Thus, although the properties of the ionic functions give some indication for the size of the matrix elements, *all* parameters are determined by the fitting procedure.

We start with the ansatz that the average band energies can be approximated by energies of the free ions corrected by the Madelung shift. This ansatz has been successfully used in an empirical LCAO fit of the band structures of thallos halides¹⁶ and has been the basis of the first LCAO scheme for the trihalogenoplumbates.¹ As in Ref. 1 the uppermost valence bands are built from $\text{Pb}^{2+} 6s$ and $\text{Cl}^- 3p$ ($\text{Br}^- 4p$) states. A careful recalculation of the contribution of the different ions to the Madelung energy of the perovskite (1-2) lattice showed, however, that in contrast to Ref. 1 the cationic *s*-type levels lie below the anionic *p*-type levels. The lowest unoccupied energy bands are mainly $\text{Pb}^{2+} 6s$ type. A further conduction band is built up from $\text{Cs}^+ 6s$ states.

Because of the high atomic number of lead we have to take the spin-orbit coupling into account; the coupling parameters were taken from data for the lead ion and the halogen ions. Thus the size of the Hamiltonian matrix is 28×28 [two $6s$, three times six $3p$ ($4p$), six $6p$, and two $6s$]. The number of the matrix elements to be fitted is determined by the restriction to third-nearest-neighbor interactions. In this approximation the following matrix elements have to be taken into account: $V_{sp}^1(\text{Pb-Br})$ and $V_{pp}^{1\sigma}(\text{Pb-Br})$, $V_{pp}^{1\pi}(\text{Pb-Br})$ between nearest neighbors, $V_{pp}^{2\delta}(\text{Br-Br})$ between second- and $V_{sp}^3(\text{Cs-Pb})$ between third-nearest neighbors; $V_{pp}^{2\sigma}$ and $V_{pp}^{2\pi}$ are negligible as compared with $V_{pp}^{2\delta}$. Owing to the large energy separation the coupling between Cs levels and the valence-band states can be neglected, too. The size of the largest parameter $V_{pp}^{1\sigma}$ can be estimated from microscopic calculations for thallos halides.¹⁵ The relative size and sign of the overlaps between the different ionic functions then approximate the other parameters. Around these starting values the five fitting parameters are independently varied.

The variation leads to significant deviations from the starting values. In particular the sign of $V_{pp}^{2\delta}$ is changed, V_{sp}^1 is reduced by 40%. These changes are mainly due to the mentioned orthogonalization effects which are even larger than those found in microscopic calculations¹⁵ of TlCl because of the

smaller nearest-neighbor distance. The center-of-mass energies E_{6s}^{Pb} , E_p^{halogen} , E_{6p}^{Pb} , E_{6s}^{Cs} are varied, too, in a small range of 1 eV around the starting values, but the results for the density of states (DOS) are much less sensitive to the variation of these than to the variations of the other matrix elements. The center-of-mass energy of the $\text{Pb } 6s$ — like band has to be taken 0.8 eV below the $\text{Br } 4p$ and 1.2 eV below the $\text{Cl } 3p$ — like band average, respectively, in order to reproduce the flat rise of the measured valence-band DOS below the top of the band.

The matrix elements with which the best agreement between the valence-band density of states and the photoemission spectrum as well as between

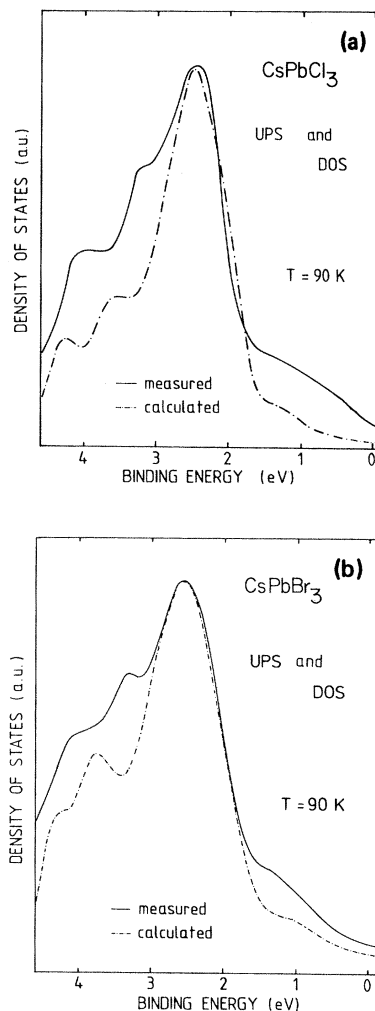


FIG. 4. Comparison of valence-band density of states calculations with experiment. The zero of energies here coincides with the extrapolated edge of the valence band. (a) CsPbCl_3 and (b) CsPbBr_3 .

the combined density of states and the optical spectrum were obtained are summarized in Table II.

