Electronic band structure, phonons, and exciton binding energies of halide perovskites CsSnCl₃, CsSnBr₃, and CsSnI₃

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The halide perovskites $CsSnX_3$, with X = Cl, Br, I, are investigated using quasiparticle self-consistent *GW* electronic structure calculations. These materials are found to have an "inverted" band structure from most semiconductors with a nondegenerate *s*-like valence band maximum (VBM) and triply degenerate *p*-like conduction band minimum (CBM). The small hole effective mass results in high hole mobility, in agreement with recent reports for CsSnI₃. The relatively small band gap changes from Cl to Br to I result from the intra-atomic Sn *s* and Sn *p* characters of the VBM and CBM, respectively. The latter is also responsible for the high oscillator strength of the optical transition in these direct-gap semiconductors and hence a strong luminescence and absorption. The band gap change with lattice constant is also anomalous. It increases with increasing lattice constant, and this results from the decreasing valence band width due to the decreased Sn *s* with anion *p* interaction. It leads to an anomalous temperature dependence of the gap. The changes in band gap in different lower-symmetry crystallographic phases is studied. The exciton binding energy of the free exciton, estimated from the Wannier-Mott exciton theory and the calculated dielectric constants and effective masses, is found to be two orders of magnitude smaller than previously claimed in literature, or of the order of 0.1 meV. The photoluminescence peak previously assigned to the free exciton is instead ascribed to an acceptor bound exciton. The phonons at the Γ point are calculated as well as the related enhancement of the dielectric constants.

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I. INTRODUCTION

The halide perovskites with the formula $CsSnX_3$, with X = Cl, Br, and I, form an interesting family of materials with unusual properties. Like the much more studied oxide perovskites, they undergo a number of phase transitions to lower-symmetry structures, starting from a cubic perovskite structure at high temperature.¹⁻⁴ These phase transitions correspond mostly to rotations and distortions of the SnX_6 octahedra, leading to a closer packing. In CsSnI₃ these structures correspond to the so-called black phase, but there is also a higher band gap yellow phase with a different, even denser structure.^{4,5} In the perovskite structure, the SnX_6 octahedra corner share, and thus each halide ion counts for one half, resulting in the formula $CsSnX_3$. The cubic structure can be understood as a CsCl packing of large Cs⁺ ions and $\text{Sn}X_3^{-1}$ units. This means that the Sn in the compounds is divalent. The bonding thus can be viewed as strongly ionic. Nevertheless, the band gaps are relatively small, of the order of 1-3 eV, compared to, for example, Cs halides, and most surprisingly, only relatively small changes occur, especially from one halide to the next, especially in the Br to I case (1.38 to 1.01 eV). As we will show in this paper, several unusual properties of this materials family result from the intracluster SnI₆ bonding. Interestingly, Cs in the structure can be replaced by other large monovalent ions, for example, Rb and Tl, or even organic radicals,¹ such as methylammonium CH₃NH₃⁺¹ and formamidinium $NH_2CH = NH_2^{+1}$.

Recently, a few of the unusual properties of black-phase $CsSnI_3$ have attracted interest for applications. Some of these result from the low-temperature process ability of the material. $CsSnI_3$ is soluble in certain organic solvents and can thus be deposited on various substrates or even inside a porous structure by solution processing.⁶ The strong luminescence at a band

gap close to that of Si^{4,7} and strong absorption at shorter wavelengths make CsSnI₃ attractive as a solar luminescent concentrator material⁸ or as a solar-cell absorber.⁹ It was recently shown⁶ that its high hole mobility⁴ make it an excellent allsolid-state replacement for the electrolyte in a dye-sensitized Grätzel-type solar cell with TiO₂. It was found that CsSnI₃ itself strongly contributes to the optical absorption, although the overall performance still is aided by the organic dyes.

However, many of its properties are still rather poorly understood. For instance, it is presently not clear whether the strong luminescence is intrinsic, i.e., due to free excitons, or due to defect bound excitons. The effects of crystal structure on the luminescence strength are poorly understood and are crucial for the indicated solar-cell-concentrator approach. Until recently,⁴ progress was strongly hampered by the difficulty in obtaining phase-pure CsSnI₃ material and the rapid conversion of the black phase to the yellow phase of CsSnI₃ in air. The electrical conductivity is only poorly understood. Although a high hole mobility of ~585 cm² V⁻¹ s⁻¹ was reported, a relatively low carrier concentration of the order of only 10^{17} cm⁻³ and a metallic-like decreasing conductivity with temperature were obtained in Ref. 4.

Besides these few applications presently under investigation, other possibilities have not yet been explored. In view of their close similarity to oxide perovskites in structure, these materials may have interesting piezoelectric or even ferroelectric properties in the lower-symmetry phases. The relatively heavy ions combined with strongly ionic bonding lead to low-frequency modes,^{10,11} which may result in large phonon enhancements of the dielectric constant. Recently,¹² third-order enhanced Raman spectra were reported for CsSnI₃. Heavy ions like Cs also make these materials suitable for capturing γ rays and, combined with their strong luminescence, may be excellent scintillation materials for detectors. This idea was recently proposed by Sing¹³ for closely related Tl- instead of Cs-containing compounds, TlGeI₃, TlSnI₃, and TlPbI₃.

Their band structures have been studied theoretically in a few previous papers.^{14–17} These papers focused mostly on the changes in band structure with crystal structure and, because they were based on density functional theory (DFT) in the local-density approximation (LDA), strongly underestimated the gaps. In the early literature, there is even significant discussion on whether they are semiconductors or semimetals.^{14,15} Only the most recent study⁴ used the screened exchange method, which gives larger gaps for CsSnI₃, but it still obtained a smaller gap than experiment for the black phase.

Here we present a study of the electronic band structure of the CsSnX₃ compounds with X = I, Br, Cl. Using the quasiparticle self-consistent GW method (QSGW).^{18,19} We first present the basic band structures in the cubic perovskite structure. Analyzing the atomic orbital character of the bands provides immediate insights into some of the questions mentioned above. These are all explained in terms of the SnI_6 intracluster nature of the band gap. The changes with crystal structure are found to be in fair agreement with previous theory work. However, it is only after adding the QSGW quasiparticle corrections that we can make a quantitative comparison of the gaps with experiment. We next address another anomaly on the exciton binding energy.²⁰ We will show that a large exciton binding energy (of the order of 12 meV) is indeed obtained if the electron-hole interaction is only screened by the high-frequency dielectric constant. However, we find that the phonons increase the dielectric constant by a factor of 9.9 and hence lead to two orders of magnitude smaller exciton binding energy if their contribution to the screening is included. The analysis of the previous experimental data is revised.

II. COMPUTATIONAL METHOD

The starting point for our band structure calculations is the LDA to the DFT. The full-potential linearized muffin-tin orbital method (FP-LMTO)^{21,22} was used for the band structure calculations. The basis set in this method is characterized by the smoothed Hankel function decay parameter κ and its smoothing radius R_{sm} . Inside muffin-tin spheres, the wave functions are augmented by ϕ and $\dot{\phi}$ functions, which are solutions to the radial Schrödinger equation and its energy derivative at some chosen linearization energy ϵ_{vRl} , specific to each orbital at atomic site R and angular momentum l. In the present calculations, we use two (κ, R_{sm}) , the first for spd and the second for sp orbitals, on Cs, Sn, and the halide ion. For Cs, we treat the 5p states as bands. A 6p orbital was added as a local orbital in some test calculations but was found to have little effect. For Br and I, we include the 4s and 5s semicore orbitals as local orbitals and the empty 5s and 6s as band orbitals, respectively. Inside the spheres augmentation is done up to $l_{\text{max}} = 4$. Brillouin zone integrations are done with a $10 \times 10 \times 10$ k-point mesh. We emphasize that although a muffin-tin construction is utilized in defining the basis set, the actual "full potential" has no shape approximations; it is neither spherical inside the atoms nor constant in between the atoms.

