

Electron energy bands and cohesive properties of CsCl, CsBr, and CsI

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Results of self-consistent first-principles calculations of the electronic band structures of the three cesium halides within the local-density functional formalism are presented. The calculations were done with the linear muffin-tin orbital (LMTO) method and relativistic effects were taken into account. The general features of the electron bands in the three compounds are very similar. In all cases the isotropic Γ_6^+ state forms the conduction-band bottom as has been speculated earlier. Effective-mass parameters for the valence and conduction bands are obtained by fitting our bands with the results of $\mathbf{k}\cdot\mathbf{p}$ perturbation theory. The nature of cohesion in the three compounds is discussed within the LMTO framework. The calculated total energy fits very well with the total energy as given by the Born-Mayer model for ionic compounds over a large range of crystal volume.

I. INTRODUCTION

The three cesium halides, viz., CsCl, CsBr, and CsI, crystallize in the $B2$ (CsCl) structure and show very similar properties. They are all insulators under normal conditions and exhibit almost identical optical spectra.^{1,2} The magnetoresistivity of CsBr has been measured³ to be isotropic indicating an s -like nature of the bottom of the conduction band. Such is also believed^{4,5} to be the case for CsCl and CsI as evidenced from their optical spectra.

Another interesting feature of these compounds is the s - d transition of the conduction-band bottom under pressure.⁶⁻⁸ At zero pressure the fundamental gap is between halogen p and cesium s states at the Γ point with the cesium d state occurring immediately above the cesium s conduction state.^{4,5,8} It has been observed^{6,7} that under a few kbar pressure there is an s - d flip of the conduction-band bottom in CsI. It seems likely that in the other two cesium halides such an s - d transition would also take place. This has interesting consequences for the nature of excitons, as the d -like conduction-band bottom implies that both the electron as well as the hole wave function are derived from degenerate bands.

Under high pressure all of the three compounds undergo a phase transition from the simple cubic to the tetragonal structure indicating a similarity of chemical binding. This transition has been the subject of extensive theoretical^{9,10} as well as experimental¹¹ investigations in the recent past.

The focus of the present paper is on the electronic band structures and the cohesive properties of the three compounds. Several early calculations of the band structure of CsI have been reported in the literature. Onodera⁵ and Rössler⁴ both obtained the electronic bands for CsI from a non-self-consistent Korringa-Kohn-Rostoker Green's-function method.¹² However, they obtained conflicting ordering of the s and d conduction bands. A self-consistent nonrelativistic symmetrized-augmented-plane-wave calculation of electron bands in CsI was recently performed by Aidun, Bukowinski, and Ross.¹³ Saks¹⁴ has

obtained valence bands for these compounds from an empirical Slater-Koster scheme. A model pseudopotential calculation of the conduction bands in CsCl has been reported by Donato *et al.*¹⁵ The latter results, however, are in direct conflict with the optical experiments of Nosenzo and Reguzzoni.² These experiments tend to suggest that electron bands in the three cesium halides should be essentially similar. To the author's knowledge, detailed band-structure calculations for CsCl and CsBr have not been performed until now.

In a recent work we have already examined the electron bands in CsI from a first-principles relativistic calculation⁸ and have emphasized that relativistic effects are indeed important. In this paper we present some further results for electron bands in CsI and compare them with the electron bands in CsCl and CsBr. The organization of the paper is as follows. In Sec. II we discuss some consequences of symmetry where we show in particular how the symmetry label of a Bloch state may be obtained by an examination of the atomic characters of the wave function. In Sec. III we present the so-called "canonical bands" in the LMTO theory^{16,17} for the simple-cubic lattice with one atom per unit cell. These canonical bands provide useful guidance also for simple-cubic solids with many atoms in the unit cell such as the cesium halides. Section IV deals with the scalar relativistic band structure in one of the compounds, viz., CsCl. In Sec. V the relativistic bands of the three cesium halides are discussed and calculated values of the deformation potentials and the effective-mass parameters are given. Section VI is devoted to the cohesive properties and the main results are summarized in Sec. VII.

II. SYMMETRY CONSIDERATION

The $B2$ (CsCl) structure with which we are concerned here, consists of a simple-cubic lattice with two atoms in the unit cell at the (0,0,0) and the $(a/2)$ (1,1,1) positions, a being the lattice constant. The crystal structure and the associated Brillouin zone (BZ) are shown in Fig. 1. The

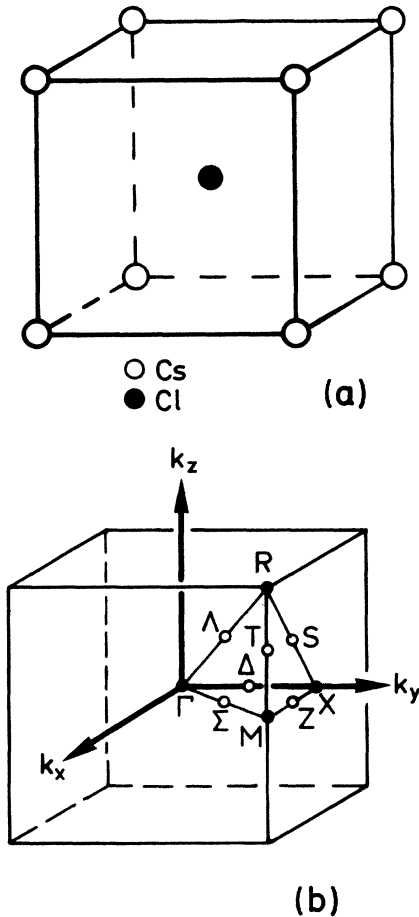


FIG. 1. (a) CsCl structure and (b) the Brillouin zone of the simple-cubic lattice.

point symmetry of the crystal is O_h . Because the point symmetry is the same about either the Cs or the Cl atom, the Bloch functions may be classified according to their symmetry properties about either of the atoms. In this paper we classify them according to the symmetry about the Cs atom. As is well known^{5,18,19} the symmetry of a Bloch function about either of the atoms is the same except when the Bloch momentum \mathbf{k} lies on the surface of the BZ. In the latter case once the symmetry about the Cs atom is known, the symmetry about the Cl atom (and vice versa) may be obtained with the use of tables given by Bell¹⁸ and by Onodera.⁵ We follow the standard Buckaert-Smolukowski-Wigner-Elliott notations²⁰ throughout to denote the irreducible representations.

