Defining the Topological Influencers and Predictive Principles to Engineer Band Structure of Halide Perovskites

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(Dated: November 21, 2019)

Complex quantum coupling phenomena of halide perovskites are examined through ab-initio calculations and exact diagonalization of model Hamiltonians to formulate a set of fundamental guiding rules to engineer the bandgap through strain. The bandgap tuning in halides is crucial for photovoltaic applications and for establishing non-trivial electronic states. Using CsSnI₃ as the prototype material, we show that in the cubic phase, the bandgap reduces irrespective of the nature of strain. However, for the tetragonal phase, it reduces with tensile strain and increases with compressive strain, while the reverse is the case for the orthorhombic phase. The reduction can give rise to negative bandgap in the cubic and tetragonal phases leading to normal to topological insulator phase transition. Also, these halides tend to form a stability plateau in a space spanned by strain and octahedral rotation. In this plateau, with negligible cost to the total energy, the bandgap can be varied in a range of 1eV. Furthermore, we present a descriptor model for the perovskite to simulate their bandgap with strain and rotation. Analysis of band topology through model Hamiltonians led to the conceptualization of topological influencers that provide a quantitative measure of the contribution of each chemical bonding towards establishing a normal or topological insulator phase. On the technical aspect, we show that a four orbital based basis set (Sn-\{s,p\}) for CsSnI₃ is sufficient to construct the model Hamiltonian which can explain the electronic structure of each polymorph of halide perovskites.

I. INTRODUCTION

Halide perovskites, enriched with structurally modulated diverse electronic phases, are promising materials for research in the fundamental area of band topology and in the applied area of optoelectronics[1–5]. These compounds with the formula ABX₃ (A is either organic or inorganic, B = Sn, Pb or Ge and X = Cl, Br or I) are structurally flexible to external stimuli such as pressure, temperature and chemical doping [6–11]. The symmetry altering structural modifications invite changes in the interplay of lattice, orbital and spin degrees of freedom to manifest trivial and non-trivial electronic phases. Studies suggest that if A is inorganic elements like Cs and Rb, then the centrosymmetric structure stabilizes [12] and in such a situation while, covalent interaction among the B and X states tune the bandgap (E₉), the strength of atomic spin-orbit coupling become deterministic towards tailoring non-trivial topological phases such as topological insulator [9, 13]. However, if A is an organic element like MA (CH₃NH₃) and FA (CH(NH₂)₂)the inversion symmetry breaks down and therefore both atomic SOC and Rashba SOC - that inflicts the spin-split in the momentum space - become deterministic in tailoring the electronic behavior of these quantum materials [14, 15].

Specific to the studies of band topology in inorganic halide perovskites, the literature, focusing on the high temperature cubic phase, hypothesizes a pressure induced phase transition from the normal insulator (NI) to topological insulator (TI) phase via an accidental Dirac semimetal (DSM) phase [9, 13]. However, experimentally halide perovskites are known to demonstrate structural polymorphs with temperature governing their stability. With lowering in temperature the cubic (α) phase yields to the tetragonal (β) phase and on further reduction of the temperature these compounds stabilize in the orthorhombic (γ) phase [16–18].

Moving from α to β and γ-phases via symmetry lowering introduces additional degrees of freedom in the form of bond length and bond angle as shown in Fig. 1. For example, unlike the case of cubic structure where the epitaxial strain is measured only through c/a, for the orthorhombic phase it is measured through c/a and b/a as well as through rotational and tilting angles θ_{ab} and θ_{c}. These additional degrees freedom introduce significant complexities to the valence and conduction bands and hence are largely avoided in the electronic structure analysis in the quest for simplifying the predictive principles. From a positive point of view, these additional degrees offer further flexibilities to tune the bandgap which is a crucial ingredient to improve the photovoltaic efficiencies as well as to open up new insight to the physics of non-trivial topology. The objective of this paper is to take into account these symmetry lowering structural distortions and possible manipulation of them through external routes such as pressure and strain so that a set of fundamental design principles can be hypothesized for tuning the electronic structure of the halide perovskite family.

The universality of the electronic structure of perovskite members as explained in our earlier works [13, 19] enables us to examine a single compound rather than the whole family and extract the insight into the band struc-
ture with regard to the anisotropic structural distortions. In this paper, it is achieved by carrying out DFT calculations on CsSnI$_3$ polymorphs. The DFT results are served as critical input to a minimal basis set based parametric Slater-Koster tight binding (SK-TB) Hamiltonian suited for each of the structural phases. Interestingly, we show that a minimal basis set consisting of 4 orbitals of single pseudo-cubic lattice formed out of the B element of ABX$_3$ is sufficient to explain its band structure. By solving the SK-TB Hamiltonian, we propose an empirical descriptor model capable of predicting the band topology of the Halide family. The model consists of a set of linear equations $[T] = [D][EC]$, where $[T]$ represents the set of hopping interactions, $D$ is the family of descriptors specific to a given compound, and EC are the externally controlled variables such as the bond lengths and the rotational and tilting angles.

In the context of CsSnI$_3$, we show that the bandgap can be manipulated to the tune of 1 eV through epitaxial strain. Furthermore, a NI to TI phase transition can be achieved either by compressive or tensile strain for the $\alpha$-phase. However, in the $\beta$-phase such a transition is plausible only through tensile strain. In the $\gamma$-phase the system cannot exhibit the TI state as either the bulk bandgap increases from its equilibrium value or the structure enters an unstable regime.

II. STRUCTURAL AND COMPUTATIONAL DETAILS:

The crystal structure of the halide perovskites in all three phases ($\alpha$, $\beta$, and $\gamma$) are shown in the upper panel of Fig. 1. The experimental structural parameters corresponding to CsSnI$_3$ are listed in Table-1 [17, 18, 20]. The $\beta$-phase emerges out of the distortion of $\alpha$-phase through minor compression of $\sim$0.015Å in the $ab$-plane and expansion of $\sim$0.05Å along the $c$-axis. The lattice distortion is also accompanied by deviation of the angle between the neighboring octahedra in the $ab$-plane ($\theta_{ab}$) from the ideal 180°. The primitive unitcell of the $\beta$-phase is formed by a $\sqrt{2} \times \sqrt{2} \times 1$ supercell. In the $\gamma$ phase the lattice experience natural compression in all three direction. Along the $a$-axis the compression is of $\sim$0.075Å, along the $b$-axis it is 0.1Å and along the $c$-axis it is 0.03Å. In this phase, both the angles, $\theta_{ab}$ and $\theta_{c}$ deviates from 180°. The primitive unitcell of the $\gamma$-phase is formed out of the $\sqrt{2} \times \sqrt{2} \times 2$ supercell.