V. DISCUSSION

As has been pointed out in the preceding section, optical as well as UPS measurements led to the conclusion that the Br 4*p* (Cl 3*p*) levels have to be positioned above the Pb 6*s* levels, the distance of the center of mass of the respective bands being 0.8 (1.2) eV. Taking this relative position of bands for granted we find an almost quantitative agreement between measured and calculated valence density of states by fitting the *s-p* matrix element between lead and the corresponding anion to the values given in Table II (see Fig. 4). A lifetime broadening of 0.4 eV is added to the theoretical density of states. The flat but pronounced tail at the top of the valence band is due to the *s*-type uppermost levels, which follow as a result of *s-p* mixing,

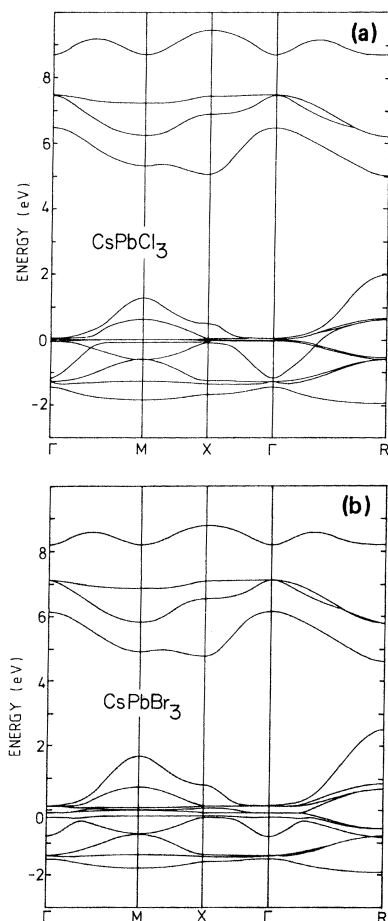


FIG. 5. Band structures of (a) CsPbCl₃ and (b) CsPbBr₃.

though the Pb 6*s* band lies below the anion *p* band. The main peak at -2.5 eV mainly consists of Br 4*p* (Cl 3*p*) contributions as is clearly visible from the band structure (see Fig. 5). The peak at -3.7 (-3.5) eV originates from crystal-field-split halogen bands and is slightly lower than the experimental value. The low-energy shoulders around -4 eV are mainly *s*-type again.

The joint density of states which has been calculated from the band structure described in Sec. IV is compared to the optical density as measured through absorption of thin films (see Sec. III B) in Fig. 6. A comparison in this case cannot be completely quantitative, of course, since no matrix element effects are considered and no many-body effects are explicitly taken into account. Although the importance of the latter for substances of the type treated here has been proven recently,¹⁷ the energetic position of structures in the optical spectrum as given in the joint density of states will be affected only slightly by these effects and by taking into account the energy dependence of matrix elements. There will be, however, a transfer of oscillator strength to the low-energy side of the spectrum and, in particular, bound excitons cannot be reproduced through a calculation of a joint density of states alone. Despite these obvious shortcom-

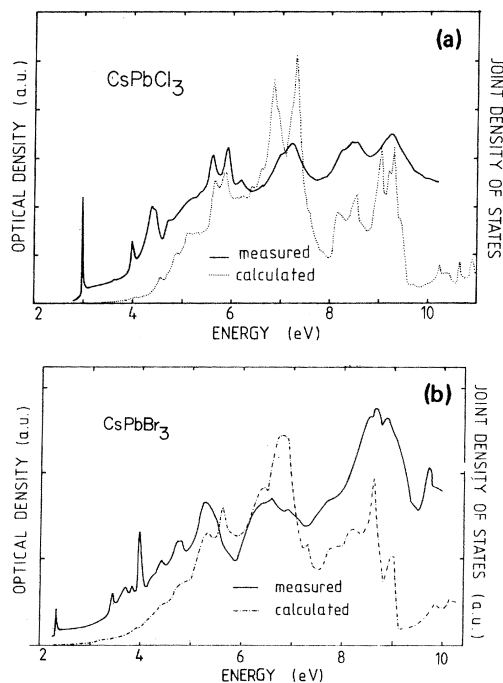


FIG. 6. Comparison of experimental absorption spectra with calculated joint density of states calculations. (a) CsPbCl₃ and (b) CsPbBr₃.

ings of the empirical tight-binding scheme all essential structural features of the experimental spectrum are well reproduced in our calculations, as may be seen from Fig. 6, and from inspection of the band structure (Fig. 5).

The first direct transition at 2.3 (3.0) eV occurs at the *R* point of the BZ, and yields an intracationic excitonic structure at the fundamental gap. A slight, but nevertheless marked, increase in the joint density of states at 3.2 (4.0) eV is due to a van Hove singularity at the *M* point of the BZ, which is the origin of a second intracationic excitonic transition experimentally measured at 3.3 (4.0) eV, named 2 in earlier references.^{1,3} The next marked step in the joint density of states occurs at 3.2 (4.4) eV and is caused by transitions from the uppermost *p*-type valence bands at *R* to the lowest conduction band. It is assigned to peaks 3,3' of the experimental spectrum in accordance with earlier assignments.^{1,3} The valence-band splitting of 0.4 eV in CsPbBr₃ is due partly to the bromine spin-orbit coupling, and partly to the crystal-field splitting induced through bromine-bromine interaction. The strong peak measured at 4 eV in CsPbBr₃, which is only weakly present in normal absorption measurements^{1,3} seems to be a superposition of several van Hove singularities at the *M* point and the *R* point including transitions to the

spin-orbit split conducting band. Its strong sensitivity against growing conditions and substrates of the CsPbBr₃ films is as yet not well understood.

The bulk of halogen *p* bands around -2 eV (Fig. 5) contribute to a series of structures in the joint density of states from 4.5 to 7.5 eV which compare favorably to experiment. The pronounced splitting between a group of transitions from 4.5 to 6 eV and a second group of transitions from 6 to 7.5 eV is due to the conduction band spin-orbit splitting.

The first transitions to the Cs conduction band are found above 7.5 eV and involve the uppermost valence band. The structures between 8 and 10 eV originate from transitions to the Cs band from the bulk of Br 4*p* (Cl 3*p*) bands.

In conclusion, in spite of all the approximations described above, the main features of the optical spectra of CsPbCl₃ and CsPbBr₃ are well described through this empirical band structure which is mainly based on the close analogy to the thallos halides.

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