The irreducible double-group representations spanned by atomic functions of different angular momenta are shown in Table I. Similar information about single-group representations can be read off from the symmetries of simple-cubic canonical bands shown in Fig. 2 and which are discussed in the next section. For example, according to Fig. 2, Cs d orbitals span the $X_2 + X_1 + X_5 + X_3$ and the Cl d orbitals the $X'_3 + X'_4 + X'_5 + X'_2$ irreducible representations at the X point. These tables contain sufficient information that the symmetry of a Bloch function may be obtained by inspecting the atomic character of the

wave function and from a knowledge of the dimensionality of various representations; an analysis of the transformation properties of the wave function under various operations of the group is not necessary. As an illustration, the conduction-band bottom at the Γ point, as we shall see later, has contributions from Cs s and halogen s orbitals and not from the p , d , or f atomic orbitals; therefore, according to Table I this Bloch state has the symmetry Γ_6^+ . However, with the information presented in Table I, one cannot differentiate between M_6^- and M_7^- , as both of them contain exactly the same, Cs p + Cl p , atomic characters. This differentiation is made from the

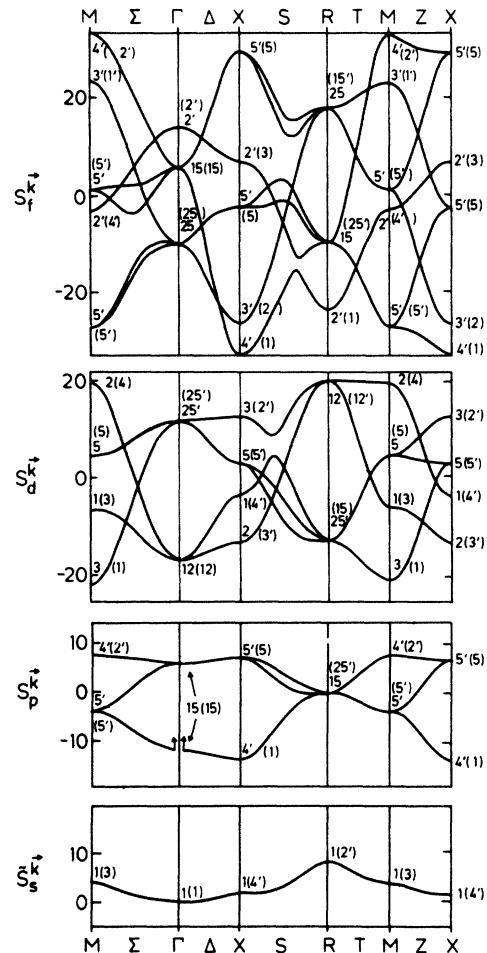


FIG. 2. Canonical bands in the simple-cubic lattice originating from the atom-centered s , p , d , and f orbitals. For the simple-cubic lattice with one atom per unit cell, an unbracketed symmetry label denotes the Bloch function symmetry about an atom. The corresponding bracketed label denotes the symmetry of the same Bloch function, but now we discuss the empty site in the unit cell with O_h point symmetry. In the $B2$ (CsCl) structure, there are two sets of canonical bands associated with either the Cs or the Cl sublattice. These two sets of bands are identical except for the symmetries. With our convention of labeling the symmetry of a Bloch state according to its symmetry about the cesium atom, the unbracketed (bracketed) labels refer to symmetries of the canonical bands associated with the Cs (Cl) sublattice in the $B2$ structure.

TABLE I. Irreducible double-group representations of the O_h point group spanned by atom-centered orbitals in the CsCl ($B2$) structure. A similar table for single-group representations may be obtained from information contained in Fig. 2.

	Γ	X	M	R
Cs s	Γ_6^+	X_6^+	M_6^+	R_6^+
Cs p	$\Gamma_6^- + \Gamma_8^-$	$2X_6^- + X_7^-$	$2M_6^- + M_7^-$	$R_6^- + R_8^-$
Cs d	$\Gamma_7^+ + 2\Gamma_8^+$	$2X_6^+ + 3X_7^+$	$2M_6^+ + 3M_7^+$	$R_7^+ + R_8^+$
Cs f	$\Gamma_6^- + 2\Gamma_7^- + 2\Gamma_8^-$	$3X_6^- + 4X_7^-$	$3M_6^- + 4M_7^-$	$R_6^- + 2R_7^- + 2R_8^-$
Cl s	Γ_6^+	X_6^-	M_7^+	R_7^-
Cl p	$\Gamma_6^- + \Gamma_8^-$	$2X_6^+ + X_7^+$	$M_6^- + 2M_7^-$	$R_7^+ + R_8^+$
Cl d	$\Gamma_7^+ + 2\Gamma_8^+$	$2X_6^+ + 3X_7^+$	$3M_6^+ + 2M_7^+$	$R_6^- + R_8^-$
Cl f	$\Gamma_6^- + 2\Gamma_7^- + 2\Gamma_8^-$	$3X_6^+ + 4X_7^+$	$3M_7^- + 4M_6^-$	$R_7^+ + 2R_6^+ + 2R_8^+$

fact that the $(z\uparrow, z\downarrow)$ atomic function based on the Cs atom transforms according to the M_6^- irreducible representation, while the same function based on the Cl atom transforms according to M_7^- . Similarly, for the single-group representations, one can differentiate between X_2 and X_3 from the fact that the Cs y^2-z^2 orbital contributes to the former and Cl y^2-z^2 to the latter Bloch function. Table I, furthermore, shows whether interaction between two atomic orbitals is forbidden by symmetry or not and which atomic orbitals are allowed to contribute to a Bloch state of a certain symmetry. We recall that with spin-orbit coupling included a Bloch state at any \mathbf{k} point in the BZ is at least twofold degenerate in a crystal that contains the inversion symmetry. This is the case for the $B2$ structure under consideration here.