The bulk and surface Brillouin zone (BZ) and the high symmetry (HS) points in the reciprocal space for each of these phases are shown in the second panel of Fig. 1. As the primitive cell in the real space gets augmented due to lowering in the symmetry, the BZ and hence the HS points of the $\beta$ and $\gamma$-phases differ from that of the $\alpha$-phase. Consequently, the TRIM $R$ of $\alpha$-phase is mapped to $Z$ and $\Gamma$ of $\beta$ and $\gamma$-phases respectively.

The electronic structure of each of the polymorphs of CsSnI$_3$, in their equilibrium and strained structures, are carried out using both density functional theory (DFT) and minimal basis set based tight-binding model Hamiltonian. For DFT, we have used the full-potential linearized augmented plane wave (FP-LAPW) method as implemented in WIEN2k simulation tool [21, 22]. The PBE-GGA approximation along with modified Becke-Johnson (mBJ) functional is used to take into account the exchange-correlation effect [23–25]. For each strain condition, structural relaxation is carried out to obtain the corresponding ground state. The basis set, employed for the SCF calculations, consists of augmented plane waves occupying the interstitial region and localized orbitals (Cs-6s, Sn-5s, 5p) and I-5p) occupying the respective muffin-tin spheres ($R_{MT}^{Cs} = 2.5$ a.u, $R_{MT}^{Sn} = 2.5$ a.u and $R_{MT}^{I} = 2.5$ a.u). The number of plane waves are determined by setting $R_{MT}K_{MAX}$ to 7.0. We find that with this cutoff, the number of plane waves lies in the range $10^3-10^4$. The Brillouin zone integration is car-
TABLE I. Crystallographic information of CsSnI$_3$. Here, the $\theta_{ab}$ and $\theta_t$ denote the angle between Sn-I-Sn in xy plane and along z direction, respectively (see Fig. 1).

| Structure          | Lattice parameter(Å) | Octahedral rotation |
|--------------------|----------------------|---------------------|
| Cubic \((a_0a_0a_0)(\alpha)\) | \(a = 6.219\)        | -                   |
| Pm-3m (221)        | \(c = 6.261\)        | \(\theta_{ab} = 161.9^\circ\) |
|                    | \(\theta_t = 180^\circ\) |                     |
| Tetragonal \((a^0a^0c^+)(\beta)\) | \(a = 8.772\)        | \(\theta_{ab} = 158^\circ\) |
| P4/mmbm (127)      | \(c = 6.261\)        | \(\theta_t = 172.3^\circ\) |
| 425-351            |                      |                     |
| Orthorhombic \((a^-a^-c^+)(\gamma)\) | \(a = 8.688\)        | \(\theta_{ab} = 158^\circ\) |
| Pnam (62)          | \(b = 8.643\)        | \(\theta_t = 172.3^\circ\) |
| \(< 351\)          | \(c = 12.378\)       |                     |

ried out with a Monkhorst-Pack grid. We used a k-mesh of \(10\times10\times10\) (yielding 35 irreducible points), \(8\times8\times12\) (yielding 60 irreducible points), and \(8\times8\times6\) (yielding 100 irreducible points) for the $\alpha$, $\beta$, $\gamma$-phases respectively. The bulk-boundary correspondence of the band topology are examined by calculating the SK-TB based surface band structure of a slab grown along (001).

III. DFT CALCULATIONS: RESULTS AND ANALYSIS

A. Electronic Structure of $\alpha$, $\beta$, and $\gamma$ Phases of CsSnI$_3$

There exist a few articles in the literature discussing the electronic structure of CsSnI$_3$ obtained from DFT calculations [9, 20, 26-29]. The focus of these articles is mainly confined to examine the bandgap of the compound and its suitability for photovoltaic applications. However, the non-trivial topological aspects, where spin-orbit coupling (SOC) plays a major role, as well as bandgap modulation as a function of strain and lattice distortion which have been largely ignored and therefore the same will be discussed in this section. The lower panel of Fig. 1 illustrates the ground state electronic structure of CsSnI$_3$ in the absence of strain which shows a monotonous increase in the bandgap as we move from the higher symmetric $\alpha$-phase to the lower symmetric $\gamma$-phase. Similar observation is also made when calculations are carried out without including the SOC [26]. Hence, it implies that this increase in bandgap with symmetry reduction is largely due to the variation in the chemical bonding.

Considering the $\alpha$-phase, for any halide and oxide perovskites ABX$_3$ we have shown that bonding and antibonding bands emerge out of strong B-{s, p}-X-p nearest neighbor covalent interactions.[13, 19] The anti-bonding and bonding bands are separated by a set of X-p dominated non-bonding bands. Furthermore, both bonding and antibonding spectrum have four bands with the lower one is formed by the B-s-X-p hybridized states and the upper three are formed by the B-p-X-p hybridized states. Also, there is a gap between the lower one and the upper three bands. In the case of halide perovskites, where the valence electron count is 20, this gap exactly lies at the Fermi level, as can be seen from Fig. 1, in order to make these compounds semiconducting or insulating. As the figure suggests, the $\beta$ and $\gamma$-phase, which stabilize with the distortion to the $\alpha$-phase, inherit these same salient features, but with a larger bandgap due to distortion induced reduction in the band width.

Though the universality of the band structure arises from the nearest-neighbor B-{s, p}-X-p covalent interactions as discussed in the previous paragraph, the second neighbor B-{s, p}-B-{s, p} interactions are found to be the driving force for engineering the bandgap as well as construing non-trivial phases [13]. In the ground state, the second neighbor interaction strength is less than 1eV (almost one-third of nearest neighbor interaction) [13, 19] which can be varied and made anisotropic easily through strain and will be discussed in the following sub-section.