Because the LDA underestimates band gaps, we next use the QSGW method to recalculate the band structures more accurately. In the GW method of Hedin²³ the exchangecorrelation self-energy of the quasiparticle excitations is obtained as a product of the one-electron Green's function G^0 and the screened Coulomb interaction W^0 , schematically, $\Sigma =$ iG^0W^0 . The screening $W^0 = \varepsilon^{-1}v = [1 - \Pi^0 v]^{-1}v$ itself is calculated in terms of the independent particle polarizability $\Pi^0 = -iG^0 \times G^0$ given in terms of the Green's function. The self-energy provides a shift of the one-electron eigenvalues as well as a lifetime through its imaginary part. The difference with QSGW is that the independent Hamiltonian H^0 from which G^0 is derived is chosen to make the difference between the quasiparticle energies and the independentparticle energies as small as possible by adding a Hermitian but nonlocal exchange correlation potential change to the LDA derived from the GW self-energy, which is then iterated to self-consistency. For details, see Refs. 18 and 19. This method has been shown to give quite accurate and systematic results for a large number of materials. In particular, band gaps are usually slightly overestimated because of the random phase approximation treatment of the screening. It was found that this can be further corrected by reducing Σ by a somewhat arbitrary ad hoc correction of a factor of 0.8. In the present work, however, we report pure QSGW results. Zero-point motion corrections are not included here because we have currently no reliable way of estimating them in these materials and they are expected to be relatively small in these low-gap materials.

The QSGW approach is used here in conjunction with the FP-LMTO implementation. An important point here is that it allows us to obtain a real-space representation of Σ in the basis of atom-centered muffin-tin orbitals. By a reverse Fourier transform, this then allows calculating the GW corrections at arbitrary \mathbf{k} points, even if the GW calculation is performed only on a relatively coarse k-point mesh. This allows us to display the full band structure at the GW level and to extract reliable effective masses from the band dispersion. The convergence of the results with the GW k-point mesh used was carefully studied along with its dependence on the parameters of the LMTO basis set. Slightly more localized basis functions than for the total-energy LDA calculations are used, and a mesh of $5 \times 5 \times 5$ was found to be adequate for the cubic perovskite structure. For the tetragonal β phase, a correspondingly dense mesh is used. Spin-orbit (SO) coupling (calculated at the LDA level) can be added as a separate term in the Hamiltonian.

The phonon calculations were performed using the density functional perturbation theory (DFPT)^{24,25} using normconserving pseudo-potentials²⁶ and within the LDA. The ABINIT code²⁷ was used for these calculations. A plane wave cut-off energy of 100 Hartree was used and a $4 \times 4 \times 4$ **k**-point mesh. Only phonons at the Γ point are calculated. The phonons were calculated at the equilibrium lattice constants of the LDA, which were found to be about 3% lower than the experimental values within the pseudopotential plane-wave method using the ABINIT code.

III. RESULTS

A. Band structures

The LDA usually slightly underestimates the lattice constants. In the present case, for the cubic phases, we obtained

TABLE I. Lattice constants for $\text{CsSn}X_3$. Note that α , β , and γ phases are cubic, tetragonal, and orthorhombic, respectively, while the *M* phase is monoclinic and the *Y* phase is orthorhombic.

Material	Space group	Lattice constants (Å)
α -CsSnCl ₃ ^a	Pm3m	a = 5.56
M-CsSnCl ₃ ^b	$P2_1/n$	a = 16.10, b = 7.425, c = 5.74
		$\beta = 93.2^{\circ}$
α -CsSnBr ₃ ^a	Pm3m	a = 5.804
β -CsSnBr ₃ ^c	P4/mbm	a = 8.195, b = 5.805
α -CsSnI ₃ ^d	Pm3m	a = 6.219
β -CsSnI ₃ ^d	P4/mbm	a = 8.772, b = 6.261
γ -CsSnI ₃ ^d	Pnam	a = 8.688, b = 8.643, c = 12.378
Y-CsSnCl ₃ ^e	Pnam	a = 10.328, b = 17.677, c = 4.765

^aBarrett *et al*.²⁸

^bPoulsen and Rasmussen.²⁹

^cScaife *et al*.³⁰

^dYamada *et al*.³

^eMauersberger and Huber.⁵

an underestimate of the lattice constant by about 1.5%-2%using the all-electron LMTO method. Therefore we prefer to use the experimental lattice constants for our band structure calculations. In Tables I and II the lattice constants and internal parameters used in this paper are summarized. For the β phase of CsSnI₃ we also performed LDA calculations to minimize the structure with respect to the internal parameters and found excellent agreement with the experimental values to 0.001 precision.

For CsSnCl₃ we also performed LDA calculations for the monoclinic phase, which has a rather different crystal structure,²⁹ and we also calculated the band structure of the yellow phase of CsSnI₃ in the LDA.

We start analyzing the band structures in the cubic perovskite phase. Figure 1 shows the band structures of $CsSnX_3$, with X = Cl, Br, I, obtained in the QSGW method without spin-orbit coupling and the corresponding partial densities of states. The dominant orbital character of the bands can be described as follows. At about -15 eV below the valence band maximum (VBM), in CsSnI₃, we find the I 5*s* bands. In the CsSnBr₃ and CsSnCl₃ cases these bands move farther down, reflecting the deeper atomic energy levels in the earlier elements of the periodic table. The next narrow band corresponds to the Cs 5*p* semicore levels. Then we find a band which is a bonding combination of Sn 5*s* and I 5*p*, followed by

TABLE II. Atomic coordinates of β and γ CsSnI₃. The position column gives the Wyckoff position and site point group.

Material	Atom	Position	x	у	Z
β -CsSnI ₃	Cs	2d(mmm)	0	0.5	0
β -CsSnI ₃	Sn	2b(4/m)	0	0	0.5
β -CsSnI ₃	I(1)	2a(4/m)	0	0	0
β -CsSnI ₃	I(2)	4h(mm)	0.210	0.290	0.5
γ -CsSnI ₃	Cs	4c(m)	0.006	-0.040	0.25
γ -CsSnI ₃	Sn	4b(T)	0.5	0	0
γ -CsSnI ₃	I(1)	4c(m)	0.476	0.000	0.25
γ -CsSnI ₃	I(2)	8 <i>d</i> (1)	0.294	0.705	-0.019

mostly I 5*p* states and a band which is antibonding between Sn 5*s* and I 5*p*. The conduction band minimum (CBM) is dominated by Sn 5*p* states, but higher up there are also I 5*p* antibonding orbital contributions, and above 5 eV, there is a significant Cs 5*d* contribution. The energy levels at the *R* point where the minimum direct gap occurs are symmetry labeled for the CsSnI₃ case, and the same labels apply for the other cases.

We can see that the band gap in all three materials is direct at the point $R = (1,1,1)\pi/a$. The VBM is nondegenerate, while the conduction band minimum is threefold degenerate without SO coupling and splits into a doublet and a quadruplet (including spin) when SO is included, as is illustrated for CsSnI₃ in Fig. 2 The spin-orbit splittings are summarized in Table III. This is opposite from what is found in most compound semiconductors with tetrahedral bonding. We therefore call it an "inverted" band structure. We note that this term should not be confused with a so-called band inversion, a term recently applied to topological insulators for the case where there is actually a negative gap in the absence of spin-orbit coupling because the cation *s*-like conduction band dips below the anion *p*-like valence band.