III. SIMPLE-CUBIC CANONICAL BANDS

The calculations reported in this paper were performed with the well-documented^{16,17} linear muffin-tin orbital in the atomic spheres approximation (LMTO-ASA) method. We solved the scalar-relativistic Dirac equation self-consistently. The Hamiltonian containing this self-consistent potential and the spin-orbit coupling term was diagonalized only once in the space and spin coordinates to obtain the relativistic bands. About 100 \mathbf{k} points in the irreducible BZ were used in the self-consistency loop and all Brillouin-zone integrations were performed with the tetrahedron integration scheme.²¹ We used two energy panels, the lower panel to obtain the Cs p valence bands, and the upper one to obtain the halogen p valence bands as well as the conduction bands.

In the LMTO-ASA theory, the scalar-relativistic Hamiltonian is given by

$$H_{\mathbf{k}} = C + \Delta^{1/2} \frac{S_{\mathbf{k}}}{1 - \gamma S_{\mathbf{k}}} \Delta^{1/2}, \quad (1)$$

where C , Δ , and γ are potential parameter matrices diagonal in the angular momentum and atom indices. These three parameter matrices are, respectively, the band center, the bandwidth, and the distortion parameters linearized about an energy E_{ν} chosen in the energy range of interest. An energy eigenvalue E obtained from the diagonalization of the Hamiltonian, Eq. (1), is correct to the second order $(E - E_{\nu})^2$. For the sake of completeness, we

might mention that the fourth potential parameter that enters in the fourth-order correction to the energy is

$$\langle \phi_{\nu}^2 \rangle \equiv \int d^3r \left[\frac{\partial \phi(E)}{\partial E} \Big|_{E=E_{\nu}} \right]^2,$$

where $\phi(E)$ is the solution of the radial Schrödinger equation inside the atomic sphere with the energy E . The numerical value of $\langle \phi_{\nu}^2 \rangle^{1/2}$ is a measure of the energy range within which the linearization is valid. The structure constant matrix $S_{\mathbf{k}}$ entering into the Hamiltonian, Eq. (1), depends only on the type of lattice and is independent of the type of atoms making the crystal. Diagonalization of $S_{\mathbf{k}}$ with neglect of the nondiagonal part between different angular momenta produces the so-called canonical bands^{16,17} which contain many general features of the band structure for a particular lattice type. The canonical bands have been tabulated for the fcc, bcc, and the hcp structures.¹⁷ Here we present results for the canonical bands in the simple-cubic structure.

In Fig. 2 the canonical bands for the simple-cubic structure have been shown and the values at four symmetry points are listed in Table II. As is well known,^{17,22} the s canonical band diverges at the Γ point as $1/k^2$ but this divergence does not enter into the Hamiltonian as is clear from the form of Eq. (1). Following previous authors we have plotted the s canonical bands using a free-electron-like scale, $\tilde{S}_s = [1 - (4/\pi^2)S_s]^{-1}$. The p canonical bands have a discontinuity at the Γ point which disappears as a result of hybridization with bands of other angular momenta. Even though we do not use the f atomic orbitals in our calculation, we nevertheless show the f canonical bands as well, which may be useful for other simple-cubic compounds where f bands play a role.

As has been mentioned already, in the simple-cubic lattice there are two sites of O_h symmetry in the unit cell. In Fig. 2 the unbracketed symmetry labels refer to the symmetry of the Bloch function about the site on which the atomic orbitals constituting the Bloch function are centered. Bracketed labels refer to the symmetry of the same Bloch function about the other site with O_h symmetry but on which the atomic orbitals in question are not centered. In the case of the $B2$ structure, which may be viewed to be made up of two interpenetrating simple-cubic sublattices, each sublattice has the same canonical bands as shown in Fig. 2 except that the symmetry labels

TABLE II. Canonical bands S_{ii}^k at points of high symmetry in the simple-cubic structure with one atom in unit cell. The symmetry point coordinates are in units of π/a .

l	Γ (0,0,0)	X (1,0,0)	M (1,1,0)	R (1,1,1)				
s	1	$-\infty$	1	0.961	1	1.837	1	2.168
p	15		4'	-13.876	5'		15	
	15	6.000	5'		5'	-3.834	15	
	15	(-12.000)	5'	6.938	4'	7.668	15	0.000
d	12		2	-13.502	3	-21.386	25'	
	12	-17.134	1	-3.931	1	-6.403	25'	
	25'		5		5		25'	-13.151
	25'		5	2.621	5	4.268	12	
	25'	11.422	3	12.192	2	19.252	12	19.726
f	25		4'	-32.994	5'		2'	-23.510
	25		3'	-26.569	5'	-27.238	15	
	25	-10.216	5'		2'	-3.193	15	
	15		5'	-2.587	5'		15	-9.796
	15		2'	6.772	5'	1.113	25	
	15	5.676	5'		3'	22.787	25	
	2'	13.622	5'	28.982	4'	32.657	25	17.632

are different. As is indicated from the above discussions, unbracketed or bracketed labels in Fig. 2 are symmetries in the CsCl structure of Bloch functions made up of Cs or Cl orbitals, respectively. This is consistent with our convention of classifying the Bloch states according to the symmetry about the Cs atom.