B. Effect of Epitaxial Strain on the Band Topology

The nature of lattice distortion due to applied epitaxial strain depends on the ground state structure. In the $\alpha$-phase, the strain brings change to the translational symmetry as only the c/a ratio changes without tilting and rotating the octahedra. In the upper panel of Fig. 2, we have shown the band structure of $\alpha$-CsSnI$_3$ for c/a = 0.9, representing the tensile strain, and for c/a = 1.1, representing the compressive strain. We see that at the TRIM $R$, the band character reverses with respect to the ground state structure (see Fig. 1) irrespective of the strain condition. Now, the Sn-p characters construct the VBM and the Sn-s character constructs the CBM. This band inversion brings a parity transformation to create a topologically invariant Dirac state at the surface as will be discussed in section 4.3. To provide a quantitative measure of band inversion, in the lower panel of Fig. 2 we have plotted the Sn-s and -p orbital weight at $R$ for band-1 - constituting the VBM - band-2 -constituting CBM - as a function of c/a. It shows that there exists two critical values of c/a one each for compressive and tensile strain. Beyond these critical values the band inversion occurs to induce the TI phase. This can be explained from the fact that with strain, the bond lengths either in the xy plane (compressive) or along the z-axis decreases. With the decrease in the bond length there is substantial increase in the hopping interaction strength (t) and hence the band width, particularly for band-1. As a consequence, the gap between band-2 and band-1 decreases. At a certain critical value of strain the gap become negative leading
and will be discussed in the context of uniform hydrostatic pressure, the \( \theta_{ab} \) increases only with compressive strain, which probably can be supplied to the system by thermal means, has its significance in optoelectronic applications \[30\]. Thirdly, with tensile strain negative bandgap emerges (see Fig. 3(b)). In the negative gap region, the band inversion occurs which lead to formation of topological insulating phase. To further reconfirm and illustrate the role of the bandgap on the band inversion, we have identified six points in Fig. 3(b) in the space spanned by \( c/a \) and \( \delta \theta_{ab} \) and plotted the respective band structures in Fig. 3(c). The points lie within the area enclosed by the dotted black line show the inversion of the s and p orbital characters between the VBM and CBM at Z. The other points exhibit the normal band insulator behavior. Interestingly, the stability curve passes through the negative to positive bandgap region as the strain changes its character from compressive to expansive. Hence, unlike the \( \alpha \)-phase, the \( \beta \)-phase can establish the TI phase only through tensile epitaxial strain.

As mentioned in section 2, the \( \gamma \)-phase represents the lowest symmetry structure among the three phases and it is characterized by both in-plane (\( \theta_{ab} \)) and out of plane (\( \theta_{c} \)) octahedral rotations. Fig. 4 summarizes the effect of strain on the stability and electronic structure of CsSnI\(_3\) in this phase. The optimized values of \( \theta_{ab} \) and \( \theta_{c} \) as a function of \( c/a \) are shown in the upper panel. The tensile strain distorts the lattice more as both the angles deviate considerably from 180°. However, the energetically expensive compressive strain brings the lattice close to the \( \beta \)-phase with \( \theta_{c} \) approaching 180°. The estimation of bandgap, plotted in blue solid line, shows that larger the octahedral rotation and tilting, larger the bandgap. One can minimize the bandgap in this phase by compression. However, we find that it is far from being negative even after 15% compression (bandgap = 0.6 eV) which further implies that cannot be induced in \( \gamma \)-CsSnI\(_3\).

**IV. MODEL HAMILTONIAN FOR THE BULK HALIDE PEROVSKITES**

The modulation of the bandgap and hence the topological phase, as revealed from DFT calculations, are found...
solid curve in Fig. b represents the minimum energy curve or the stability curve with optimized value of c/a calculations for suitably chosen 42 odd points in the dotted lines separate the NI from the TI phase. The total energy and the bandgap maps are obtained by carrying out DFT calculations for the (I) second neighbor Sn-Sn interaction, (II) the octahedral rotation/tilting angles δθab, δθ, and (III) the c/a ratio induced through strain. Therefore, formulation of an empirical relationship between E_g and the influencing factors (c, t, δθ, c/a) is desirable. To fill the void, such calculations can be carried out. To fill the void, the minimal basis set based tight-binding calculations, following the Slaker-Koster formalism [31], are adopted in this work.

In this regard, while the all-electron DFT calculations are best suitable for the purpose, being computationally expensive, only a discrete, and hence incomplete, set of such calculations can be carried out. To fill the void, the minimal basis set based tight-binding calculations, following the Slaker-Koster formalism [31], are adopted in this work. The appropriate SK-TB Hamiltonian for the family of ABX3, in the second quantization notation, is expressed as

\[
H = \sum_{i, m} \epsilon_i c_{i m}^\dagger c_{i m} + \sum_{\langle (ij); m, n \rangle} t_{i m j n} (c_{i m}^\dagger c_{j m} + h.c.) + \lambda L \cdot S. \tag{1}
\]

Here, \((ij)\) and \(m (n)\) are site \((B)\) and the orbitals \((s, p_x, p_y, p_z)\) indices respectively. The parameters \(\epsilon_{i m}\) and \(\lambda t_{i m j n}\) respectively represent the on-site energy and the strength of hopping integrals. The spin-orbit coupling (SOC) is included in the third term of the Hamiltonian with \(\lambda\) denoting the SOC strength. The SOC requires doubling of the Hilbert space in the spin-domain. Since the unitcell of \(\alpha, \beta\) and \(\gamma\) phases consists of one, two and four formula units, the order of the Hamiltonian matrix for these phases in the same sequence is 8, 16 and 32. Furthermore, in the present consideration, the Hamiltonian needs to obey the time reversal symmetry which can be achieved by ensuring the following relation [32].

\[
H = \begin{pmatrix} H_{\uparrow\uparrow} & H_{\uparrow\downarrow} \\ H_{\downarrow\uparrow}^\dagger & H_{\downarrow\downarrow} \end{pmatrix}; H_{\downarrow\downarrow} = (H_{\uparrow\uparrow})^\dagger, H_{\downarrow\uparrow} = (H_{\downarrow\uparrow})^\dagger. \tag{2a}
\]