To obtain further insight into why this happens, we analyze the atomic orbital character of the bands. This is shown in Fig. 3. In Fig. 3, the color intensity indicates how much a chosen atomic orbital is present in the eigenstates at each **k** point. One can see that the CBM is composed mostly of Sn p states. The VBM, on the other hand, is a mixture of I p and Sn s states. These two form an antibonding combination. The reason why there is a strong $Sn \ s$ to anion p orbitals at this particular **k** point is that at **k** point *R*, the *p* orbitals on opposite sites of the unit cell differ by a phase factor $e^{i\mathbf{k}\cdot\mathbf{T}} = -1$, and hence the p orbitals all point with the same lobe of the orbital inward toward the Sn s, as shown in Fig. 4. They thus belong to the same irreducible representation a_{1g} of the cubic group and have a strong interaction with each other. This means that the gap is to a large extent intra-atomic between Sn s and Sn p.

In fact, further group theoretical analysis, following the notation of Bose *et al.*,¹⁵ shows that the CBM has R_{15} symmetry, while none of the I 5*p* orbital combinations on the faces of the unit cell belong to this irreducible representation. It also does not interact with the Cs 5*p* below. There is some interaction with the I 5*s* states, which do form a R_{15} linear combination at point *R* but which lie very deep so that the upper state has little I 5*s* contribution. There is also some interaction with Cs 5*d* states higher up which also belong to R_{15} . This interaction will tend to reduce the gap. On the other hand, the I 5*p* with Sn *s* interaction leading to the two states of symmetry R_1 is clearly very strong because the levels are close to each other and thus there is a very strong hybridization. The Cs 6*s* on the corners of the unit cell form a $R_{2'}$ irreducible representation, which would only interact with *f* states at the center.

The natures of the CBM and VBM explain a number of the intriguing properties of these materials. First, they explain the "inverted" nature of the band structure. Second, they show that strong optical transitions are expected between the VBM and the CBM because they have an allowed $\Delta l = 1$ dipole character on the same atom. Third, they show that the gap is essentially controlled by the Sn *s* to I *p* covalent



FIG. 1. (Color online) QSGW band structures and partial densities of states of α -CsSnI₃, α -CsSnBr₃, and α -CsSnCl₃.



FIG. 2. (Color online) Energy bands of $CsSnI_3$ in the QSGW method near the gap including spin-orbit coupling.

antibonding interaction. For instance, with an increasing lattice constant, one expects this interaction to become weaker, and hence the valence band width will be decreased and the gap will be increased. We will see below that this is confirmed directly by the calculations, and it also explains the anomalous temperature behavior of the gap. It also explains why to zeroth order the gap is not as strongly dependent on the anion as one might think. In fact, it is in some sense intra-atomic in nature on Sn. In particular, we note that the gaps of CsSnI₃

TABLE III. Spin-orbit splitting in α -structure and tetragonal crystal field splitting in β -structure in meV.

Compound	Δ_{so}	Δ_c
CsSnCl ₃	448	
CsSnBr ₃	437	215
CsSnI ₃	420	254



FIG. 3. (Color online) Dominant orbital character of (top) CBM and (bottom) VBM for α -CsSnI₃. For the selected orbitals ϕ_i mentioned, the plots show **k**- and *E*-resolved "spectral functions," $A(\mathbf{k}, E) = |\langle \phi_i | \psi_{n\mathbf{k}} \rangle|^2 \delta(E - E_{n\mathbf{k}})$, with the δ function replaced by a Gaussian, using the color scale shown on the right. So the light green areas and white areas indicate zero contribution from that orbital, while the red areas indicate a strong contribution from that orbital. The thin red lines show the band superposed on the color graph.

and CsSnBr₃ are rather close, especially if we consider the fact that the larger spin-orbit coupling in I, which reduces the gap, partially overcomes the expected increase in gap on going from I to Br. Still, of course, the degree of antibonding mixing of the anion p orbital in the VBM will decrease from Cl to Br to I because the anion p levels move farther down. This explains the decreasing trend of the gaps from Cl to I.

Next, we consider the changes in band gap due to the structural distortions in the lower-symmetry phases. The structural phases of interest can be summarized as follows. Starting from the cubic α phase, a rotation of the octachedra in the *xy* plane results in the tetragonal β phase. Chabot *et al.*¹⁶ pointed out that this is related to the imaginary frequency of the lowest acoustic mode at point *M* in the Brillouin zone. The symmetry lowering from cubic to tetragonal symmetry leads to a crystal-field splitting of the CBM in addition to the spin-orbit coupling. The crystal-field splittings are included in Table III. When both spin-orbit and crystal-field splittings are included for the β phase, the VBM splits into three levels, similar to what



FIG. 4. (Color online) Schematic drawing of the anion p orbitals pointing toward Sn s at the center of the unit cell for the VBM Bloch state at point R at the corner of the Brillouin zone.

is observed for the VBM in tetragonally distorted tetrahedrally bonded semiconductors, such as chalcopyrites.³¹ A further tilting of the tetrahedra away from the z axis results in the orthorhombic γ phase. These structural distortions have been discussed in detail in Refs. 17 and 4. The yellow phase, on the other hand, involves a much more involved rearrangement of the atoms. The LDA band structures of all four CsSnI₃ phases are shown in Fig. 5. The Brillouin zones (BZ) and the labeling of the high-symmetry points are shown in Fig. 6. Note that the relation between the α and β phases involves a rotation by 45° and a folding. The Γ -*M* line of α phase folded about its midpoint, which we labeled B in Fig. 6, becomes the Γ -X line of the β phase. We can clearly see in the band structure figures that the bands along M-B of the α phase are similar in dispersion to those along the Γ -X line in the β phase. Point R in α becomes folded onto the Z point in the β BZ. In fact the whole M-R line is folded onto the Γ -Z line. We included point L in the middle of the M-R line, although it is not a higher-symmetry point. It becomes equivalent to point H in the β structure. The transformation from β to γ structure involves a doubling of the cell in the c direction or folding of the bands along Γ -Z about the halfway point H so that Z of β now becomes folded on to the Γ point of γ and point H becomes the new Z point where the bands are doubly degenerate because of the folding. However, the tetragonal symmetry is also broken, so that the Γ -X and Γ -Y directions become distinct.

Our results on the band gap changes obtained in LDA are in good agreement with previous studies. For β -CsSnI₃ we also carried out the full QSGW calculation. This allows us to check that the GW gap correction is not very sensitive to the structure. Although the structural changes between the α , β , and γ phases are mild, the changes for the monoclinic phase of CsSnBr₃ and the yellow phase of CsSnI₃ are more severe. Nonetheless, one may argue that the GW corrections are mostly dependent on the average electron density and not too sensitive to structural details. The degree to which this holds may be judged from the agreement between our thus estimated gaps for these phases with experiment. Thus, once we have obtained the gap correction for the α phase, we can also apply it to the gaps of the other phases. The QSGW band



FIG. 5. (Color online) LDA band structure of α -CsSnI₃, β -CsSnI₃, γ -CsSnI₃, and *Y*-CsSnI₃.

structures of the β phase materials are shown in Fig. 7 for both CsSnI₃ and CsSnBr₃.

The results on the band gaps are summarized in Table IV. The band gap differences between β and α and between γ and



FIG. 6. (Color online) Brillouin zone of cubic (α phase), tetragonal (β phase), and orthorhombic (γ and Y phases) structures, from left to right.