The canonical bands contain valuable information as regards hybridization between various orbitals. The X_2 state, as seen from Fig. 2, for instance, is a pure Cs d state (omitting the Cl f contribution). An M_1 state on the other hand can be a combination of Cs s , Cs d , and Cl d states. This information is similar to what is already presented for double-group representations in Table I. The amount of hybridization between different atomic orbitals depends, of course, on the type of atoms constituting the crystal, i.e., through the band-center and the bandwidth parameters in Eq. (1).

As seen from Fig. 2, a general feature of the d bands in a simple-cubic solid with one atom in the unit cell is that the Γ_{12} state is always below the Γ'_{25} state. The interaction of s , p , and f orbitals with these two states is forbidden by symmetry. In the $B2$ structure the d orbitals of the two different species of atoms span the same $\Gamma_{12} + \Gamma'_{25}$ irreducible representations and therefore interact. As a result, the ordering of the Γ_{12} and Γ'_{25} states can, in principle, be reversed. As we shall see, in the case of the cesium halides, the hybridization between the d orbitals of the two atoms is sufficiently small that Γ_{12} is still below Γ'_{25} . When both atoms in the CsCl structure are the same, one obtains the bcc structure. In this case the Γ_{12} and Γ'_{25} states belonging to the Cs sublattice may be expected to interact rather strongly with the states of the same symmetry belonging to the Cl sublattice. One sees from canonical bands in the bcc structure¹⁷ that this interaction is so strong that now in fact Γ_{12} is above Γ'_{25} . Incidentally, this is also the case for the fcc structure as well. Generally speaking, these features of the canonical bands are retained in the electron band structure except for shifting

and rescaling of energy as seen from Eq. (1).

We now wish to estimate the magnitude of Γ_{12} - Γ'_{25} splitting in the sc, bcc, and fcc crystals with the same volume per atom (i.e., the same Wigner-Seitz sphere radius). From the canonical bands (Table II and Ref. 17) one sees that this splitting should be in the ratio 6.875 (fcc): 8.992 (bcc): -28.556 (sc) with the assumption that the bandwidth parameter Δ_d is the same for the three structures. Because of interaction between d orbitals based on the Cs or the Cl atoms, in the CsCl structure the Γ_{12} - Γ'_{25} separation might be different from the above-mentioned value of -28.556 units, depending on the strength of the interaction. In our calculation this separation turns out to be about -25 units for the cesium halides. Rössler⁴ has performed band calculations for CsI both in the fcc (rocksalt) as well as in the sc ($B2$) structure. His result that the Γ'_{25} - Γ_{12} separation is large (2.0 eV) in the sc structure and is quite small (0.2 eV) in the fcc structure is consistent with our results from the canonical bands as discussed above. Rössler correctly attributed this to differences in the crystal structure from a tight-binding analysis of interaction between the d orbitals.

IV. SCALAR-RELATIVISTIC CsCl BANDS

The scalar-relativistic bands in CsCl shown in Fig. 3, indicate the general features of the electronic band structure in the cesium halides with the spin-orbit coupling excluded. The Cl $3p$ bands constitute the highest valence bands with the Cs $5p$ bands occurring immediately below in energy. The lowest conduction bands are primarily of Cs s and Cs d atomic characters.

The valence Cl $3p$ bands generally resemble the canonical p bands, Fig. 2, in shape. Of course, as discussed before, the Γ_{15} state is triply degenerate unlike the canonical Γ_{15} state derived from the p orbitals. In the canonical p bands, M'_2 forms the top of the band, with Γ_{15} occurring

even below the X_5 state, i.e., the ordering is $M'_2 > X_5 > \Gamma_{15}$. In the electron bands this ordering could be modified as a result of interaction of the p orbitals with other orbitals as follows. The X_5 state is pushed down in energy as a result of interaction with Cs d orbitals. Omitting contributions from $l \geq 3$ orbitals, in the $B2$ structure M'_2 is a pure Cl p state, while the Cl- p -derived Γ_{15} state is pushed up in energy through the interaction with the lower-lying Cs p orbitals. Thus, depending on the strength of interaction between the valence cation p and anion p orbitals, either M'_2 or Γ_{15} forms the valence-band top. This might, of course, be modified through spin-orbit coupling. In the CsCl scalar-relativistic bands, M'_2 occurs just below Γ_{15} so that the direct band gap at Γ is the fundamental gap.

The Γ_{15} state consists of antibonding Cl p orbitals (97%) with about 3% admixture from the Cs p orbitals. Along the Δ line, the highest valence state with Δ_5 symmetry has increasing admixture from the Cs d orbitals at the expense of the Cs p orbitals. The X_5 state which is the highest valence state at the X point has about 96% Cl p and the rest Cs d character. Along the Σ line starting from Γ , the Cl p character of the Σ_3 valence-band top first decreases slightly before increasing so that the M'_2 state is a pure Cl p state. The X_1 state constituting the bottom of the Cl p valence bands consists of bonding Cl p orbitals pointed along the direction of the Bloch vector.

The lowest conduction bands are primarily of Cs s and Cs d characters. From the canonical simple-cubic d bands, M_3 should be the lowest of the Cs d bands lying below Γ_{12} . In spite of hybridization with other orbitals, this feature is still retained in the CsCl scalar-relativistic bands. The conduction-band bottom has Γ_1 symmetry and has about 51% Cs s and the rest Cl- s character. It may be mentioned here that if relativistic effects are totally omitted, then Γ_1 lies above Γ_{12} in energy,^{8,13} an ordering that is inconsistent with experiments. The importance of the relativistic effects for the conduction-band struc-

ture for CsI was observed by Onodera⁵ quite early. As we have discussed earlier in connection with canonical bands, the occurrence of the Γ_{25} state above the Γ_{12} state is a consequence of the simple-cubic crystal structure.

