## Impact of symmetry breaking and spin-orbit coupling on the band gap of halide perovskites

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Halide perovskite (HP) materials have recently emerged as a class of semiconductors with immense promise for various optoelectronic applications, ranging from solar cells to light-emitting diodes. One of the unique attributes of HPs is their tunable band gaps with different factors governing their value. The first factor is related to relativistic corrections ["mass-Darwin," connected to the *ns*<sup>2</sup> lone pairs, and spin-orbit coupling (SOC)] that induce an orbital shift or degeneracy splitting, resulting in a band-gap reduction. The second factor involves the structural configuration: in HPs the local symmetry of each Wyckoff position tends to be broken, inducing an opening of the band gap. Based on high-throughput density functional theory calculations, this paper systematically studies a possible self-cancelation on the band-gap correction for HPs when the polymorphous configuration—structural effects—and the SOC—electronic effects—are included. Our results indicate that the nature of interplay between SOC and symmetry breaking (SB) is that they are independent decoupling effects to describe the band-gap magnitude in halide perovskites. As a result of that, we observe a transitivity of the band-gap description; i.e., if we know the band gap of halide perovskites without SB and SOC, we can independently add the effects of band-gap reduction due to SOC and band-gap opening due to SB, regardless of the order in which these effects are considered.

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#### I. INTRODUCTION

Three-dimensional halide perovskites (HPs) are structured as corner-sharing octahedra (thus, "perovskites") with the empirical formula  $ABX_3$ , where A represents a monovalent cation metal (K, Rb, Cs) or organic molecular cation [methylammonium (MA), formamidinium (FA)], B represents a column IV metalloid element (Ge, Sn, Pb), and X a halogen anion (Cl, Br, I) [1,2]. The HPs have recently emerged as a highly promising class of materials because of their ability to offer a broad range of insulating band gaps and, therefore, have attracted attention for optoelectronic applications, including solar cells, light-emitting diodes, lasers, and photodetectors [3–6]. The emphasis on optical uses has directed scrutiny toward the factors influencing the band gaps of these semiconductors.

It is known that different factors can influence the bandgap description in materials. For III-V semiconductors, the relativistic physical effects such as spin-orbit coupling (SOC) drastically change the dispersion in the vicinity of the valenceband maximum and conduction-band minimum, inducing a spin splitting and a band-gap reduction that can reach 0.3 eV [7]. The band gap can also be affected by structural distortions, where the disorder in the atomic occupation, resulting in a local symmetry breaking, affects the overlap between the band edges' orbital character, which is observed in spinel oxide structures such as  $Al_2MgO_4$  [8]. Both relativistic physical effects and symmetry breaking are observed in most of the three-dimensional halide perovskites, and in this paper we discuss their effects on the electronic structure of these materials.

Regarding *bonding effects associated with relativistic physics*, we note that the scalar relativistic ("mass-Darwin" [9]) effect shifts orbital energies without splitting degeneracy.

This effect has its origin in the  $ns^2$  lone pair of the *B* atom's sublattice. Also important is the nonscalar relativistic impact of SOC, which leads to splitting of degeneracy, which here induces a band-gap reduction [10–15]. The scalar relativistic formation of the lone-pair orbital in halide perovskites causes the  $ns^2$  orbital of Pb (Sn) to hybridize with halogen p orbitals, forming an antibonding state as the valence-band maximum (VBM). This state is thus repelled to higher energy, so the VBM ionization energy (with respect to the vacuum) in halide perovskites becomes smaller than in the standard halide salts. such as NaCl or CsCl, that do not have an antibonding VBM. This upward repulsion of the VBM leads, in halide perovskites (and also in nonperovskites such as PbTe [16]), to a decreased band gap [10] relative to ordinary halides. The lone pairs also affect the dispersion of the VBM, reducing the hole's effective mass [17,18], and indirectly affecting properties such as defect tolerance, dielectric constant, thermal expansion, and others [19–23]. The lone pairs of elements can hardly be controlled in the density functional theory (DFT) calculations because it depends on the pseudopotentials and the electrons considered in the valence states. On the other hand, the SOC is easy to control and can be added to DFT calculations.