While \(H_{\downarrow\downarrow}\) is the time reversal partner of \(H_{\uparrow\uparrow}\), the off-diagonal component \((H_{\downarrow\uparrow})\) is position independent and its conjugate transpose enable the hopping between the partners. In the expanded form, these sub-matrices are found to be

\[
H_{\uparrow\uparrow} = \begin{pmatrix} 
\epsilon_i + f_0 & 2it_{\uparrow \uparrow}^pS_x & 2it_{\uparrow \uparrow}^pS_y & 2it_{\uparrow \uparrow}^pS_z \\
-2it_{\uparrow \downarrow}^pS_x & \epsilon_p + f_1 + i\lambda & -i\lambda & 0 \\
-2it_{\uparrow \downarrow}^pS_y & i\lambda & \epsilon_p + f_2 & 0 \\
-2it_{\uparrow \downarrow}^pS_z & 0 & 0 & \epsilon_p + f_3
\end{pmatrix}, \tag{2b}
\]

\[
H_{\downarrow\uparrow} = \begin{pmatrix} 
0 & 0 & 0 & 0 \\
0 & 0 & \lambda & 0 \\
0 & 0 & -i\lambda & 0 \\
0 & \lambda & 0 & 0
\end{pmatrix}. \tag{2c}
\]

The dispersion relations \(f\) are obtained by using the Slater-Koster TB relations [31]. For the (un)strained \(\alpha\)-phase they

![FIG. 3. (a) The variation of total energy (relative to ground state structure) and (b) bandgap as a function of c/a and δθab for β-CsSnI3. In this paper we define c/a as the ratio between the nearest Sn-Sn bond length - which is also the lattice parameter in the α-phase - along \(\hat{z}\) and along \(\hat{x}\). The color-bar indicates the magnitude of bandgap measured at the TRIM Z. The red solid curve in Fig. b represents the minimum energy curve or the stability curve with optimized value of δθab. The black dotted lines separate the NI from the TI phase. The total energy and the bandgap maps are obtained by carrying out DFT calculations for suitably chosen 42 odd points in the c/a-δθab plane. (c) Orbital resolved DFT band structure of some of the representative points (1 to 6) indicated in Fig. b. As expected, the band inversion occurs for the points with negative bandgap.](image)
lower panel) suggests that the cation Sn does not 
which shows that the bandgap is 
(c, d) The representative band 
strain on the band topology. 
ǫ(c/a) and δθ. The following questions can be asked. Do 
the nearest neighbor Sn-I covalent 
through ϵ and t, the following questions can be asked. Do 
we really need the real crystal unit cell to construct a TB 
model in order to capture the essential electronic behavior in 
the vicinity of the Fermi surface? Can a smaller unit cell, 
sufficient to reduce the basis set of the TB Hamiltonian, be 
designed so that the formation of a large intractable Hamiltonian 
matrix (e.g. the 32×32 for the γ-phase) can be avoided? 
A closer inspection of the crystal structure of the three phases 
(see Fig. 5 lower panel) suggests that the cation Sn does not 
change its symmetry (Wyckoff) position due to change in 
the crystal phase. Hence, the lattice of Sn alone is same for all 
the phases, except the change in the length of the lattice vectors 
as can be noticed from the lower panel of Fig. 5. The later is equivalent to application of anisotropic strain to the 
cubic lattice. Therefore, the TB model for the α-phase can 
be accepted as a common TB model (CTB) for the family 
of halide perovskites. With this model, the phases will be 
distinguished from each other through the strength of the in-
teraction parameters. Therefore, the dispersion relation of 
Eq. (3) remains the same for the CTB model except the fact 
that each of the t are now explicitly function of c/a and θ. The 
band structure for the β and γ-phases, obtained with the CTB 
model, are shown in Fig. 6 which shows that the bandgap is 
well reproduced. In fact, the TB band structure for the real 
unit cell of the β and γ-phases can be reconstructed from the 
CTB band structure through band downfolding.

B. Construction of a Descriptor Model

The structural optimization carried through DFT calculations 
in the previous sections have revealed that with strain, 
the bond lengths and bond angles such as rotation and tilting 
(specific to the β and γ-phases) change. As a result, the TB 
parameters change and consequently the band structure 
differs from the equilibrium configuration. Therefore, in order to 
gain insight on the band topology of the halide polymorphs, it 
is crucial to examine the variation of the TB parameters with 
strain. This has been carried out in this work for the case of 
α and β-phases and the results are illustrated in Fig. 7. 
The blue and red solid lines correspond to the strained α and 
β-phases respectively. In general the interaction strengths in-
crease with decrease in bond length and it is well reflected 
through the blue lines. The deviation of the parameters of
FIG. 5. First row: DFT (red) and TB (blue) band structure of different phases of CsSnI$_3$. Second row: The cubic units of the $\alpha$-phase and the distorted-cubic units of lower symmetry $\beta$ and $\gamma$ phases. If I and Cs are ignored, the lattice of Sn alone (blue lines) in the $\beta$- and $\gamma$- phases can be represented as strained $\alpha$ phases.

FIG. 6. The band structure of unstrained $\beta$- and $\gamma$-CsSnI$_3$ as obtained with a minimal basis set based common tight-binding (CTB) model as discussed in the text. The TB parameters of Table-II are used to calculate the band structure. The effect of each of the parameters on the band structure in the vicinity of the Fermi level can be explained by calculating the eigenvalues at the TRIM $R$ by diagonalizing the CTB matrix of Eq. (2). They form four degenerate pairs as expressed below.

\[
E_{1,2} = \epsilon_s - 4t_{ss}^2 - 2t_{xz}^2,
\]

\[
E_{3,4} = \frac{(\epsilon_p^x + \epsilon_p^z - \lambda)}{2} - 2t_{ppxx} - \zeta - \frac{\sqrt{8\lambda^2 + (\lambda + \chi)^2}}{2},
\]

\[
E_{5,6} = \epsilon_p^x + \lambda - 2t_{ppxx} - 2t_{xz}^2 - 2t_{zz}^2,
\]

\[
E_{7,8} = \frac{(\epsilon_p^x + \epsilon_p^z - \lambda)}{2} - 2t_{ppxx} - \zeta + \frac{\sqrt{8\lambda^2 + (\lambda + \chi)^2}}{2}.
\]