 β in CsSnI₃ are 0.158 and 0.050 eV. These values are in fair agreement with those of Borriello *et al.*,¹⁷ 0.133 and 0.080 eV, but are not as well in agreement with those of Chabot *et al.*,¹⁶ 0.179 and 0.244 eV.

The comparison with experimental gaps requires a little discussion. For Cl and Br materials, these gaps are not as well established as for the I material because we rely on rather old literature data. Voloshinovskii et al.32 presented photoluminescence (PL) and photoluminescence excitation (PLE) as well as optical absorption data for CsSnCl₃ in its hightemperature cubic and low-temperature monoclinic forms. For the α phase they show a broad PL band centered around 555 nm, or 2.2 eV. This is probably due to defect bound excitons rather than being intrinsic. The PLE shows a peak centered at 368 nm, or 3.4 eV; however, it extends clearly to about 400 nm, or 3.0 eV. The absorption extends even somewhat further to 420 nm, or 2.9 eV. This is in good agreement with our gaps of 2.7 eV (with spin-orbit coupling) and 3.0 eV (without spin-orbit coupling). The monoclinic phase clearly has a higher gap. The peak of the PLE and optical absorption lies near 4.46 eV.³² We only calculated this material in the LDA (see Fig. 8), but assuming the same gap shift to GW as for the cubic phase, we would estimate a gap of 4.7 eV. Ohno and Sasaki³⁴ obtained two phase materials and associated a 2.11-eV PL band with α -CsSnCl₃, with a PLE peak at 3.5 eV and onset just above 3.1 eV, and a 2.65-eV PL band with monoclinic CsSnCl₃, with PLE peaking at 4.23 eV.



FIG. 7. (Color online) QS*GW* band structure of β -CsSnI₃ (red solid lines) and β -CsSnBr₃ (blue dashed lines).

TABLE IV. Band gaps for $CsSnX_3$ (eV) in various structures. Note that for the α and β phases, actual QSGW calculations were performed, while for the other cases, they are estimates assuming a structure-independent gap correction beyond LDA.

Material	LDA	QSGW	QSGW + SO	Other calc.	Expt.
α -CsSnCl ₃	0.744	2.997	2.693	0.950 ^a	2.9 ^b
M-CsSnCl ₃ ^c	2.743		4.7 ± 0.1	2.845 ^a	4.5 ^b
α -CsSnBr ₃	0.351	1.690	1.382	0.58 ^d	
β -CsSnBr ₃	0.574	1.918	1.740		1.8 ^e
α -CsSnI ₃	0.295	1.354	1.008	0.462, ^f 0.348 ^a	
β -CsSnI ₃	0.453	1.494	1.288	0.641, ^e 0.481 ^a	
γ -CsSnI ₃ ^c	0.503		1.3 ± 0.1	0.885, ^e 0.561 ^a	1.3 ^g
Y-CsSnI ₃ ^c	2.026		2.7 ± 0.1	2.53 ^h	2.55 ^g

^aBorriello *et al.*¹⁷ GGA pseudopotential plane-wave method. ^bVoloshinovskii *et al.*³²

^cQSGW results are estimates only.

^dBose *et al.*¹⁵ LDA with LMTO ASA.

eClark et al.33

^fChabot *et al.*¹⁶GGA pseudopotential plane-wave method.

^gChen et al.²⁰

^hChung et al.⁴

Clark et al.³³ report a band gap of 1.8 eV for α -CsSnBr₃ from optical absorption and low-temperature band gap luminescence at 1.72–1.75 eV depending on temperature. Myagkota et al.35 also assigned a peak at 1.72 eV to intrinsic luminescence of CsSnBr₃ in a sample that was a mixture with other phases. It is not entirely clear whether these reports correspond truly to cubic CsSnBr₃ or to the tetragonal β form, whose structure is reported in Scaife et al.³⁰ We find that our gap for the β phase of CsSnBr₃ agrees much better with experiment than the for the α phase. We note that our gap of α -CsSnBr₃ is rather close to that of CsSnI₃, and hence this material is also worth considering for photovoltaic applications if it can be stabilized. In fact, as mentioned in Ref. 4, the smaller cage size in this material may lead to a stabler bonding of Cs, and hence it avoids the undesirable larger-gap yellow phase of CsSnI₃ but stays in a perovskite-derived structure.

We note that in the past literature, ^{14,15,36} it was unclear if this material was a semiconductor or semimetal. For example, in the first semiempirical linear combination of atomic orbitals



FIG. 8. (Color online) LDA band structure of *M*-CsSnCl₃.

(LCAO) band structure calculation of Parry *et al.*³⁶ and the semiempirical pseudopotential calculation of Lefebvre *et al.*¹⁴ the Sn *p*-derived states at *R* are reversed with the Sn *s*-derived states, and hence the material appeared to be semimetallic, which was thought to be consistent with the high electrical conductivity. Already in Bose *et al.*'s¹⁵ LMTO calculations in the atomic sphere approximation (ASA) this was reversed, and a semiconducting band structure was concluded, but the gap was still strongly underestimated by the LDA with a gap of the order of 0.58 eV.

These authors noted that the main difference between the earlier empirical LCAO band structure and theirs was the absence of any Cs orbitals in the LCAO basis set. However, at the *R* point where the minimum gap occurs, the Cs 6s states belong to irreducible representation $R_{2'}$ and hence cannot interact with the R_1 VBM. The Cs 5d orbitals of symmetry t_{2g} can interact with the Sn p at the center because they both belong to R_{15} symmetry. For example, the Cs d_{xy} orbitals at the corners of the cell interact with the Sn p_z at the center, taking into account the Bloch function phase factors as discussed above. However, since the Cs 5d lie above the Sn p, omitting the Cs orbitals or pushing them up will reduce this interaction and thus move the Sn p CBM up, which would increase the gap. The Cs 5p states cannot interact with the Sn p or Sn seither. Thus we conclude that the absence of Cs orbitals did not play a major role in the opening of the gap. However, if we shift the Sn levels down with respect to Br or I or Cl orbitals, we can increase the Sn s with X p interaction sufficiently to make the R_1 state shift above the R_{15} state, thereby closing the gap and pinning the Fermi level at the R_{15} state. Note that the X s states at **k** point *R* form a state of R_{15} symmetry, which interacts with the Sn p orbitals at the center of the unit cell, and this interaction tends to increase the gap. However, this interaction is much weaker because the halogen X s orbitals lie rather deep. Thus the origin of the wrong band structures in the early work is because the position of the Sn s versus the X p levels, which depends on charge transfer, was not properly taken into account. In pseudopotential language, this corresponds to a too deep Sn pseudopotential, as was speculated by Bose *et al.*¹⁵

Interestingly, it was recently proposed by Yang *et al.*³⁷ that some of these materials could be close to a topological insulator condition when a strain is applied so as to induce a band inversion, i.e., negative gap. The gap would then indeed result purely from spin-orbit coupling. These calculations, however, were done at the generalized gradient approximation (GGA) level, which underestimates the gaps significantly, as shown here. With our present results, the strains required to induce a topological insulator behavior would become unrealistic.