Regarding the effect of *specific crystallographic phases*, we note that the high-symmetry cubic perovskite phase Pm-3m (often the most utilized phase in HP solar cell applications) was recently noted to be, in many cases, a "virtual average phase" denoting an average over possible octahedra distortions, leading to ideal high-symmetry crystallographic configurations [24]. In many instances, the cubic phase is not high symmetry but rather a phase that is cubic *globally* but can locally include a range of octahedral distortions (a polymorphous distribution of motifs). Recent local characterization tools such as pair distribution function (PDF)



FIG. 1. The most accurate calculation for halide perovskites is represented in the polymorphous phase configuration with spinorbit coupling (SOC) correction  $(E_g^{poly})$  and can be obtained by two different paths: (i) in the red path, on top of the band gap of the monomorphous phase without SOC  $(E_g^{mono})$ , we add the correction for symmetry breaking (SB),  $\Delta E_g$ (SB), and spin-orbit coupling (SOC),  $\Delta E_g$ (SOC), following this sequence; (ii) in the blue path, on top of the band gap of the monomorphous phase without SOC  $(E_g^{mono})$ , we add the corrections for SOC,  $\Delta E_g$ (SOC), and SB,  $\Delta E_g$ (SB), following this sequence.

measurements [17,25] and Raman spectra [26] have evidenced that the cubic phase is locally different from what the x-ray diffraction average structure has indicated. If these local symmetry-breaking phases exist, they can change the electronic structure, and significantly increase the band gap [24,27–32]. Interestingly, analogous local distortions, in combination with local magnetic moments, have been recently shown to control the band gap in oxide  $ABO_3$  perovskites, explaining, in effect, the origin of Mott insulators as a consequence of such symmetry breaking [33,34].

The competition between the local bonding effects and the structural effects is dominant in halide perovskites, and here arises one important question: Are the effects that change the band gap in halide perovskites transitive? In other words, if we start from the band gap of the monomorphous phase, i.e., high-symmetry Pm-3m ( $E_g^{mono}$ ), and add to it the effects of SOC ( $\Delta E_g(SOC)$ ) and symmetry breaking ( $\Delta E_g(SB)$ ), in different orders, can we obtain a different band gap for the polymorphous phase  $(E_g^{poly})$ ? Figure 1 schematically represents these questions by the two different paths, the red and blue. The red path indicates the evolution of the band gap from monomorphous configuration without SOC  $(E_{\rm g}^{\rm mono})$  to polymorphous configuration  $(E_g^{poly})$  with SOC by adding the band-gap opening due to symmetry breaking (SB),  $\Delta E_g$ (SB), and band-gap closing due to SOC,  $\Delta E_g$ (SOC), following this order, whereas the blue path indicates the evolution of the band gap from monomorphous configuration without SOC  $(E_g^{mono})$  to polymorphous configuration  $(E_g^{poly})$  with SOC by adding the band-gap closing due to SOC,  $\Delta E_g(SOC)$ , and in the sequency the band-gap opening by SB,  $\Delta E_g(SB)$ .

To address the raised question, in this paper we select a large number of possible halide perovskites from the Open Quantum Materials Database (OQMD) and run highthroughput calculations controlling the relativistic effects such as SOC and the structural effects and check its influence on the band gap. We demonstrate that SOC is strong in systems composed of  $ns^2$  lone pairs, and it leads to a large reduction in the band gap and is largely independent of structural factors. In contrast, the band gap opening by symmetry breaking is explicitly structure dependent. The main point of the nature of interplay between SOC, a correction that depends primarily on atomic number and lives inside the nucleus, and SB, a correction that depends primarily on bonding outside the nucleus, is that they are independent effects to describe the band-gap magnitude in halide perovskites. As a result of that, we observe a transitivity of the band-gap description (independent of the path, red or blue, in Fig. 1); i.e., if we know the band gap of halide perovskites without SB and SOC, we can independently add the effects of band-gap reduction due to SOC and band-gap opening due to SB, regardless of the order in which these effects are considered. This transitivity provides a computationally efficient method for describing the band gaps of halide perovskites. First, compute the band-gap reduction due to SOC using the high-symmetry cubic Pm-3m structure (lower number of electrons), and calculate the bandgap opening in the polymorphous cell (higher number of electrons). Then, combine these effects in the band gap of the monomorphous cubic Pm-3m cell.