Where,

\[
\chi = \epsilon_p^x - \epsilon_p^z + 2(t_{ppxx}^x + t_{ppxx}^z - t_{ppxx}^z - t_{ppxx}^z),
\]

\[
\zeta = t_{ppxx}^x + t_{ppxx}^z + t_{ppxx}^z + t_{ppxx}^z.
\]

The superscripts $x$ and $z$ refers to in-plane and out-of-plane interactions. The pair $E_{1,2}$ form the VBM and the pair $E_{3,4}$ form the CBM. These two pairs determine the band topology as $E_{5,6}$ and $E_{7,8}$ lies above $E_{3,4}$. The pre-factor to the TB parameters of $E_{1,2}$ and $E_{3,4}$ can be defined as topology-influencers (TIF) and they are listed in Table 3. Fig. 7 and Table 3 together can be referred to provide a physical interpretation for TIF. For example, for change of 0.3 in $c/a$ ratio,
the $t''_{sp}$ changes by $\sim 0.1$ eV. However, it shifts the VBM at $R$ by $0.4$ eV. On the other hand, though for the same change in $c/a$ $t''_{sp}$ changes by $0.4$ eV, it does not disturb the VBM and CBM at all.

![Diagram](image)

**FIG. 8.** (a) Variation of the bandgap as a function of $c/a$ for constant $\theta_{ab}$ and (b) vice-versa as estimated using the descriptor method. The DFT bandgap values are denoted with red dots, which shows excellent agreement with the descriptor method.

**TABLE III.** The topological influencers for different interaction parameters.

| $e_s$ | $\epsilon_{11}$ $\epsilon_{12}$ $\epsilon_{13}$ | $t''_{sa}$ | $t''_{sp}$ | $t''_{pp\sigma}$ | $t''_{pp\pi}$ | $\delta'_{c/a}$, for CsSnI$_3$. |
|-------|--------------------------------|------------|------------|-----------------|----------------|-------------------------------|
|       |                                 |            |            |                 |                 |                               |
| 2.22  | 0                                | 0          | 6.01       | 3.12            | 1.7            |                               |
| 6.07  | 4.2                              | 16.9       | -0.22      | -0.61           | -2.33          |                               |
|       | -0.22                            | 1.23       | -4.2       |                 |                |                               |
| 0.50  | 1.18                             | -0.28      | 0.48       | -1.93           | 5.26           |                               |
| 0.83  | 0.63                             | -0.145     | 0.86       | -0.77           | 1.5            |                               |
| 0.09  | 0.47                             | -0.64      | 0.09       | 0.61            | 1.89           |                               |

| $e_s$ | $\xi_{11}$ $\xi_{12}$ $\xi_{13}$ | $t''_{sa}$ | $t''_{sp}$ | $t''_{pp\sigma}$ | $t''_{pp\pi}$ | $\delta'_{c/a}$, for CsSnI$_3$. |
|-------|--------------------------------|------------|------------|-----------------|----------------|-------------------------------|
|       |                                 |            |            |                 |                 |                               |
| 2.19  | 0.57                            | -0.402     | 6.0        | 0.14            | -1.11          |                               |
| 6.0   | 0.59                            | 0.30       | -0.22      | 0.07            | 0.29           |                               |
|       | -0.22                            | 0.04       | 0.50       | -0.04           | -0.86          |                               |
| 0.83  | 0.09                             | -0.57      | 0.09       | 0.04            | -0.04          |                               |
| 0.09  | 0.04                             | -0.04      |           |                |                |                               |

Note: Here, $\delta\theta$ is in terms of radian.

Using Eq. (4) and the descriptor matrices of Eq. (5) and (6), we can estimate the $E_g$ ($= E_{3,4} - E_{1,2}$) as a function of $\delta c/a$ and/or $\delta \theta$ and few selected plots are shown in Fig. 8. We found that the bandgap obtained from above equations for constant $\delta \theta$ and $c/a$ shows substantial agreement with DFT bandgap (red dots). These formulations assist in analyzing the bandgap as a function of strain. From the literature it is evident that most of the halide perovskites follow similar band structure [27, 28] and thus the descriptor model universalize the $E_g$ variation under different types of strain. Also, in the context of uniform expansion or compression it has been shown that irrespective of the exchange-correlation (XC) functional, the variation of the bandgap with compression and expansion remains the same [13, 34–36]. The same is expected for the case of epitaxial strain. Therefore, the descriptors are expected to be independent of XC and hence have universal appeal.
C. Surface Band Structure

The bulk electronic structure study has enabled us to identify the possible trivial and non-trivial phases and phase transition among them in CsSnI$_3$ polymorphs. However, the practical observation of these phases comes from the calculation of surface band structure. In this section, we develop a Slater-Koster based TB Hamiltonian for slabs grown along (001) to obtain the surface band structure. Here, the slab consist of alternative stacking of CsI and SnI$_2$ layers. However, as discussed in section 2, there is no contribution of Cs and I orbitals at the Fermi level, the model is restricted to Sn-[s, p] orbital basis. The appropriate Hamiltonian for the slab consisting of n unit cells (001) is

$$H_{slab} = \begin{pmatrix} H^{\uparrow\uparrow} & H^{\uparrow\downarrow} \\ H^{\downarrow\uparrow} & H^{\downarrow\downarrow} \end{pmatrix}. \tag{7}$$

Here, $H_{jj}$ is the Hamiltonian for $j^{th}$ layer of the slab, and it is given by,

$$H_{jj} = \begin{pmatrix} \epsilon_s + f_0 & 2it^{\sigma_p}S_x & 2it^{\sigma_p}S_y & 0 \\ -2it^{\sigma_p}S_x & \epsilon_{p} + f_1 & -i\lambda & 0 \\ -2it^{\sigma_p}S_y & i\lambda & \epsilon_{p} + f_2 & 0 \\ 0 & 0 & 0 & \epsilon_{p} + f_3 \end{pmatrix}. \tag{8}$$