For CsSnI₃ our gap for the γ phase comes rather close to the experimental value of 1.3 eV recently established. The change in the gap between the β and γ phases is rather small. In any case, our gaps are clearly all significantly larger than the LDA gaps and the gaps reported in previous work, including the sx-LDA gap reported in Ref. 4. With improved materials, it should become possible to probe the nature of the spin-orbit split gaps using circularly polarized light. For *Y*-CsSnI₃, Chung *et al.*⁴ found a direct gap of 2.53 eV for the yellow phase, in good agreement with the observed 2.55 eV onset of absorption, but they also found a somewhat lower indirect gap of 2.46 eV. They



FIG. 9. (Color online) Band gap vs lattice constant.

did not report a value for the gap for the γ phase, but from their figure it appears to be about 0.7 eV, thus significantly smaller than the 1.3 eV measured. Our LDA band structure of *Y*-CsSnI₃ is shown in Fig. 5. Both the direct gap, 2.026 eV, and indirect gap, 1.943 eV, are close to the *X* point. If we add the same amount of energy change shown in the α -CsSnI₃ case, we will get around 2.7 eV for the band gap after QSGW and SO correction, which is close to the experimental value of 2.55 eV.

Finally, we show in Fig. 9 the changes in band gap with lattice constant for CsSnI₃, CsSnBr₃, and CsSnCl₃. We confirm the already mentioned increase of gap with lattice constant. In view of the thermal expansion, this also implies an increasing band gap with increasing temperature, which is opposite most materials. This is because in most semiconductors, the gap is between anion p- and cation s-dominated bands. The increasing covalent interaction between the two when atoms are brought closer together then increases the gap with decreasing lattice constant. However, here the gap is, to first approximation, intra-atomic. The decreasing lattice constant results in an increasing band width of the valence band, pushing up the VBM by the increased interaction between Sn s and anion p. This then results in the anomalous gap behavior. Such anomalous gap behavior was reported recently for CsSnI₃ (Ref. 8) but can also be seen in the data for the 1.72-eV CL band in Myagkota et al.³⁵ for CsSnBr₃. We find a gap deformation potential $a_g = dE_g/d\ln a$ of 4.65 eV in LDA and 7.35 in QSGW for CsSnI₃. For the other materials, a_g are shown in Table V. While it is often assumed that the gap deformation potentials can be obtained accurately within LDA even when the gaps themselves are underestimated because one expects similar errors for each lattice constant, the present results indicate that the GW corrections also are required for the gap changes. The increase in gap from α to β structure is

TABLE V. Gap deformation potential a_g in α structure (in eV).

Compound	a_g in LDA	a_g in QSGW
CsSnCl ₃	5.62	9.05
CsSnBr ₃	5.34	8.99
CsSnI ₃	4.65	7.35

TABLE VI. Effective masses at the band gap edges (in electron mass). These correspond to the bands without spin-orbit coupling.

Sample	m_h^*	$m_{he}^*[100]$	$m_{he}^{*}[111]$	$m_{le}^{*}[100]$	$m_{le}^{*}[111]$
α -CsSnCl ₃	0.140	0.741	0.272	0.088	0.149
α -CsSnBr ₃	0.082	0.635	0.201	0.053	0.084
α -CsSnI ₃	0.069	0.573	0.154	0.041	0.068

related to a similar effect. While the overall structure becomes denser under this transformation, we found that the Sn halogen distance actually increases. This reduces the Sn *s*-halogen–*p* interaction, and hence the gap increases. The change from β to γ is more difficult to interpret because the tilting of the octahedra makes the orbital interactions more complex.

B. Effective masses and exciton binding energies

In Table VI we report the effective masses obtained by fitting parabolic dispersion curves to our first-principles energy band structures. For the holes, this is straightforward because the band is nondegenerate and the band dispersion is isotropic and parabolic near the VBM. We can see that rather low hole masses are found decreasing from the Cl to the Br to the I compound. These results are obtained for the cubic phase for simplicity, but they do not differ very much in the other phases. The low hole masses clearly play an important role in the observed high hole mobility, which was reported⁴ to be of the order of ~585 cm² V⁻¹ s⁻¹. In view of the general relation $\mu = e\tau/m^*$ they indicate a carrier relaxation time τ of about 2.29 × 10⁻¹⁴ s.

Because of the threefold degeneracy of the CBM in the absence of SO coupling, the masses depend on direction. Along the [100] direction, there are two bands, and we label these masses as the heavy (*he*) and light electron (*le*), in analogy with the usual terminology for holes in tetrahedrally bonded semiconductors. Similarly, in the [111] direction we also have a splitting. This situation can best be described by the Kohn-Luttinger (KL) Hamiltonian based on the theory of invariants. Although we are here dealing with electrons instead of holes and with a different **k** point, namely, *R* instead of Γ , the form of the Hamiltonian is still applicable because of the cubic symmetry. The KL Hamiltonian is given by

$$\hat{H} = \frac{1}{3} \Delta_0 \vec{L} \cdot \vec{\sigma} + Ak^2 - (A - B) (L_x^2 k_x^2) + L_y^2 k_y^2 + L_z^2 k_z^2) - 2C(\{L_x, L_y\}k_x k_y) + \{L_y, L_z\}k_y k_z + \{L_x, L_z\}k_x k_z),$$
(1)

where $\{L_i, L_j\} = (L_i L_j + L_j L_i)/2$, Δ_0 is the spin-orbit splitting, and the parameters A, B, and C are related to the effective masses in different directions as follows:

$$A = \frac{1}{m_{le}^*[100]},$$

$$B = \frac{1}{m_{he}^*[100]},$$
(2)

$$\frac{A+2B-C}{3} = \frac{1}{m_{he}^*[111]},$$
$$\frac{A+2B+2C}{3} = \frac{1}{m_{le}^*[111]}.$$
(3)

TABLE VII. Calculated inverse mass parameters A, B, and C of the Kohn-Luttinger Hamiltonian.

Sample	Α	В	С	ε_{∞}	ε_0	\tilde{E}_b (meV)	$E_b ({\rm meV})$
α -CsSnCl ₃ α -CsSnBr ₂	11.4 18.7	1.35 1.57	3.05 6.92	4.80 5.35	29.4 32.4	37.0 19.2	0.696 0.345
α -CsSnI ₃	24.2	1.74	8.28	6.05	48.2	12.2	0.124

In Table VII we list the *A*, *B*, and *C* parameters obtained by fitting to these equations.

The exciton binding energy is of great importance to understanding the relation between absorption and luminescence in these materials. In a recent paper, Chen *et al.*²⁰ deduced the exciton binding energy from the temperature dependence of the photoluminescence intensity and found a rather high value of 18 meV. They further remarked that this implies a large deviation of the empirical Haynes' rule, which relates exciton binding energies to band gaps. In fact on a logarithmic scale the exciton binding energies appear linear when plotted versus band gap on the linear scale.

Using the effective mass approximation, the exciton binding energy within the Wannier exciton theory can be obtained from the electron and hole effective masses and the screened Coulomb interaction between the electron and hole. In the simplest form of the theory, this lead to a hydrogenic model with the binding energy being the effective Rydberg. This scales proportionally to the reduced mass and inversely proportionally to the dielectric constant squared. This model can be further elaborated to take into account the degenerate nature of the CBM described by the Kohn-Luttinger Hamiltonian. For the usual situation of a degenerate VBM and a nondegenerate CBM, the theory was worked out in detail using group theoretical analysis by Baldereschi and Lipari.³⁸ Within a so-called spherical approximation, they obtained

$$E_b = \frac{2\pi^2 \mu_0 e^4}{h^2 \varepsilon_0^2} \left[1 + \frac{10}{7} \left(\frac{\mu_0}{\mu_1} \right)^2 + \frac{5}{28} \left(\frac{\mu_0}{\mu_2} \right)^2 \right], \quad (4)$$

with $\mu_0^{-1} = (m_h^*)^{-1} + 2(A+2B)/3$, $\mu_1^{-1} = (A-B)/3$, and $\mu_2^{-1} = 2C/\sqrt{3}$.