#### II. THEORETICAL APPROACH AND COMPUTATIONAL DETAILS

#### A. DFT calculations

Our first-principles calculations are based on DFT as implemented in the Vienna Ab initio Simulation Package (VASP) [35,36]. The interaction between valence electrons and the ionic cores is treated according to the projector augmented wave (PAW) method [37,38]. We used the Perdew-Burke-Ernzerhof (PBE) semilocal exchange and correlation functional for the volume optimization [39]. This process was done only in the cubic Pm-3m (5 atoms and 1 f.u.), where a cutoff energy of 600 eV was used for the plane wave expansion during the minimization of the stress tensor. At the same time, the forces were minimized in all the atoms until they became smaller than 0.01 eV/Å. For the Brillouin zone integration in the cubic Pm-3m cell, we used a k mesh of  $7 \times 7 \times 7$  for CsPbI<sub>3</sub> and the same k density for all the remaining compositions. This k density enables us to determine the fundamental band gap, regardless of whether its nature is direct or indirect.

The polymorphous cell was built up based on a repetition of  $2\sqrt{2} \times 2\sqrt{2} \times 4$  of volume-optimized *Pm-3m* cubic perovskites, resulting in a supercell composed of 32 *ABX*<sub>3</sub> f.u. (160 atoms). In this polymorphous configuration, we nudge the atoms by a random displacement of 0.15 Å in all directions, and in the sequence, we relax the atomic forces (keeping the volume constant). Because of the large supercell of the



FIG. 2. Elements that compose our database of halide perovskites used to study the effects of symmetry breaking and spin-orbit coupling in the band gap.

polymorphous configuration, we used only the  $\Gamma$  point for the Brillouin zone integration.

For the band-gap calculation, we run one full selfconsistent (one shot) calculation using the Heyd-Scuseria-Ernzerhof (HSE) hybrid exchange-correlation functional [40,41]. Under this approach, 25% of the exchange is calculated through the Fock operator, i.e., in the exact form, and added into the short-range region, defined by a screening factor  $\omega = 0.20 \text{ Å}^{-1}$ . In the long range, all the exchange is calculated from the PBE approach. In some systems, we also add the relativistic effect of SOC into the HSE calculation. It is important to mention that the use of HSE + SOC leads to very expensive calculations, especially for polymorphous cells due to the large number of atoms and electrons. We did not include dispersion corrections, such as van der Waals, in our calculations; this dispersion improves cohesion (i.e., reduced equilibrium volume) but the reduced volume does not have a significant effect on electronic structure.

#### **B.** Selection of the database

From the OQMD [42] we select 1022 systems with the  $ABX_3$  chemical formula. This does not mean that we need to have the perovskite crystal structure, does not mean that the materials need to be stable, and does not mean that they need to be cubic. After that, we apply a quantum stability filter where we select only systems that have decomposition energy (relative to their competing phases; e.g., for CsPbI<sub>3</sub> the components are PbI<sub>2</sub> and CsI) smaller than 150 meV/ f.u. After the stability filter, we have a total of 642 *ABX*<sub>3</sub> compounds that are stable by the relative cutoff defined earlier. From these materials, we select the systems that are composed of nonmagnetic elements, which results in our database of 229 *ABX*<sub>3</sub> compounds. Figure 2 indicates the possible

combinations of elements in the A, B, and X sites that compose this database, and all the systems are shown in the Supplemental Material [43].

In the next step of our screening process, we proceed to "cubicize" all compounds. Despite the potential existence of alternative crystal structures among the selected 229 materials (nonperovskites, or perovskites but not cubic), we standardize their structure into cubic perovskites. In essence, regardless of the crystal structure originally removed from OQMD in these 229 materials, we compute them as cubic perovskite systems. For the most known perovskite systems, the cubic *Pm-3m* phase is a high-temperature structure and tends to be stable near room temperature. In addition, our focus is to describe the band-gap variation with symmetry breaking, which is more pronounced in the cubic crystallographic structure. Because of that, we do not run the calculation for the low-symmetry and low-temperature (ground-state configuration) perovskite structure.

The band gap, therefore, is calculated using the HSE exchange-correlation functional for 229  $ABX_3$  perovskites in the cubic Pm-3m and polymorphous phase. As mentioned before, HSE + SOC can be very expensive, especially for polymorphous configurations. Because of that, we select a subset of compounds that are based on Cs in the A site and add the SOC correction. In most of the halide perovskites, the A site does not contribute to the band edge's orbital character and, therefore, does not directly influence the band gap and the SOC effects. This subset contains 49  $CsBX_3$  compounds, and is also shown in the Supplemental Material [43].