The block $H_{jj-1}$ describe the interaction between layer j and j-1.

$$H_{j-1j} = (H_{jj-1})^T = \begin{pmatrix} t^{\sigma_p} & 0 & 0 & t^{\sigma_p} \\ 0 & t^{\sigma_{pp}} & 0 & 0 \\ 0 & 0 & t^{\sigma_{pp}} & 0 \\ -t^{\sigma_p} & 0 & 0 & t^{\sigma_{pp}} \end{pmatrix}. \tag{9}$$

The off diagonal block emerging from the SOC is of the form

$$H_{\uparrow\downarrow} = \begin{pmatrix} G_{11} & 0 & 0 & 0 & \cdots \\ 0 & G_{22} & 0 & 0 & \cdots \\ 0 & 0 & G_{33} & 0 & \cdots \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & G_{n-1n-1} & 0 \\ 0 & 0 & 0 & 0 & G_{nn} \end{pmatrix}. \tag{10}$$

where,

$$G_{jj} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \lambda \\ 0 & -\lambda & 0 \end{pmatrix}. \tag{11}$$

As mentioned in Eq. 2, $H^{\downarrow\downarrow} = (H^{\uparrow\uparrow})^*$ and $H^{\uparrow\downarrow} = H^{\downarrow\uparrow}$, which assures the time reversal symmetry of the Hamiltonian matrix [32].

Considering a slab of 30 layers thick, in Fig. 9, we have shown the surface band structure of $\alpha$- and $\beta$- CsSnI$_3$ for different strain conditions. Bands with deep blue color corresponds to bulk structure and bands with red color are from the surface. The figure justify the prediction that, s-p band inversion arising from negative bulk bandgap yields TI phase. For example, in the upper row of the figure the strain condition creates negative $E_g$ and hence invariant surface Dirac states, which is a must for the TI phase, is formed. However, for the lower row, the strain condition is such that it creates positive $E_g$. Therefore, no invariant Dirac states are formed. We find that the SK-TB formalism is appropriate to examine the surface phenomena and it can considered as an alternate tool besides the widely used $k$-$p$ theory and Wannier formalism.

The band structure shown in first row of Fig. 9 corresponds to trivial phase, since there is no Dirac kind of states at the Fermi level as bulk counterpart does not show any band inversion. Whereas, in the second row, the band structure has time-reversal protected Dirac states at $E_F$, in which the bulk band structure exhibits band character inversion. In non-trivial phase, the topological surface states are seen within the bulk bandgap. The Dirac point (DP) occurs at M high symmetry k-point of the surface Brillouin zone. Here, we emphasize that, the method used in the present work to obtain the surface band structure is computationally inexpensive as compared to the Wannier function based methods and is easy to implement.
V. SUMMARY AND OUTLOOK

In summary, we have taken CsSnI$_3$ as a prototype for examining the electronic structure of sp-element based halide perovskites which are promising for optoelectronic applications and possess the right crystal and orbital symmetries to demonstrate non-trivial quantum states. However, bandgap engineering is crucial to realize either of these two aspects. In this work, we have adopted a dual approach, ab-initio DFT studies and design of parametric tight-binding Hamiltonian based on the framework of LCAO formalism and came up with predictive principles that are fundamental to carry out the bandgap engineering via strain in the halide perovskite family. Some of the crucial conclusions are as follows. (I) In the cubic phase, one can apply both compressive and tensile strains to reduce the bandgap from the equilibrium bulk value and eventually a critical value the system exhibits negative bandgap and therefore the non-trivial topological insulator phase. (II) In the tetragonal phase, while tensile strain reduces the bandgap and thereby there is a possibility of normal insulator to topological insulator phase transition, compressive strain enhances it and hence can be used as a controllable factor for optoelectronic applications. (III) Interestingly, the halide structure establishes stability plateau in the configuration space spanned by strain and octahedral rotations in the crystal. In this plateau, while the total energy of the system remains almost flat, the variation range of the bandgap is close to 1 eV. (IV) The orthorhombic phase enhances the bandgap with tensile strain and reduces it with the compressive strain. Also, we find that the compressive strain tries improve the symmetry as system gradually enters to the tetragonal phase, but at a higher energy cost. (V) Our model study led to conceptualization of topological influencers (TIF) which basically provide a quantitative measure of the ability of each electron hopping interaction to alter the band structure at the Fermi surface/chemical potential and hence the band topology of the system. These influencers are independent of chemical composition of the compound and hence have universal appeal. (VI) We realize that a basis set consisting of only four orbitals (e.g. Sn-s, p) is sufficient to include in the tight-binding (TB) Hamiltonian so that the electronic structure of each of the structural phases can be explained. (VII) The TB studies further led to the design of a descriptor model which describes the effect of structural distortion due to strain on the interaction parameters.

The value of the critical temperatures at which the structural phase transition occurs, vary with the chemical composition of the perovskite. As can be seen from Fig. 10, while some of the compounds have cubic phase at the room temperature, some others have tetragonal or orthorhombic phases. Therefore, the conclusions (I - IV) listed above can act as fundamental guideline to room temperature engineering of the bandgap, with respect to the equilibrium bulk value, of a given material via strain. Accordingly, the application perspective can be decided.

Furthermore, centrosymmetricity of the compound plays a vital role in the electronic properties of the halides. The organic halides are non-centrosymmetric and hence create an internal electric field leading to removal of momentum degeneracy through Rashba coupling. Therefore, such a coupling should be considered while designing a model Hamiltonian, with the objective of explaining the band phenomena of all members of halide perovskites (inorganic, organic and hybrid). We find that the TB model in present paper addresses this aspect. We find that if the Rashba coupling is included in the designed TB Hamiltonian (i.e. $H_{\text{centro}} + \alpha_{\text{R}}(\mathbf{k} \times \hat{z}) \cdot \hat{\sigma}$), it provides the appropriate band structure. For example, in Fig. 10 lower panel, we show that the invariant surface Dirac state, exhibited by a centrosymmetric perovskite, yield two Dirac states with the inclusion of Rashba coupling. This is due to the breakdown of Kramers degeneracy in noncentrosymmetric systems and it is an well established fact[32]. Therefore, from the topological perspective, the present work provides an universal TB Hamiltonian and also proposes a new set of numbers called TIF to engineer the topology of a given halide perovskites.