V. RELATIVISTIC ELECTRON STATES IN THE CESIUM HALIDES

A. Electron band structure

The calculated electron bands for the three cesium halides, with inclusion of the spin-orbit coupling, are shown in Fig. 4. The major effect of the spin-orbit coupling, as is indicated by a comparison of Figs. 3 and 4(a), is to split the Cs $5p$ and halogen p valence bands. The splitting of the Cs $5p$ valence bands at the Γ point is more or less the same for all three compounds, about 0.135 Ry. As might be expected, the spin-orbit splitting of the halogen p valence bands increases as the halogen atom becomes heavier. At the Γ point this splitting is 0.014 Ry for CsCl, 0.043 Ry for CsBr, and 0.088 Ry for CsI. The corresponding splittings, as obtained from the experiments of Ref. 2, are, respectively, 0.017, 0.038, and 0.076 Ry. These values are roughly the same as the spin-orbit splitting in the atom. The low-lying conduction bands, being of s and d atomic characters in general, are not affected appreciably by the spin-orbit coupling term.

The calculated bands for the three compounds are very similar. Contrary to the early results of Donato *et al.*,¹⁵ we find that the band gap is direct and occurs at the Γ point in each case. As in all local-density calculations, the magnitudes of the band gaps are underestimated, but the experimental trend (gaps of CsCl > CsBr > CsI) is reproduced from our calculation.

The conduction-band bottom has the Γ_6^+ symmetry in all cases with the d -like Γ_8^+ state occurring immediately above in energy. The interband edge at the M point occurs close in energy to the fundamental gap at the Γ point and may be relevant to the interpretation of the optical spectra.⁵ At the M point the valence-band top has the M_7^- symmetry in all three cases, while the symmetry of the lowest conduction state changes from M_7^+ for CsCl to M_6^+ for CsI. For CsBr the M_7^+ and M_6^+ states lie very close to each other in energy. The topology of bands around the X and R points also show some differences.

B. Deformation potential

The calculated deformation potentials $dE/d \ln V$ for the two interband transitions $\Gamma_8^- \rightarrow \Gamma_6^+$ and $\Gamma_8^- \rightarrow \Gamma_8^+$ are given in Table III. The calculated deformation potentials for CsI are in reasonable agreement with the corresponding experimental values as is discussed in Ref. 8. To the author's knowledge similar experiments for CsCl and CsBr have not been performed.

The increase in energy of the s -like Γ_6^+ conduction state under volume compression can be understood in terms of the kinetic energy increase due to confinement. In contrast, the energy of the Γ_8^+ conduction state decreases because the shorter lattice constant increases the magnitude of the bonding interaction between the d orbitals.²³ The

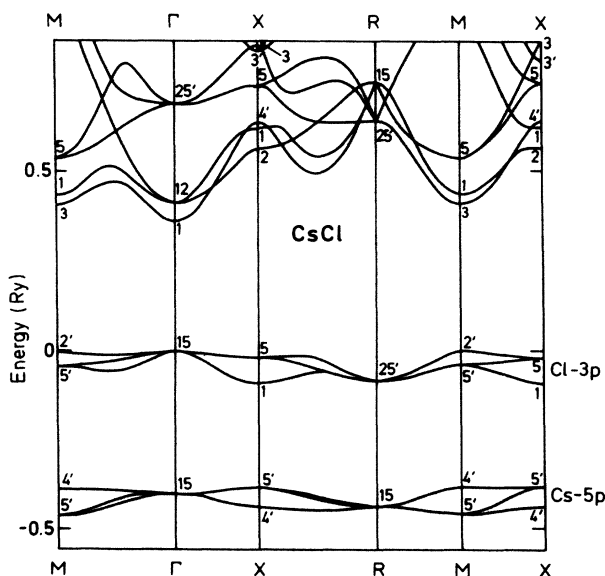


FIG. 3. Scalar-relativistic electron bands in CsCl.