#### **III. RESULTS**

The discussion of electronic effects (relativistic SOC) and structural effects (symmetry breaking) on the band gap of

TABLE I.	Calculated	and experiment	al values for b	and gaps for	r the most	t studied	inorganic	halide pe	erovskites.	This tab	ole is se	parated
according to th	e structural	configuration, n	nonomorphous	or polymorp	hous, and	with the i	inclusion of	r not of th	ne spin-orbi	it effects	In pare	ntheses
we show the de	eviation bet	ween theoretical	and experimen	ital results, w	here a pos	sitive (ne	gative) valu	ue means	overestima	ation (un	derestin	nation).

System	Band gap (eV)									
	Monomorphous	Polymorphous	Monomorphous + SOC	Polymorphous + SOC	Expt.					
CsPbCl <sub>3</sub>	2.92 (-2.67%)	3.35 (11.67%)	1.78 (-49.67%)	2.27 (-24.33%)	3.00 <sup>a</sup>					
CsPbBr <sub>3</sub>	2.41 (8.07%)	2.87 (28.70%)	1.25 (-43.95%)	1.79 (-19.73%)	2.23 <sup>b</sup>					
CsPbI <sub>3</sub>	2.00 (15.61%)	2.46 (42.20%)	0.77 (-55.49%)	1.35 (-21.96%)	1.73 <sup>°</sup>					
CsSnCl <sub>3</sub>	1.56 (-46.21%)	2.38 (-17.93%)	1.17 (-59.66%)	2.13 (-26.55%)	2.90 <sup>d</sup>					
CsSnBr <sub>3</sub>	1.10 (-38.89%)	1.81 (0.56%)	0.70 (-61.11%)	1.53 (-15.00%)	1.80 <sup>e</sup>					
CsSnI <sub>3</sub>	0.81 (-37.69%)	1.50 (15.38%)	0.37 (-71.54%)	1.18 (-9.23%)	1.30 <sup>f</sup>					
CsGeBr <sub>3</sub>	1.13 (-52.52%)	1.56 (-34.45%)	1.02 (-57.14%)	1.45 (-39.08%)	2.38 <sup>g</sup>					

<sup>a</sup>Reference [44].

<sup>b</sup>Reference [45].

<sup>c</sup>Reference [46].

<sup>d</sup>Reference [47].

<sup>e</sup>Reference [48].

<sup>f</sup>Reference [49].

<sup>g</sup>Reference [50].

halide perovskites will be separated into three different sections, where the agents for band-gap variation can be treated separately. In Sec. IIIA we consider the effects of symmetry breaking in the polymorphous configuration, *not* including the effects of SOC, and we compare the results with the system in a monomorphous high-symmetry configuration (*Pm-3m*). In Sec. IIIB we examine the effects of SOC in the band gap of a cubic *Pm-3m* unit cell (monomorphous), *not* including the symmetry breaking. In Sec. IIIC we discuss the effects of symmetry breaking *and* SOC in the band gap of halide perovskites; i.e., both effects are included simultaneously. The band gaps calculated in different structural configurations and with or without SOC are shown in Table I for the most common inorganic halide perovskites.

#### A. Symmetry-breaking effects on the band gap: Monomorphous versus polymorphous configuration

In this section, we investigate the effects of symmetry breaking in the band gap of halide perovskites. The symmetry breaking was induced in a supercell by a random nudge in all the atoms. When the calculation for atomic relaxation is performed, it allows the possibility of capturing bond disproportionation, atom displacements, and octahedral rotation in different local chemical environments. Because of that, each local chemical environment could be different, and the perovskite structure is not composed by a spatial repetition of one single motif as in the monomorphous phase. We, therefore, call this nonsymmetric atomic configuration a polymorphous phase. It is important to mention that allowing a nonaverage unit cell that affords a distribution of local environments can already lower the total internal energy [24]. This is static energy lowering. This polymorphous effect occurs primarily for the nominal cubic phase Pm-3m, though some compounds, such as BaZrO<sub>3</sub> and others that will be presented here, have negligible static cubic polymorphous energy lowering. Other, lower-symmetry phases such as in orthorhombic perovskite

have but a negligible static lowering in total energy. In addition to static (nonthermal) energy lowering there is the conventional effect of thermal agitation creating a distribution of local displacements around the static polymorphous network (not around the cubic Pm-3m). The latter, thermal shift was considered in earlier molecular dynamics studies [34,51] and is not included here in this paper.