The only remaining unknown parameter in this theory is the dielectric constant. This is a rather subtle point. If the exciton binding energy is small, at the time scale of the relative motion of the electron and hole, the ions have time to relax and contribute to the screening. One should then use the static dielectric constant including the phonon contributions. On the other hand, if the time scale of the excitons is fast relative to the vibrational periods, then the phonons cannot contribute, and one should use the high-frequency dielectric constant. In most semiconductors, where the Wannier theory of excitons applies, the static dielectric constant is applicable.

However, in CsSnI₃ the highest optical phonon energies are of the order the of 18 meV, as we discuss in the next section. The static dielectric constant is larger than the high-frequency dielectric constant by a factor of 9.9. The high-frequency dielectric constant can be obtained from our *GW* calculations. By taking the $q \rightarrow 0$ and $\omega \rightarrow 0$ limit of $\varepsilon^{-1}(q,\omega)$ we obtain what is usually called ε_{∞} . Using this high-frequency dielectric constant, we obtain an exciton binding energy \tilde{E}_b of about 12 meV for α -CsSnI₃. This is of the same order of magnitude as the phonon frequencies but still lower than the highest phonon frequencies. Therefore, in principle, at least the higher-energy phonons should contribute to the screening. It is not entirely clear if we should take into account the full phonon enhancement factor of the phonons as some of the lower phonon frequencies are lower than our exciton binding energy. However, according to the Lyddane-Sachs-Teller relation

$$\prod_{i} \left(\frac{\omega_{Li}}{\omega_{Ti}}\right)^2 = \frac{\varepsilon_0}{\varepsilon_{\infty}},\tag{5}$$

we can think of each mode as contributing a separate factor to the enhancement of the dielectric screening. The highest modes show the highest contribution because they have the highest LO-TO splitting. They already increase the dielectric constant by a factor of 1.5 and so would reduce the binding energy by a factor of 2.3. But then the next phonon frequency is already higher than this binding energy, so we need to also include it. Ultimately, this means a factor of 9.9 for the dielectric constant and a decrease of our exciton binding energy by a factor of 98, or, in other words, two orders of magnitude. Thus we expect the exciton binding energy to be of the order of 0.1 meV. While these are all fairly rough estimates because a full dynamic theory of excitons including electron-phonon coupling is beyond present-day capabilities of first-principles calculations, the reduction of the exciton binding energy by the phonons by about two orders of magnitude should remain valid. In that case it is not at all in contradiction with Haynes's rule; in fact, it is even somewhat low. The same conclusion applies to the other materials which all end up with exciton binding energies of about 0.1 meV. This disagrees with Chen *et al.*²⁰

We now discuss the reasons for the discrepancy. Chen *et al.*²⁰ claimed that the exciton is a free rather than bound exciton based on their excitation power dependence study, which shows a linear dependence and no saturation over several decades, and on the fact that the shape of the exciton indicates a single peak which is just shifting and broadening with temperature, rather than shifting weight from a bound exciton at low temperature to a free exciton at higher temperature. However, this is not entirely convincing because their PL is rather broad. Second, their approach for extracting the exciton binding energy relies on a number of assumptions. They fitted the decay of the exciton intensity as a function of temperature to the expression

$$R_{\rm spon}(T) = R_G[1 - e^{-E_b/k_B T}],$$
(6)

where R_G is the generation rate of excitons, k_B is Boltzmann's constant, and the underlying assumption is that the decay is given by the dissociation of excitons as a function of temperature only. In other words, no nonradiative processes are in competition with the radiative one. This equation makes sense if we assume the exciton is a bound exciton and there is no kinetic energy related to the exciton moving as a whole: the probability at temperature T of the decay of the exciton is then given by the Boltzmann equation, and only the excitons surviving can give rise to radiation. However, they also tried to justify this equation for a free exciton. In order to arrive at the same expression under the assumption of a free exciton, they

had to assume that the exciton motion is two-dimensional (2D) so that there is a steplike density of states of exciton kinetic energies. In that case the number of excitons would be

$$N(T) = \int D(E)e^{-\frac{E}{k_B T}} dE \propto T \left[1 - e^{-\frac{E_b}{k_B T}} \right]$$
(7)

if we integrate up to E_b , which presumably one could justify by assuming that when an exciton gets kinetic energy above the binding energy, it will decay. In the case of a threedimensional (3D) distribution $D(E) \propto \sqrt{E}$, and we would obtain $N(T) \propto T^{3/2} \gamma(3/2, E_b/k_B T) / \Gamma(3/2)$, with $\gamma(a, x)$ and $\Gamma(a)$ being the incomplete gamma function and gamma function, respectively.³⁹ This N(T) must then be divided by the partition function of free electrons, which is proportional to T in 2D and to $T^{3/2}$ in 3D, to obtain the rate of survival of excitons. The reason is that we consider electrons to either be bound to a hole or free, but we only consider minority carriers (electrons) since the material is p type. On the other hand, the theory of exciton decay for free excitons in a 2D quantum well was considered by Feldmann et al.⁴⁰ Slightly generalizing their approach to either 2D or 3D, the decay rate of excitons is given by

$$\frac{1}{\tau} \propto \frac{E_b \mu \gamma \left(\frac{D}{2}, \frac{\Delta}{k_B T}\right)}{M \Delta \Gamma \left(\frac{D}{2}\right)},\tag{8}$$

where D is the dimensionality of the motion, $M = m_e + m_h$ is the total mass of the exciton, μ is the reduced mass, and Δ is the spread of energies of the exciton due to their nonzero kinetic energy, which arises from interaction with acoustic phonons. In other words, $\Delta(T)$, which in general depends on T, is the linewidth of the exciton peak. This approach appears similar to that of Chen *et al.*²⁰ but is arrived at by integrating the density of excitons only up to Δ rather than to E_b . It turns out that for D = 2 this reduces to a form similar to Eq. (6) because $\gamma(1,x) = [1 - e^{-x}]$, but the important point is that the relevant parameter Δ , in this equation, is not the exciton binding energy but the linewidth of the exciton. A fit of the data to this equation with the assumption D = 3 would give $\Delta \approx 30$ meV, which agrees roughly with half the linewidth of the PL peak. The measured exciton lifetimes as a function of temperature by Chen *et al.*²⁰ show a curve which is essentially inversely proportional to the exciton-integrated intensity as a function of temperature, as expected. However, if their exciton were really free and this theory were applicable, it does not tell us anything about the exciton binding energy but merely about the exciton linewidth.

On the other hand, the study of Chung *et al.*⁴ showed that after high-temperature cycling (300–600 K), the PL increased in intensity and that this increase is also accompanied by an increase in conductivity. This indicates that chemical changes are taking place in the material, leading to an enhanced hole concentration (since the material was found to have *p*-type conduction). Their calculations, in fact, ascribe this to the formation of Sn vacancies V_{Sn} . These observations are clear indications that the PL in question is in fact due to an acceptor bound exciton rather than a free exciton. Even material as grown before the heat treatments is already *p* type with concentrations of the order of 10^{17} cm⁻³. In that case, Chen *et al.*'s²⁰ first analysis in terms of a simple rate equation,

assuming a single-exciton binding energy but no kinetic energy of the excitons, may be considered to be valid as a way to obtain the exciton binding energy, but it is then the energy of a bound exciton and is therefore not in contradiction with our conclusion that the free-exciton binding energy is two orders of magnitude smaller. Essentially, the energy is lowered by the binding energy of the acceptor, which may easily be of the order of 20 meV. Their analysis leading to the conclusion of a 2D motion, however, is clearly invalid. In fact, there is also no

C. Phonons

support for 2D motion of the electrons (or excitons) from our

band structure or from the crystal structure.