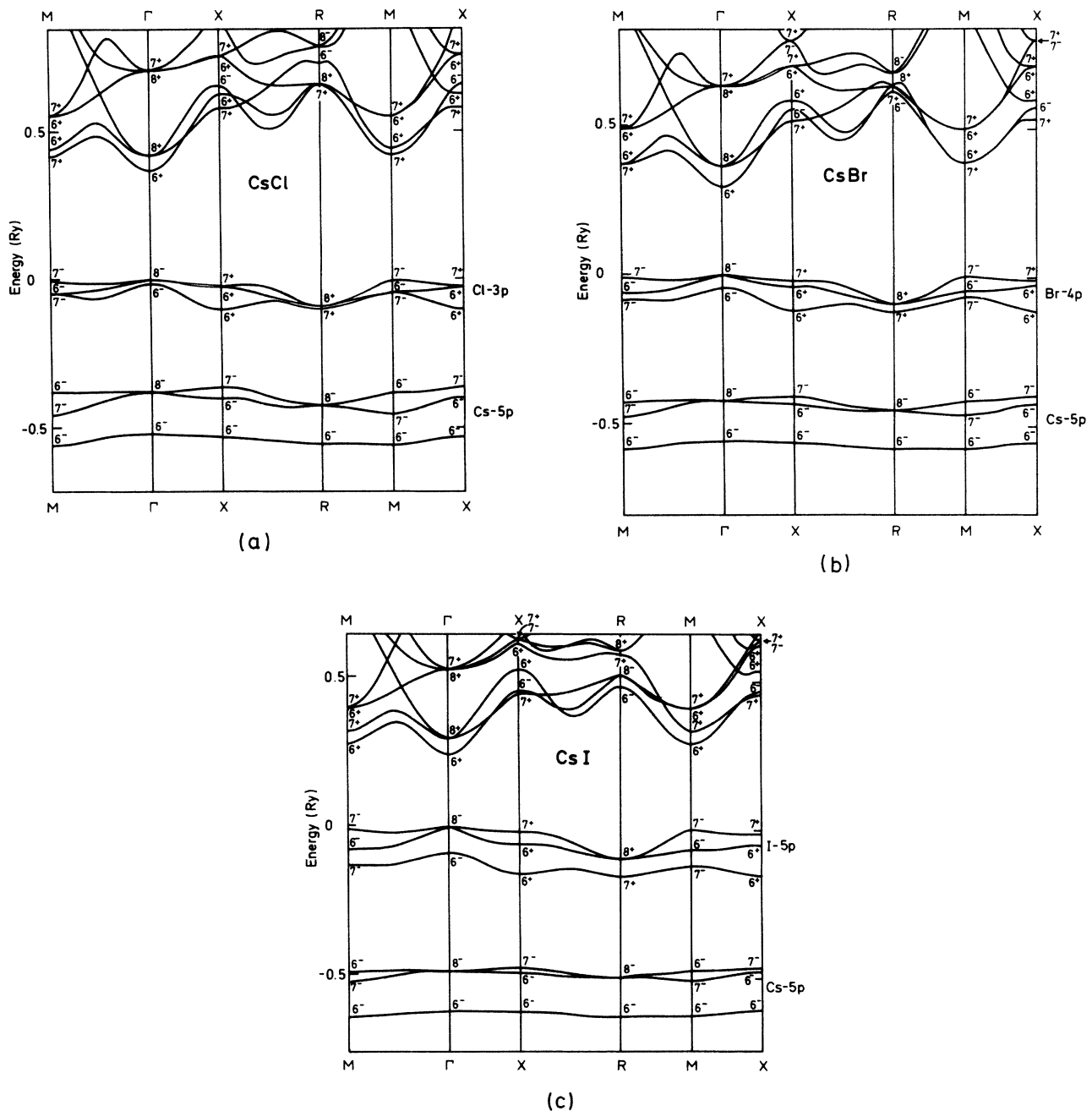


FIG. 4. Relativistic electron bands in the cesium halides: (a) CsCl, (b) CsBr, and (c) CsI.

opposite shifts indicate that under pressure the Γ_6^+ and Γ_8^+ states should cross and beyond a critical pressure the d -like Γ_8^+ state should become the conduction-band bottom. Such an s - d transition has indeed been observed for CsI. Similar experiments for CsCl and CsBr would be of interest.

TABLE III. Calculated deformation potentials $dE/d \ln V$ for interband transitions. Energies are in units of eV.

Transition	CsCl	CsBr	CsI
$\Gamma_8^- \rightarrow \Gamma_6^+$	-5.28	-4.16	-3.51
$\Gamma_8^- \rightarrow \Gamma_8^+$	0.79	1.31	2.25

From our calculated $\Gamma_8^+ - \Gamma_6^+$ separation and the calculated deformation potentials, we estimate that the s - d transition should occur at a volume compression of about 0.12 for CsCl and CsI and about 0.18 for CsBr. The corresponding pressures, using the experimental values of the bulk moduli, are about 20, 26, and 14 kbar for CsCl, CsBr, and CsI, respectively. However, as is indicated from the experiments on CsI where the s - d transition occurs around 5 kbar, our results seem to overestimate the transition pressures by a factor of 2 to 3. It is furthermore clear from what has just been said concerning the s - d transition of the conduction-band bottom and the signs of the deformation potentials shown in Table III that under pressure the fundamental band gaps of all

TABLE IV. Calculated effective-mass parameters for the cesium halides. The parameters are defined in the text.

Parameter	CsCl	CsBr	CsI
Valence Γ_6^- : $(2m_e/\hbar^2)A$	-0.76	-0.87	-0.98
Valence Γ_8^- : $(2m_e/\hbar^2)A'$	-0.92	-1.16	-1.54
$(2m_e/\hbar^2) B $	0.60	0.85	1.24
$(2m_e/\hbar^2)^2C^2$	-0.17	-0.97	-3.12
Conduction Γ_6^+ : $(2m_e/\hbar^2)A''$	3.25	3.70	4.02
Conduction Γ_8^+ : $(2m_e/\hbar^2)(J+K)$	1.62	1.70	1.95
$(2m_e/\hbar^2) J-K $	1.16	1.22	1.40

three cesium halides should at first increase before finally decreasing in magnitude.

C. Effective-mass parameters

From $\mathbf{k}\cdot\mathbf{p}$ perturbation theory²⁴ the electron energy in the neighborhood of the Γ point for various bands is given by

$$E(\mathbf{k}) = E(\Gamma_6^-) + Ak^2, \quad (2a)$$

$$E(\mathbf{k}) = E(\Gamma_8^-) + A'k^2 \pm [B^2k^4 + C^2(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)]^{1/2}, \quad (2b)$$

$$E(\mathbf{k}) = E(\Gamma_6^+) + A''k^2, \quad (2c)$$

$$E(\mathbf{k}) = E(\Gamma_8^+) + k^2 \left[\frac{\hbar^2}{2m_e} + J + K \right] \pm (J - K)[k^4 - 3(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)]^{1/2}. \quad (2d)$$

We found that our calculated bands can be fitted very well with the above expressions in the neighborhood of the Γ point and the effective-mass parameters obtained this way are tabulated in Table IV. The calculated effective masses for the isotropic valence band and the conduction band, viz., $(2m_eA/\hbar^2)^{-1}$ and $(2m_eA''/\hbar^2)^{-1}$, decrease as one

goes down the series from CsCl to CsI. We expect this trend in the effective masses to be correct; however, we do not believe that the absolute values of the effective masses, especially for the conduction bands, can be reproduced from the local-density calculations.²⁵ Unfortunately, experimental values of the effective masses for the cesium halides do not yet exist in the literature.