One important parameter to compare the polymorphous and monomorphous phases is the total energy. In Fig. 3(a), taking the monomorphous phase as a reference, we show the variation in total energy  $(E_{tot}^{poly}-E_{tot}^{mono})$ . We can see that in almost all the cases the total energy variation is negative, which indicates that the polymorphous phase is more stable than the monomorphous phase. There are some examples where the variation in the total energy is neglectable, indicating a degenerated state between monomorphous and polymorphous configurations. In other words, during the atomic relaxation of the polymorphous phase, all the atoms return to the ideal Wyckoff position of cubic Pm-3m, recovering the monomorphous phase. Therefore, the polymorphous configuration is more stable, or at least with the same total energy per formula unit, than the monomorphous phase.

To check the effects of symmetry breaking in the band gap, in Fig. 3(b) we plot the band gap for the polymorphous phase as a function of the monomorphous phase. The dashed line indicates the equality condition in the band gap for the two atomic configurations. An upper deviation from the dashed line means that the band gap of the polymorphous configuration is opening, while a lower deviation indicates that the band gap is closing. From these results, we can separate the band gap of the polymorphous phase into three categories: (i) invariant band gaps (i.e., monomorphous and polymorphous gaps are equal), (ii) compounds with band-gap opening, and (iii) compounds with band-gap closing.

For compounds with invariant band gap, i.e., where the band gaps of the polymorphous and monomorphous structures



FIG. 3. (a) Total energy difference between the polymorphous and monomorphous configurations for all the halide perovskites in our data set. The negative values indicate that the polymorphous phase is more stable than the monomorphous one. (b) Polymorphous band gap  $(E_g^{\rm poly})$  as a function of the monomorphous band gap  $(E_g^{\rm mono})$ . The dashed line indicates the condition for equality in the band gap for both atomic configurations.

are the same, the atomic relaxation process done in the supercell with nudged atoms makes it return to the original Wyckoff position of the cubic Pm-3m configuration, and therefore the full Pm-3m symmetry is restored. In other words, the polymorphous configuration after relaxation is identical, or very close, to the monomorphous configuration. These systems are examples where the total energies of monomorphous and polymorphous configurations are identical. This condition is observed for just a few compounds with halogen species of F and Cl, with one exception that is CsMgBr<sub>3</sub>. In all the cases, there are no B atoms composed of elements with  $ns^2$  lone pairs, and the band gap is always larger than 3.0 eV. Chemical elements that are very ionic (F and Cl) can make the bonds more rigid, creating difficulty for the octahedral rotations and bond disproportionation, therefore inducing small-amplitude symmetry breaking.

In the second category of symmetry-breaking effects on the band gap, we discuss the systems where the band gap of the polymorphous phase is larger than that of the

monomorphous phase. From Fig. 3(b), we can see that the majority of polymorphous HPs belong to this category. In these examples, the nudging induces at least one type of symmetry breaking, which is octahedral rotation, bond disproportionation, or atom displacement. The symmetry breaking reduces the total energy of the compound (when compared to the monomorphous phase), and the band gap opens. The intensity of band-gap opening is more pronounced for compounds that have monomorphous band gaps smaller than 4.0 eV and are composed mainly of heavier halogen atoms, such as I and Br. Note the large number of systems that have a near-metallic band gap in the monomorphous phase ( $E_g^{mono} = 0$ ); however, the symmetry breaking induces a band-gap opening, resulting in an insulator. Systems with wider band gaps (>6.0 eV) and composed of highly ionic halogen elements (F and Cl) have more rigid bonds, as mentioned before, and the effects of symmetry breaking are not so pronounced, which leads to a small variation in the band gap.

The most studied inorganic halide perovskites belong to this category of materials where the band gap opens upon symmetry breaking; these include Pb and Sn perovskites, shown in Table I. The symmetry breaking induces a bandgap opening around 0.5 eV in all these common compounds. However, the type of symmetry breaking in each one of these Pb- and Sn-based HPs are different. While in  $CsPbX_3$  (X = F, Cl, Br, and I) the predominant symmetry breaking is the octahedral rotation and Cs displacement, for  $CsSnX_3$  (X = F, Cl, Br, and I), the bond disproportionation (in addition to the octahedral rotation and Cs displacement) is very strong. For example, in CsSnF<sub>3</sub> the Sn atoms are bonded with three F atoms in an elongated bond, which is around 30% larger than the other three shorter Sn-F bonds. The bond disproportionation tends to decrease when the halogen size increases and becomes around 12% different in the CsSnI<sub>3</sub>. In fact, previous studies demonstrated that the contribution of band-gap changing are different from the different effects such as charge transfer, octahedral tilting, and lattice expansion [2,27].