The previous section already relied on some of our results on phonons. Here we present the results of our phonon calculations. Group theoretical analysis shows that in the cubic perovskite structure, there are three infrared active modes of irreducible representation T_{1u} and one silent mode of symmetry T_{2u} . Since each of these are threefold degenerate, they account for all the modes (N - 1)3, with N = 5 being the number of atoms in the unit cell.

The calculated frequencies of the modes are shown in Table VIII along with some other properties and experiment results from Donaldson et al.⁴¹ We note that Donaldson et al.⁴¹ reported three infrared bands for CsSnCl₃ at 70, 172, and 310 cm^{-1} and three for CsSnBr₃ at 68, 118, and 218 cm⁻¹. These seem significantly higher than our calculated modes and do not distinguish between TO and LO modes. However, we notice that the lowest optical mode in our calculations had an oscillator strength that is between 12 and 21 times weaker than the higher-frequency ones. We thus assume that it may have been missed in the experiment and ascribe the lowest experimental mode to our second-lowest mode $T_{1\mu}^2$. One can see a reasonable agreement between the average of our TO and LO modes, i.e., the middle of the absorption band as it would be seen in reflectivity, and the experimental value. For CsSnCl₃ our values for $(\omega_{TO} + \omega_{LO})/2$ for T_{1u}^2 and T_{1u}^3 are 77 and 182 cm⁻¹, while the two lowest observed IR bands are at 70 and 172 cm⁻¹. The higher observed band of 310 cm⁻¹ is close to but somewhat lower than $2T_{1u}^3$, although one would expect two-phonon absorption to be weak. In two-phonon absorption one rather expects to see a density of states, which may be more influenced by zone-boundary phonons. Based on the phonon-dispersion curves shown by Chabot et al.,¹⁶ we expect these zone boundary phonons to be somewhat lower than our T_{1u}^3 . For CsSnBr₃ we similarly find 64 and 145 cm⁻¹ as average modes for T_{1u}^2 and T_{1u}^3 , which can be compared with the lowest two IR bands at 68 and 118 cm⁻¹. Our calculation would overestimate the experiment by about 23%, which is expected in view of the overbinding of LDA. Again, the third observed IR band at 218 cm⁻¹ is not too far from $2T_{1u}^3$ at 290 cm⁻¹ but again is somewhat lower because we expect it to be a two-phonon density of states band. For CsSnI₃ we could not find infrared absorption data in the literature. Donaldson et al.⁴¹ also calculated the silent $T_{2\mu}$ mode by using force constants extracted from the observed IR active T_{2u} modes, but in view of the, in our opinion, erroneous assignment of the modes, these values are not trustworthy.

We next analyze the Lyddane-Sachs-Teller relation, already mentioned in the previous section in Eq. (5). We can see

TABLE VIII. Phonon frequencies ω (in cm⁻¹), oscillator strength *S* (in a.u., with 1 a.u. = 253 m³/s²), generalized Lyddane-Sachs-Teller relation, and dielectric constants in α -CsSnX₃. These dielectric constants ε_{∞} differ from the ones in Table VII because they are obtained from the DFPT at the LDA level instead of from *GW*.

	Mode	ТО	LO	S	Expt. ^a	ω_L/ω_T	$\prod_i \left(\frac{\omega_{Li}}{\omega_{Ti}}\right)^2$	$\frac{\varepsilon_0}{\varepsilon_\infty}$	\mathcal{E}_{∞}	ε_0
CsSnCl ₃	$T_{1\mu}^{1}$	25	32	1.4×10^{-5}		1.311				
	$T_{1\mu}^{2}$	76	78	1.3×10^{-5}	70	1.029				
	T_{1u}^{3}	121	243	2.9×10^{-4}	172	2.003				
	T_{2u}	53					7.29	7.30	4.03	29.4
CsSnBr ₃	$T_{1\mu}^{1}$	19	26	1.1×10^{-5}		1.381				
	T_{1u}^{2}	59	69	3.7×10^{-5}	68	1.165				
	T_{1u}^{3}	108	183	1.6×10^{-4}	118	1.697				
	T_{2u}	37					7.45	7.45	4.34	32.4
CsSnI ₃	$T_{1\mu}^{1}$	12	18	9.5×10^{-6}		1.483				
	T_{1u}^{2}	45	63	5.5×10^{-5}		1.412				
	T_{1u}^{3}	101	152	1.1×10^{-4}		1.506				
	T_{2u}	29					9.93	9.93	4.86	48.2

^aDonaldson *et al*.⁴¹

that the static to high-frequency dielectric constant ratio is close to the expected value from the Lyddane-Sachs-Teller relation. We observe indeed a very strong contribution of the phonons to the static dielectric constant by a factor of 7–10 increasing from Cl to I. This is expected in view of the strong ionic bonding. Relatedly, we have rather large Born effective charges, obtained from DFPT, as shown in Table IX. The Born effective charge for the X atom in the direction parallel to the polarization of the mode is different from that in the direction perpendicular to it. It is interesting that even though Sn is nominally divalent in this material, its Born effective charge is nonetheless larger than 4. The Cs effective charge, on the other hand, is close to 1.

Returning to the dielectric constants, the values obtained for the high-frequency dielectric constant obtained from the DFPT calculations are somewhat larger than those in the previous section. This is not surprising because, first, they are obtained in a rather different manner, namely, from the polarization in response to a static electric field and only including electronic contributions and calculated via the Berry phase method. In the previous section they were obtained from the low-frequency limit of the polarizability calculated as function of frequency in the region above the band gap. Furthermore that calculation was based on the QSGW band structure, while the present one uses the LDA band structure. In view of these widely different approaches, the agreement between the two can be viewed as satisfactory and certainly sufficient for our main present purpose of estimating the exciton binding energies in the previous section.

TABLE IX. Born effective charges obtained within DFPT (in units of e).

	Cs	Sn	X_{\parallel}	X_{\perp}
CsSnCl ₃	1.162	4.462	-3.471	-1.077
CsSnBr ₃	1.109	4.701	-3.295	-1.258
CsSnI ₃	1.060	4.954	-3.110	-1.452

IV. CONCLUSIONS

In this paper, we have presented quasiparticle selfconsistent GW band structures of the family of $CsSnX_3$ compounds, with X = (Cl, Br, I). Spin-orbit coupling effects were included. The changes in band structure with the structural distortions of the α , β , and γ phases were investigated. The band gap of 1.3 ± 0.1 eV was found to be in good agreement with experiment for γ -CsSnI₃, for which the best experimental data are available. For α -CsSnCl₃, our gap of 2.7 eV is in good agreement with the PLE data of Voloshinovskii et al.,³² giving an estimate of 2.9 eV. We also obtained good agreement for the much higher gap of the monoclinic phase (of the order of 4.5 eV) if we assume the same LDA to QSGW gap correction applies. For α -CsSnBr₃, our calculations predict a gap of 1.38 eV, while for the β phase we obtain 1.7 eV, in good agreement with experiment (1.8 eV) by Clark et al.³³ While this gap is a little larger than optimal for solar-cell applications, the increased stability of the desirable perovskite phase for the Br compound makes this material of further interest for photovoltaics. The Br material, having a somewhat smaller lattice constant, appears to avoid the competing so-called yellow phase of CsSnI₃.