ACKNOWLEDGMENT:

This work is supported by Department of Science and Technology, India through Grant No.EMR/2016/003791.
Appendix A: Tight binding model for lower symmetry polymorphs of CsSnI$_3$:

The tight binding Hamiltonian discussed in the main text (Eq. (1) and Eq. (2)) for α-phase is extendable to lower symmetry β and γ-phases with appropriate number of basis. Here, we elaborate the TB Hamiltonian for β and γ-phases to obtain the TB band structure.

1. β-phase:

As discussed in section-II of the main text, the presence of octahedral rotation in $ab$-plane in β-phase creates two in-equivalent Sn atoms in the unit cell. We denote them as Sn$_A$ and Sn$_B$. Now the basis set include eight eigen states, $\{s_{\alpha A}^{\text{Sn}} , p_x^{\text{Sn}} , p_y^{\text{Sn}} , p_z^{\text{Sn}} , s_{\alpha B}^{\text{Sn}} , p_x^{\text{Sn}} , p_y^{\text{Sn}} , p_z^{\text{Sn}} \}$. The corresponding SOC included 16×16 Hamiltonian matrix is given as,

$$
H_{TB} = \begin{pmatrix}
H_{\uparrow\uparrow} & H_{\uparrow\downarrow} \\
H_{\downarrow\uparrow} & H_{\downarrow\downarrow}
\end{pmatrix}, \quad H_{\uparrow\downarrow} = (H_{\downarrow\uparrow})^* = \begin{pmatrix}
H_{AB} & H_{AB}^* \\
(H_{AB})^* & H_{BB}
\end{pmatrix}^{\uparrow\uparrow},
$$

and

$$
H_{AB}^{\uparrow\uparrow} = H_{BB}^{\uparrow\downarrow} = \begin{pmatrix}
\epsilon_x + f_0 & 2i(t_{sp}^{AB})^A S_x & 2i(t_{sp}^{AB})^A S_y & 2i(t_{pp}^{AB})^A S_z \\
-2i(t_{sp}^{AB})^A S_x & \epsilon_p + f_1 -i\lambda & 0 \\
-2i(t_{sp}^{AB})^A S_y & i\lambda & \epsilon_p + f_2 & 0 \\
-2i(t_{sp}^{AB})^A S_z & 0 & 0 & \epsilon_p + f_3
\end{pmatrix}, H_{\downarrow\uparrow}^{\uparrow\downarrow} = \begin{pmatrix}
g_0 & g_1 & g_2 & 0 \\
g_1 & g_4 & g_5 & 0 \\
g_2 & g_5^* & g_4 & 0 \\
0 & 0 & 0 & g_6
\end{pmatrix}
$$

$$
\begin{align*}
f_0 &= 2(t_{sp}^{AB})^A \cos(k_x a) + \cos(k_y a) + 2(t_{sp}^{AB})^A \cos(k_z a) \\
f_1 &= 2(t_{pp}^{AB})^A \cos(k_y a) + 2(t_{pp}^{AB})^A \cos(k_z a) + 2(t_{pp}^{AB})^A \cos(k_x a) \\
f_2 &= 2(t_{pp}^{AB})^A \cos(k_z a) + 2(t_{pp}^{AB})^A \cos(k_x a) + 2(t_{pp}^{AB})^A \cos(k_y a) \\
f_3 &= 2(t_{pp}^{AB})^A \cos(k_x a) \\
g_0 &= 4t_{sp}^{AB} \cos(k_y a) \cos(k_z a) \\
g_1 &= 2\sqrt{2} t_{sp}^{AB} \sin(k_x a) \cos(k_z a) \\
g_2 &= 2\sqrt{2} t_{sp}^{AB} \sin(k_y a) \cos(k_z a) \\
g_4 &= 2(t_{pp}^{AB} + t_{pp}^{AB}) \cos(k_z a) \cos(k_y a) \\
g_5 &= 2(t_{pp}^{AB} - t_{pp}^{AB}) \sin(k_z a) \sin(k_y a) \\
g_6 &= 4t_{pp}^{AB} \cos(k_x a) \cos(k_y a)
\end{align*}
$$

FIG. 11. The schematic representation of different hopping interactions in $ab$-plane of β-CsSnI$_3$. Here, the $t^{AA}$ hopping interaction are weak as compared to $t^{AB}$, as they do not involve Iodine mediation.
Here, the \((t_i^x/t_i^z)^{AA}\) interaction strengths are weak (~0.01 eV) as they do not involve iodine mediated hopping, we can safely neglect them. The significant parameters are listed in Table 2 of main text. In Fig. 7 of the main text, for \(\beta\)-CsSnI₃, we have shown the variation of various interactions parameters as a function of \(c/a\), where the deviation from \(\alpha\)-phase is due to existence of in-plane octahedral rotations. Here, in Fig. 12 and 13, we present the effect of \(c/a\) for constant \(\theta_{ab}\) and vice versa.

\begin{equation}
H_{\uparrow\downarrow} = \begin{pmatrix}
H_{\uparrow\uparrow}^{AA} & 0 \\
0 & H_{\downarrow\downarrow}^{BB}
\end{pmatrix}, \quad H_{\uparrow\downarrow}^{AA} = H_{\downarrow\downarrow}^{BB} = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & \lambda & 0 \\
0 & \lambda & 0 & -i\lambda \\
0 & -i\lambda & 0 & 0
\end{pmatrix}.
\end{equation}

(Fig. 12). Variation of different interaction parameters of \(\beta\)-CsSnI₃ as a function \(c/a\) for a constant \(\theta_{ab}\) (= 162°).