The symmetry breaking also directly affects the band edges' orbital character in the halide perovskites. Considering compounds with *B* atoms with  $ns^2$  lone pairs (e.g., CsPbI<sub>3</sub>) in the monomorphous configuration, where there is no distortion, the overlap between the halogen *p* orbitals and the *B*  $ns^2$  lone pairs is large. The octahedral rotation observed in the polymorphous configuration decreases the overlap between the *B*  $ns^2$  lone pairs and halogen *p* orbitals. This symmetry breaking results in pushing less the antibonding states of VBM to higher energies [52], as shown in Fig. 4 (right-hand panel). At the same time, deeper VBM states tend to become more localized, and this is clearly observed in the charge isosurface in polymorphous structures that have the smallest area when compared to the monomorphous phase in Fig. 4 (left-hand panel).

For compounds that contain *B* atoms without  $ns^2$  lone pairs, such as CsMgI<sub>3</sub>, the octahedral rotation induced by the symmetry breaking is not so pronounced, and the variation in the band gap is small. However, even in this condition the VBM is pushed to deeper energies and induces a charge localization, as shown in Fig. 4.

The last category of band-gap variation, according to the symmetry breaking, contains the compounds with band-gap



FIG. 4. Left: Comparison of charge density for the valence-band maximum in halide perovskites composed of *B* atoms with and without lone pairs. The cutoff for the charge density isosurface was chosen to be 10% of the maximum in each case. Right: Schematic representation of band-edge orbital character composition for halide perovskites composed of *B* atoms with and without lone pairs. In both comparisons, the results are shown for the monomorphous (cubic Pm-3m) and polymorphous structural configurations.

closing. In these compounds, the atomic configuration is not so different from the compounds where the band gap opens; i.e., it is possible to observe all types of symmetry breaking. In addition, the total energy of the polymorphous phase is smaller than the total energy of the monomorphous phase. However, the band gap closing due to symmetry breaking can be addressed to the electronic structure and the band edges' orbital characters. Most of these compounds contain Tl and In in the A site. Since the formal oxidation state for the A atom is 1+, the s orbitals of Tl and In form a lone pair that contributes in the vicinity of the valence-band maximum and makes a hybridization with halogen p orbitals. The conduction-band minimum comprises p orbitals of the A atom hybridized with halogen s orbitals. This is a different composition of bandedge orbital characters when compared to standard halide perovskites, where atom A has deep occupied states lying far away from the vicinity of the VBM, and shallow unoccupied states lying far away from the CBM [52,53]. Hence, the presence of  $ns^2$  lone pairs on the A site introduces states at the band edges that come from these A atoms, and the symmetry breaking leads to a closing in the band gap of these halide perovskites. This behavior contrasts with the typical observation in standard halide perovskites, where the B atom possesses  $ns^2$  lone pairs and the symmetry breaking opens the band gap.

#### B. Spin-orbit coupling effects on the monomorphous band gap

The calculations that use hybrid exchange-correlation functionals with the addition of SOC tend to be computationally very expensive, especially when the number of electrons is very large as in the polymorphous configuration. In the Pm-3m structure, HSE + SOC is not a problem from a computational point of view; however, to be consistent and compare with the polymorphous phase, we decided to select a subclass of HP that has Cs in the A site. This subset of halide perovskites includes the most studied systems with the largest interest from the experimental community. The analysis of the SOC effect will be similar to the other systems with different A bases since the A atom is not important for the band edges of halide perovskites, and therefore does not affect directly the electronic configuration, which is one important factor for SOC. The unique exceptions are the system with low importance, which has the band-gap reduction mentioned before and is composed of Tl and In in the A site.

The SOC tends to affect the band-gap energy, and the intensity depends on two important factors: (i) the atomic number Z of each element that composes the HP (heavier elements have stronger SOC) and (ii) the band-edge orbital character (orbitals with higher angular momentum have stronger SOC). It is worth reminding that Fig. 4 (right-hand panel) shows a schematic composition of valence and conduction bands from most of the cases in our database, which include all the Cs-based compounds. Therefore, discussing SOC effects on the band gap of halide perovskites focuses on these two important factors.