The most important finding is that all these materials have a rather unusual "inverted" band structure with a nondegenerate s-like valence band and a degenerate p-like conduction band. This was shown to result from the strong Sn s character of the valence band maximum, which is an antibonding state, or anion p states with Sn s. The reason why the VBM occurs at the Brillouin zone corner R is that at this point in \mathbf{k} space, the anion p orbitals on the corners of the octahedron surrounding the Sn atom point with their lobes of the same sign toward the center of the octahedron and hence give the strongest interaction. The strong intra-atomic nature of the gap explains various features: the relatively weak dependence on the anion, the strong optical luminescence and band gap absorption, and the anomalous temperature dependence, increasing the gap with increasing temperature.

The effective masses were determined for the band edges, and the low hole mass in $CsSnI_3$ is found to be responsible for the high hole mobility observed in this material. The other materials also have relatively low hole masses and may thus also be expected to be excellent *p*-type semiconductors.

The free-exciton binding energy was estimated to be of the order of 0.1 meV in $CsSnI_3$, in contrast to a recent report²⁰ which claimed an anomalously high value of 18 meV. Our low value is obtained when using the static dielectric constant rather than the high-frequency one. This is consistent with the fact that, while the vibrational frequencies are rather low, they still are expected to contribute to the dielectric screening of the electron-hole interaction. We also find no evidence for 2D motion of excitons as claimed by Chen *et al.*²⁰ and showed that their method of determining the binding energy of the excitons is flawed. Further, we propose that their PL should rather be interpreted as an acceptor bound exciton than as a free exciton.

- ¹S. Sharma, N. Weiden, and A. Weiss, Z. Phys. Chem. **175**, 63 (1992).
- ²M. Mori and H. Saito, J. Phys. C 19, 2391 (1986).
- ³K. Yamada, S. Funabiki, H. Horimoto, T. Matsui, T. Okuda, and S. Ichiba, Chem. Lett. **20**, 801 (1991).
- ⁴I. Chung, J.-H. Song, J. Im, J. Androulakis, C. D. Malliakas, H. Li, A. J. Freeman, J. T. Kenney, and M. G. Kanatzidis, J. Am. Chem. Soc. **134**, 8579 (2012).
- ⁵P. Mauersberger and F. Huber, Acta Crystallogr., Sect. B **36**, 683 (1980).
- ⁶I. Chung, B. Lee, J. He, R. P. H. Chang, and M. G. Kanatzidis, Nature (London) **485**, 486 (2012).
- ⁷K. Shum, Z. Chen, J. Qureshi, C. Yu, J. J. Wang, W. Pfenninger, N. Vockic, J. Midgley, and J. T. Kenney, Appl. Phys. Lett. **96**, 221903 (2010).
- ⁸C. Yu, Z. Chen, J. J. Wang, W. Pfenninger, N. Vockic, J. T. Kenney, and K. Shum, J. Appl. Phys. **110**, 063526 (2011).
- ⁹Z. Chen, J. J. Wang, Y. Ren, C. Yu, and K. Shum, Appl. Phys. Lett. **101**, 093901 (2012).
- ¹⁰M. H. Kuok, L. S. Tan, Z. X. Shen, and C. H. Huan, Solid State Commun. **97**, 497 (1996).
- ¹¹Z. X. Shen, W. L. Loo, M. H. Kuok, and S. H. Tang, J. Mol. Struct. **326**, 73 (1994).
- ¹²C. Yu, Z. Chen, and K. Shum, J. Raman Spectrosc. 44, 262 (2013).
- ¹³D. J. Singh, J. Appl. Phys. **112**, 083509 (2012).
- ¹⁴I. Lefebvre, P. E. Lippens, M. Lannoo, and G. Allan, Phys. Rev. B 42, 9174 (1990).
- ¹⁵S. K. Bose, S. Satpathy, and O. Jepsen, Phys. Rev. B **47**, 4276 (1993).
- ¹⁶J.-F. Chabot, M. Côté, and J.-F. Brière, in *High Performance Computing Systems and Applications and OSCAR Symposium (Proceedings)*, edited by D. Senechal (NRC Research Press, Ottawa, 2003), p. 57.
- ¹⁷I. Borriello, G. Cantele, and D. Ninno, Phys. Rev. B **77**, 235214 (2008).
- ¹⁸M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).
- ¹⁹T. Kotani, M. van Schilfgaarde, and S. V. Faleev, Phys. Rev. B 76, 165106 (2007).
- ²⁰Z. Chen, C. Yu, K. Shum, J. J. Wang, W. Pfenninger, N. Vockic, J. Midgley, and J. T. Kenney, J. Lumin. **132**, 345 (2012).

We presented also results for the phonons at the Γ point of the cubic perovskite and for the static and high-frequency dielectric constants. The phonon frequencies for CsSnBr₃ and CsSnCl₃ are in reasonable agreement with experimentally observed infrared absorption bands, provided we assume that the lowest vibrational modes have too low an oscillator strength to be observed.⁴¹

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- ²¹M. Methfessel, M. van Schilfgaarde, and R. A. Casali, in *Electronic Structure and Physical Properties of Solids: The Use of the LMTO Method*, edited by H. Dreyssé, Lecture Notes in Physics Vol. 535 (Springer, Berlin, 2000), p. 114.
- ²²T. Kotani and M. van Schilfgaarde, Phys. Rev. B 81, 125117 (2010).
- ²³L. Hedin, Phys. Rev. **139**, A796 (1965).
- ²⁴X. Gonze, Phys. Rev. B 55, 10337 (1997).
- ²⁵X. Gonze and C. Lee, Phys. Rev. B 55, 10355 (1997).
- ²⁶C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B **58**, 3641 (1998).
- ²⁷X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, and D. C. Allan, Comput. Mater. Sci. 25, 478 (2002).
- ²⁸J. Barrett, S. R. A. Bird, J. D. Donaldson, and J. Silver, J. Chem. Soc. A **1971**, 3105 (1971).
- ²⁹F. R. Poulsen and S. E. Rasmussen, Acta Chem. Scand. 24, 150 (1970).
- ³⁰D. E. Scaife, P. F. Weller, and W. G. Fisher, J. Solid State Chem. 9, 308 (1974).
- ³¹S. Limpijumnong and W. R. L. Lambrecht, Phys. Rev. B **65**, 165204 (2002).
- ³²A. Voloshinovskii, S. V. Myagkota, N. S. Pidzyrailo, and M. V. Tokarivskii, J. Appl. Spectrosc. **60**, 226 (1994).
- ³³S. J. Clark, C. D. Flint, and J. D. Donaldson, J. Phys. Chem. Solids 42, 133 (1981).
- ³⁴N. Ohno and K. Sasaki, UVSOR Acta Rep. 2001, 122 (2002).
- ³⁵S. V. Myagkota, P. V. Savchin, A. S. Voloshinovskii, T. M. Demkiv, Y. V. Boïko, R. S. Vus, and L. S. Demkiv, Phys. Solid State 50, 1473 (2008).
- ³⁶D. E. Parry, M. J. Tricker, and J. D. Donaldson, J. Solid State Chem. 28, 401 (1978).
- ³⁷K. Yang, W. Setyawan, S. Wang, M. B. Nardelli, and S. Curtarolo, Nat. Mater. 11, 614 (2012).
- ³⁸A. Baldereschi and N. O. Lipari, Phys. Rev. Lett. 25, 373 (1970).
- ³⁹M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).
- ⁴⁰J. Feldmann, G. Peter, E. O. Göbel, P. Dawson, K. Moore, C. Foxon, and R. J. Elliott, Phys. Rev. Lett. **59**, 2337 (1987).
- ⁴¹J. D. Donaldson, S. D. Ross, and J. Silver, Spectrochim. Acta, Part A **31**, 239 (1975).