2. Orthorombic phase:

The \(\gamma\)-phase of CsSnI₃ is characterized by in plane \((ab)\) rotation as well as out of plane \((along c)\) octahedral tilting. This dual rotation creates four inequivalent Sn atoms. We denote them as Sn\(_A\), Sn\(_B\), Sn\(_C\) and Sn\(_D\). Therefore, the basis set augmented and include sixteen eigen states and the corresponding SOC included \(32\times 32\) Hamiltonian matrix is given as,

\begin{equation}
H_{TB} = \begin{pmatrix}
H_{\uparrow\uparrow} & H_{\uparrow\downarrow} \\
H_{\downarrow\uparrow} & H_{\downarrow\downarrow}
\end{pmatrix}, \quad H_{\uparrow\uparrow} = H_{\downarrow\downarrow} = \begin{pmatrix}
H_{\uparrow\uparrow}^{AA} & H_{\uparrow\uparrow}^{AB} & H_{\uparrow\uparrow}^{AC} & H_{\uparrow\uparrow}^{AD} \\
(H_{\uparrow\downarrow}^{AB})^\dagger & H_{\uparrow\downarrow}^{BB} & (H_{\uparrow\downarrow}^{AC})^\dagger & (H_{\uparrow\downarrow}^{AD})^\dagger \\
(H_{\downarrow\uparrow}^{AC})^\dagger & (H_{\downarrow\uparrow}^{BC})^\dagger & H_{\downarrow\downarrow}^{CC} & (H_{\downarrow\downarrow}^{CD})^\dagger \\
(H_{\downarrow\downarrow}^{AD})^\dagger & (H_{\downarrow\downarrow}^{BD})^\dagger & (H_{\downarrow\downarrow}^{CD})^\dagger & H_{\downarrow\downarrow}^{DD}
\end{pmatrix}^\dagger,
\end{equation}

and

\begin{equation}
H_{\uparrow\downarrow}^{ii}(i = A, B, C, D) = \begin{pmatrix}
\epsilon_i^x + f_0 & 2i(t_{s p}^x)^{AA}S_x & 2i(t_{s p}^x)^{AA}S_y & 0 \\
-2i(t_{s p}^x)^{AA}S_x & \epsilon_i^x + f_1 & -i\lambda & 0 \\
-i\lambda & \epsilon_i^x + f_2 & 0 & 0 \\
0 & 0 & 0 & \epsilon_i^x + f_3
\end{pmatrix}, \quad H_{\downarrow\downarrow}^{ii} = H_{\uparrow\uparrow}^{ii} = \begin{pmatrix}
g_0 & g_1 & g_2 & 0 \\
g_1^* & g_3 & g_4 & 0 \\
g_2^* & g_5 & g_6 & 0 \\
0 & 0 & 0 & g_6
\end{pmatrix}.
\end{equation}
FIG. 13. Variation of different interaction parameters of $\beta$-CsSnI$_3$ as a function $\theta_{ab}$ for constant $c/a$ (= 1).

FIG. 14. The schematic representation of different hopping interactions in $ab$-plane and along $c$ direction of $\gamma$-CsSnI$_3$.

\begin{equation}
H_{11}^{AC} = H_{11}^{BD} = \begin{pmatrix}
    f_4 & 0 & 0 & f_5 \\
    0 & f_6 & 0 & 0 \\
    0 & 0 & f_6 & 0 \\
    f_5^* & 0 & 0 & f_7
\end{pmatrix}, \quad H_{11}^{AD} = H_{11}^{BC} = \begin{pmatrix}
    0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0
\end{pmatrix}.
\end{equation}

(A5)
\[ f_0 = 2(t_{zz}^x)^{AC} \cos(k_x a) + 2(t_{zz}^y)^{AC} \cos(k_y b) \]
\[ f_1 = 2(t_{ppp}^x)^{AA} \cos(k_x a) + 2(t_{ppp}^y)^{AA} \cos(k_y b) \]
\[ f_2 = 2(t_{ppp}^x)^{AA} \cos(k_x b) + 2(t_{ppp}^y)^{AA} \cos(k_y a) \]
\[ f_3 = 2(t_{ppp}^x)^{AA} \cos(k_x a) + 2(t_{ppp}^y)^{AA} \cos(k_y b) \]
\[ f_4 = 2(t_{zz}^x)^{AC} \cos \frac{k_x c}{2} \]
\[ f_5 = 2i(t_{zz}^y)^{AC} \sin \frac{k_x c}{2} \]
\[ f_6 = 2(t_{ppp}^z)^{AC} \cos \frac{k_z c}{2} \]
\[ f_7 = 2(t_{ppp}^z)^{AC} \cos \frac{k_z c}{2} \]

(A6)

\[ g_0 = 4t_{zz}^{AB} \cos \left( \frac{k_x a}{2} \right) \cos \left( \frac{k_y b}{2} \right) \]
\[ g_1 = 4 \cos (\theta_1) t_{zz}^{AB} \sin \left( \frac{k_x a}{2} \right) \cos \left( \frac{k_y b}{2} \right) \]
\[ g_2 = 4 \cos (\theta_2) t_{zz}^{AB} \sin \left( \frac{k_y a}{2} \right) \cos \left( \frac{k_x b}{2} \right) \]
\[ g_3 = 4f(\theta_1) \cos \left( \frac{k_x a}{2} \right) \cos \left( \frac{k_y b}{2} \right) \]
\[ g_4 = 4f(\theta_2) \cos \left( \frac{k_y a}{2} \right) \cos \left( \frac{k_x b}{2} \right) \]
\[ g_5 = 4f(\theta_{12}) \sin \left( \frac{k_x a}{2} \right) \sin \left( \frac{k_y b}{2} \right) \]
\[ g_6 = 4t_{ppp}^{AB} \cos \left( \frac{k_x a}{2} \right) \cos \left( \frac{k_y b}{2} \right) \]

\[ f(\theta_1) = (t_{ppp}^{xy})^{AB} \cos^2(\theta_1) + (t_{ppp}^{xy})^{AB} \sin^2(\theta_1) \]
\[ f(\theta_2) = (t_{ppp}^{xy})^{AB} \cos^2(\theta_2) + (t_{ppp}^{xy})^{AB} \sin^2(\theta_2) \]
\[ f(\theta_{12}) = ((t_{ppp}^{xy})^{AB} - (t_{ppp}^{xy})^{AB}) \cos(\theta_1) \cos(\theta_2) \]

(A7)

Here, \( \theta_1 \) and \( \theta_2 \) arise due to slight difference in the lattice parameter \( a \) and \( b \).