Figure 5 shows the effects of SOC on the band gap of all Cs-based monomorphous (cubic Pm-3m) halide perovskites. We observe a band-gap reduction in all the systems, with



FIG. 5. Band-gap reduction induced by spin-orbit coupling (SOC) in the monomorphous atomic configuration. These calculations were done in the class of  $CsBX_3$  compounds and separated into groups according to the halogen chemical species. The systems based on Pb and Sn are indicated by the marks in the bars.

the exception of the ones that already have a metallic gap before the inclusion of SOC. When we exclude the compounds that contain *B* atoms with  $ns^2$  lone pairs (Sn and Pb), the reduction in the band gap tends to be very weak, around 0.2 eV. However, the SOC effect is stronger in I-based compounds, followed by Br, while for F- and Cl-based materials it is very similar. This trend can be observed by the average band-gap reduction indicated by the red dashed line in Fig. 5.

In the absence of  $ns^2$  lone pairs from the *B* atom, the conduction band is composed mainly of halogen *s* orbitals hybridized with *s* orbitals from the *B* atom; because of that, the SOC is very weak. The valence band, nevertheless, is composed mainly of halogen *p* orbitals, where the SOC can exist and be stronger as the halogen atom is heavier, following the trend described before.

Considering the systems composed of *B* atoms with  $ns^2$  lone pairs, the valence band is not strongly affected by the SOC, since on these compounds there is a hybridization of the halogen *p* orbital with *s* orbitals of the *B* atom. On the other hand, the conduction band is strongly affected due to the main contribution of *p* orbitals of the *B* atom. The reduction in the band gap should be stronger when the *B* atom is heavier, as observed for Sn and Pb, marked with special characters in the bars of Fig. 5.

Considering the most studied inorganic halide perovskites, shown in Table I, in the case of Pb, the SOC effect can reduce the band gap by values larger than 1.00 eV, and with the largest value of 1.23 eV found for CsPbI<sub>3</sub>. For the Sn compounds, the band-gap reduction due to SOC is around 0.40 eV, which is much smaller than the Pb ones. Despite the electronic structure being more accurately described when the SOC is included, the band-gap value for the monomorphous phase becomes largely underestimated. For the case of CsSnI<sub>3</sub>, the theoretical band gap is around 70% of the experimental band gap.



FIG. 6. Comparing the band-gap reduction due to spin-orbit coupling in monomorphous versus polymorphous configurations. The highlighted points inside the red ellipse denote systems characterized by CsPb $X_3$ , with X = I represented in purple, X = Br in orange, X = Cl in green, and X = F in blue.

# C. Spin-orbit coupling effects on polymorphous halide perovskites

Considering the same Cs-based halide perovskites discussed in Sec. IIIB, we now calculate the effects of SOC in the band gap of the system that includes symmetry breaking (polymorphous configuration). This section takes into account both mechanisms (relativistic physical effects and configurational composition) that induce a band-gap variation. It is important to note that symmetry breaking not only opens the band gap of halide perovskites, but also can change the electronic structure of the band-edge orbital characters, as shown in the schematic right-hand panel of Fig. 4. The octahedral rotation, bond disproportionation, and atom displacement can increase the charge localization (when compared to the monomorphous phase) and reduce the hybridization of the states at the valence and conduction bands. As a consequence, the symmetry breaking, in principle, can affect the SOC.

The results for band-gap variation due to SOC in the polymorphous configuration compared to the monomorphous system are shown in Fig. 6. There is a larger similarity between the SOC effects on calculations of halide perovskites with and without symmetry breaking (polymorphous vs monomorphous). In both scenarios, the inclusion of SOC leads to a reduction in the band gap, and the magnitude of this reduction is similar, as the systems are notably concentrated nearer to the main diagonal in Fig. 6, indicated by the black dashed line. The key differentiation arises in certain systems that exhibit metallic behavior in the monomorphous phase. With the incorporation of symmetry breaking, the band gap opens, allowing SOC to exert its influence, ultimately diminishing the band gap in these systems.

Given the comparable band-gap reduction induced by SOC in both monomorphous and polymorphous phases, we can infer that the factors influencing the intensity of this reduction resemble those discussed in Sec. IIIC. Specifically, (i) a system with a higher atomic number Z has a larger magnitude of band-gap reduction (I > Br > Cl ~ F); a system with heavier B atoms, and with  $ns^2$  lone pairs (Pb and Sn), has a strong band-gap reduction; and (iii) systems composed of B atoms without  $ns^2$  lone pairs have a weak band-gap reduction.