VI. COHESIVE PROPERTIES

As might be expected from the atomic sizes (for example, covalent radii are $r_{\text{Cs}}=2.35$ Å, $r_{\text{Cl}}=0.99$ Å, $r_{\text{Br}}=1.14$ Å, and $r_{\text{I}}=1.33$ Å), the lattice constant down the series from CsCl to CsI increases in magnitude experimentally.²⁶ The calculated lattice constants also reproduce this trend, as may be seen from Table V. The cohesive energy per ion pair—defined here as the total energy of the ion pair in the solid minus, that of the free, neutral atoms—is a quantity easily measured from thermochemical experiments. The calculated cohesive energies in agreement with the experimental values²⁷ show that the cohesive energy decreases down the series, i.e., CsCl > CsBr > CsI.

The cohesive natures in the three compounds are very similar to one another, as one might expect. The calculated partial pressures and the partial bulk moduli are shown

TABLE V. Theoretical and experimental equilibrium lattice properties of the cesium halides. (Theoretical results are as obtained from scalar-relativistic calculations.)

Parameter	CsCl	CsBr	CsI
Lattice constant (Å)			
Theoretical	4.085	4.241	4.475
Experimental	4.120	4.295	4.567
Bulk modulus ^a B (kbar)			
Theoretical	206	169	111
Experimental	167	143	119
Pressure derivative dB/dP			
Theoretical	5.84	5.99	6.40
Experimental	5.98	5.95	5.93
Cohesive energy ^{b,c} (Ry/atom pair)			
Theoretical	-0.42	-0.39	-0.28
Experimental	-0.49	-0.46	-0.41

^aThe theoretical B and dB/dP reported here are calculated at the experimental lattice constant.

^bThe cohesive energies are with respect to the energy of the neutral atoms.

^cExperimental cohesive energy is at $T=298$ K evaluated from Ref. 26.

in Fig. 5. The principal contribution to the repulsive pressure comes from the Cs and the halogen p orbitals which may be interpreted to be caused by the increase of the electron kinetic energy due to confinement. The repulsive term is balanced by an attractive pressure coming from the Madelung term as well as from the Cs d and halogen d orbitals. The d bands are *unoccupied* in the cesium halides; however, admixture of the bonding d orbitals

with the valence states, which increases with compression, produces an attractive pressure. The partial pressures of the s orbitals are comparatively far lower.

Traditionally, cohesive properties of the ionic solids are understood in terms of the Born-Mayer model. In this model the total energy consists of an attractive Madelung energy plus a repulsive energy term:

$$E = -\frac{A}{d} + B \exp(-d/\rho). \quad (3)$$

Here d is the bond length, A is the Madelung constant, and B and ρ are repulsive parameters. The Madelung constant referred to the bond length is $A = 1.865534 \text{ Ry } \text{Å}$ for the $B2$ structure. The repulsive term of the type b/d^n (b is a constant) is sometimes used instead of the exponential form $\exp(-d/\rho)$, but the latter form is favored from quantum-mechanical considerations.²⁸ It turns out that within this model the cohesive energy coming from the Madelung term is reduced by only about 10% because of the repulsive term. Within this model the trend in the cohesive energy (Table V) can be understood in terms of the increasing bond length down the series $\text{CsCl} < \text{CsBr} < \text{CsI}$. The increasing separation between the two ions results in a diminishing value of the Coulomb interaction. This indicates a decreasing trend in the cohesive energy consistent with the experimental as well as with our calculated results.

The Born-Mayer model, although oversimplified, is physically appealing and describes cohesive properties of ionic solids remarkably well. In this model no attempt is made to evaluate the repulsive energy parameters from a quantum-mechanical calculation, rather these parameters are calculated from the experimental lattice data. With the aim of seeing if the Born-Mayer model total energy fits with our calculated total energy, we subtracted the classical Madelung term (i.e., with unit charge transfer) from the calculated total energy. The remaining energy defines the repulsive term $E_R(d)$ which is plotted in Fig. 6 as a function of the bond length d . We find that we can fit the calculated "repulsive energy" extremely well with either of the two forms:

$$E_R(d) = 2.2 \times 10^4 \exp[-d/(0.291 \text{ Å})] \text{ Ry}$$

or

$$E_R(d) = 1.9 \times 10^5 \text{ Ry}/d^{11.3}.$$

Here, d is the bond length in Å . The Born-Mayer total energy with these repulsive terms, by construction, reproduces the theoretical lattice constant as well as the bulk modulus. For comparison, the empirical, Born-Mayer repulsive term fitted to reproduce correctly the experimental data is

$$E_R(d) = 1.2 \times 10^4 \exp[-d/(0.312 \text{ Å})] \text{ Ry}$$

or

$$2.4 \times 10^5 \text{ Ry}/d^{11.07}.$$

The Born-Mayer model has the *ad hoc* assumption that there is a unit charge transfer in CsI. Charge transfer in a solid is, of course, an ill-defined quantity since charge