Considering the most studied inorganic halide perovskites shown in Table I, we can see that the reduction of the band gap due to SOC in the *polymorphous* configuration is comparable to the monomorphous configuration. For Pb-based compounds, the band-gap reduction can reach 1.00 eV and is stronger for CsPbI<sub>3</sub>. For the Sn case, the SOC effect reduces the band gap to around 0.40 eV. When the band gap is described with both effects (symmetry breaking and SOC), we still see an underestimation of the band gap for Pb-based compounds when compared to the experimental results. However, this is known, and for calculations with the hybrid functional, one way to solve it is to increase the exact exchange concentration [20,54]. On the other hand, calculations with symmetry breaking and SOC for Sn- and Ge-based compounds get closer to the experimental results when compared to the monomorphous configuration with SOC.

### D. Transitivity of SOC and symmetry breaking on the band-gap description

Despite the octahedral rotation, bond disproportionation, and atom displacement induced by the symmetry breaking, these effects are not able to significantly change the effects of SOC in the band gap when compared to the systems without symmetry breaking. Because of that, we can say that the band-gap reduction through SOC effects depends only on the elements' composition; i.e., it does not depend on the structural configuration (polymorphous vs monomorphous).

The calculations presented in this paper in Table I and in the Supplemental Material [43] follow the red path in Fig. 1. First, we calculate the polymorphous phase, which leads to an increase in the band gap by  $\Delta E_{g}(SB)$  and is presented in Sec. III A. In Sec. III A, we include the effects of SOC on the polymorphous phase, decreasing the band gap  $\Delta E_{\alpha}(SOC)$ , and fully describe the halide perovskites. However, if we follow the blue path in Fig. 1, we can calculate how much the band gap decreases by relativistic effects  $\Delta E_{g}(SOC)$  in the monomorphous phase (shown in Sec. IIIB), and use the results of the band gap increasing by symmetry breaking,  $\Delta E_{g}$ (SB), shown in Sec. IIIA. The maximum difference in the band-gap description occurs for CsPbCl<sub>3</sub>. While the red path results in 2.13 eV for the band gap, the blue path results in 1.99 eV (0.14 eV underestimated). This demonstrates that the band-gap description in halide perovskites, according to the relativistic physical effects and symmetry breaking, is transitive, i.e., independent of the path.

It is important to mention that different paths in Fig. 1 have very different computational costs. Considering, for example, CsPbI<sub>3</sub>, there are 34 valence electrons in the monomorphous phase, while in the polymorphous supercell there are 1088 valence electrons. While the red path applies the SOC correction in the polymorphous system, which is very large due to the supercell requirement, and has many electrons, the blue path applies SOC correction in the primitive high-symmetric cubic Pm-3m configuration, which contains only five atoms. Following the blue path in Fig. 1, several hours of calculation can be saved when the band-gap description is required. As a result, when handling large data sets of halide perovskites with a primary focus on band-gap description, it suffices to incorporate SOC effects within the computationally inexpensive monomorphous cubic cell (Pm-3m) and compute the band-gap reduction, and to compute the band-gap opening through symmetry breaking (without SOC) and add both band-gap variations in the monomorphous absolute band gap.

#### **IV. CONCLUSION**

In this work, we study the effects of relativistic corrections ("mass-Darwin" effect and spin-orbit coupling) and structural configuration (symmetry breaking) on the band-gap description in halide perovskites. We isolate these effects into three distinct categories: (i) with SB and without SOC, (ii) without SB and with SOC, and (iii) with SB and with SOC. In summary, we observe that SB, which can be composed of a combination of octahedral rotations, atom displacements, and bond disproportionation, tends to open the band gap in most halide perovskites by changing the overlap between the orbitals that constitute the band edges. In contrast, the SOC effect decreases the band gap of halide perovskites and the intensity is dependent on the band edges' orbital character and the mass of the elements that constitute the halide perovskites. The main point of the nature of the interplay between SOC, a correction that depends primarily on atomic number and lives inside the nucleus, and SB, a correction that depends primarily on bonding outside the nucleus, is that they are independent effects to describe the band-gap magnitude in halide perovskites. As a result of that, we observe a transitivity of the band-gap description; i.e., if we know the band gap of halide perovskites without SB and SOC, we can add the effects of band-gap reduction due to SOC and band-gap opening due to SB, regardless of the order in which these effects are considered. This transitivity provides a computationally efficient method for describing the band gaps of halide perovskites: first, compute the band-gap reduction due to SOC using the high-symmetry cubic Pm-3m structure (lower number of electrons), and calculate the band-gap opening in the polymorphous cell (higher number of electrons). Second, add these effects in the band gap of the monomorphous cubic Pm-3m cell. The band-gap result will be very similar to the band gap of the polymorphous cell with SOC, which requires a large computational cost.

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