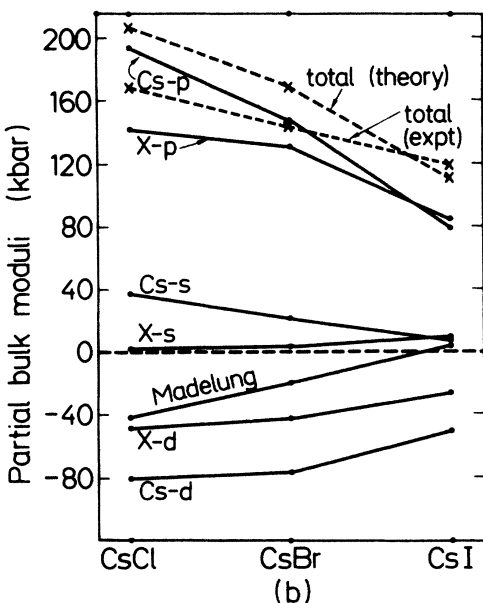
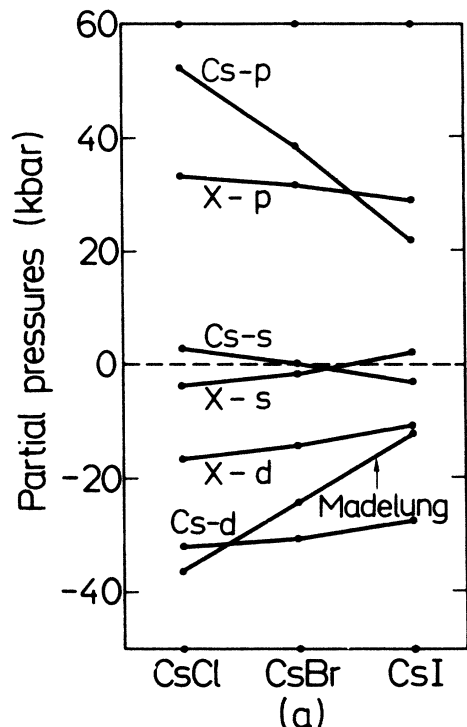


FIG. 5. (a) Partial pressures and (b) partial bulk moduli at the equilibrium lattice volume for the cesium halides. Straight lines are drawn to help the eye. The attractive Madelung and d pressures counterbalance the repulsive pressure originating from the p orbitals.

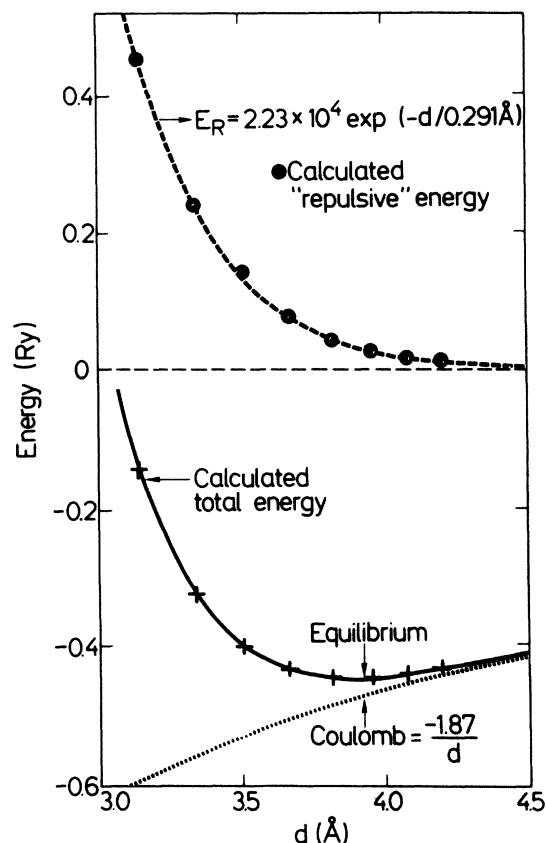


FIG. 6. Calculated total energy of CsI and its partition into a Coulomb term and a "repulsive" term. The repulsive part can be fitted very well with an exponential Born-Mayer repulsive energy over the entire range of the lattice constants for which calculation was performed.

cannot be partitioned among the atoms in an unambiguous way. With the definition that the charge belonging to an atom in the solid is that contained within the atomic muffin-tin sphere, at equilibrium about 0.6 electrons are transferred from the Cs to the I atom, assuming equal atomic sphere radii for the two atoms.⁸ Any other reasonable choice of the sphere radii does not drastically change this number. The corresponding calculated charge transfers for CsBr and CsCl are about 0.7 and 0.8, respectively.²⁹ The calculated charge-transfer trend is consistent with Pauling's rule³⁰ connecting the amount of ionic character in a single bond to the electronegativities of the two atoms, according to which CsCl should be the most ionic

and CsI the least. Apart from incomplete charge transfer (i.e., less than unit charge transfer between the two ions), its magnitude varies as the crystal volume is changed. Considering this, it is not physically apparent why the Born-Mayer total-energy expression should fit the first-principles calculated total energy so well.

VII. SUMMARY

The calculations presented here demonstrate that the electron bands in CsCl, CsBr, and CsI in the *B2* structure are essentially similar, in agreement with the speculations of Nosenzo and Reguzzoni² based on an analysis of optical experiments. The band gap is direct and occurs at the Γ point between the Γ_8^- valence state and the Γ_6^+ conduction state, in all cases. From the similarity of the bands in the three compounds, we speculate that as in the case of CsI, crossover between the conduction Γ_6^+ and Γ_8^+ states would also occur in CsBr and CsCl as pressure is applied. Consequently, the fundamental gap at the Γ point for all three compounds should first increase before finally decreasing as pressure is applied.

The calculated lattice constants, bulk moduli, cohesive energies, etc., show a clear trend in agreement with experiments. Equilibrium in the solid is determined through the competition between *p* orbitals which generate repulsive forces and the *d* orbitals, as well as the Madelung term which give rise to the counterbalancing attractive force. We find that for CsI the calculated total energies (over the entire range of lattice constants $a = 3.1$ to 4.2 Å for which calculation was performed) can be fitted very well to the total-energy expression, a classical Madelung term plus a repulsive term, of the Born-Mayer model. Our quantum-mechanical results are, however, equally compatible with an exponential or a power-law form for the Born-Mayer repulsive energy.

Apart from the above results for the cesium halides, we also presented the simple-cubic canonical bands as well as some symmetry properties of the Bloch states which are applicable to the entire class of compounds in the *B2* structure. These canonical bands are, furthermore, relevant for crystals in which a simple-cubic sublattice of identical atoms is present.

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