Multi-orbital tight-binding Hamiltonian and strength of spin-orbit interaction in strained Mg$_2$X (X = Si, Ge, Sn, Pb)

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We have developed multi-orbital tight-binding (MOTB) Hamiltonian models to describe the electronic characteristics of intermetallic compounds Mg$_2$Si, Mg$_2$Ge, Mg$_2$Sn, and Mg$_2$Pb subject to strain. We have incorporated spin-orbital mediated interactions and calibrated the MOTB models to the band structures of density functional theory (DFT) by a massively parallelized multi-dimensional Monte-Carlo search algorithm. The results show that a five-band tight-binding (TB) model reproduces the key aspects of the band structures in the entire Brillouin zone. The five-band TB model reveals that the compressive strain localizes the contribution of the 3$s$ orbital of Mg to the conduction bands and the outer shell $p$ orbitals of X to the valence bands. The tensile strain, in contrast, has a reversed effect and weakens the contribution of the 3$s$ orbital of Mg and the outer shell $p$ orbitals of X to the conduction bands and valence bands, respectively. We have found that the $\pi$ bonding in the Mg$_2$X compounds is negligible compared to the $\sigma$ bondings, follow the hierarchy $|\sigma_{sp}| > |\sigma_{pp}| > |\sigma_{ss}|$, and the largest variation against strain belongs to $\sigma_{pp}$. Moreover, the five-band TB model allowed for estimating the strength of SOC in Mg$_2$X and obtaining its functionality with respect to the atomic number of X and strain. Additionally, the calculations find significant band gap tuning and band splitting due to strain. It is shown that a compressive strain of $\sim$10% can open a band gap at the $\Gamma$ point in metallic Mg$_2$Pb whereas a tensile strain of $\sim$10% closes the semiconducting band gap of Mg$_2$Si. Also, $\sim$5% of tensile strain can remove the three-fold degeneracy of valence bands at the $\Gamma$ point in semiconducting Mg$_2$Ge. Our results and model approach can be useful in designing devices made of Mg$_2$X more accurately.

I. INTRODUCTION

Intermetallic compounds Mg$_2$X(X = Si, Ge, Sn) are mainly considered to be semiconductors and their addition to, e.g., metallic matrices can form solid solutes and grains. These Mg$_2$X solid solutes can desirably change the electronic, mechanical, and macroscopic properties of these metallic matrices.$^{[1–5, 12]}$ Furthermore, Mg$_2$X(X = Si, Ge, Sn) are chemically and thermally stable, nontoxic, resistive against oxidation, economically inexpensive, environmentally friendly, relatively light weight, and therefore have a great potential for large-scale production.$^{[2, 7, 8]}$ More importantly, they possess a high figure of merit and can serve as good solid-state thermoelectric materials for converting waste heat to electricity. These excellent characteristics have fuelled robust effort to explore various aspects of Mg$_2$X and find ways to improve and optimize their favorable performance. For instance, one main approach followed to manipulate the electrical transport of these compounds was by intercalation with differing elements.$^{[4, 5, 7–19]}$ It was found that the intercalation can result in non-linearity in the band gap, enhanced spin-orbit interaction (SOI), and band splitting. The controllable and efficient thermoelectric materials are promising in designing micro-scale self-powered sensors, solar thermal elements, and waste heat recovery devices.$^{[20–27]}$

An intensive theoretical study has so far been performed on these compounds, mainly using density functional theory (DFT).$^{[1, 14, 15, 28–31]}$ The theoretical studies can provide deep and independent insight into the physics of these compositions and shed light on delicate aspects. For example, one can attain better view over the physical mechanisms and possibly harnessing them in the future experiments, to create new opportunities, achieve more reliable analysis, and avoid introducing detrimental effects during the implementation process. Additionally, there are multiple works discussing various aspects of these compounds by using an effective single-band parabolic approximation.$^{[8, 12, 14]}$ The common assumption of these works is the homogeneity of the alloys and generalization of the rigid-band structure approach to obtain the band structure of the intermediate alloy systems.

Motivated by the above, we have constructed multi-orbital tight-binding (MOTB) models, accounting for the \{s, p, d, s$^*$\} orbitals. Our investigations demonstrate that a simple five-band tight-binding (TB) model is sufficient to describe the electronic properties of strained Mg$_2$X(X = Si, Ge, Sn, Pb) close to the Fermi level. The results of the five-band TB model show that compressive (tensile) strain enhances (suppresses) the strength of spin-orbit interaction (SOI) in Mg$_2$X. The Mg-X interactions were found to dominate over Mg-Mg and X-X counterparts. The $\pi$ bonding is negligible whereas the dominate variation against strain appears in $\sigma_{pp}$. We have found that a tensile strain on the order of $\varepsilon = 5\%$ eliminates the three-fold degeneracy of the valence bands at the $\Gamma$ point in Mg$_2$Ge. A two-fold band degeneracy, however, remains intact throughout $\varepsilon \in [-10\%, +10\%]$
in Mg2Si. Our results illustrate that the band gap of Mg2X is highly tunable through a uniform strain so that, despite their unstrained characteristics, the Mg2X compounds can acquire semiconductor (metallic) characteristics. These findings point into an excellent opportunity for band engineering of Mg2X-based materials [27] and can be helpful when analyzing and designing devices made of Mg2X. Moreover, unlike the simple single-band parabolic models, our five-band TB model is able to capture key features of the DFT band structure within the entire Brillouin zone and therefore, can be employed to perform large-scale molecular dynamics simulations and quantum transport studies as further improvements are desired for a practical implementation of Mg2X-based thermoelectric generators. Furthermore, our approach can be generalized for further investigation of the related compositions to Mg2X, intercalated with other elements, and develop more accurate models than the single-band parabolic models. Note that DFT can support systems with a few hundreds of atoms only and once different elements are included, the calculations to search for favorable compositions are computationally very challenging and impossible in many cases. [32] However, the MOTB approach usually demands trivial computational cost, provides an explicit Hamiltonian that can accommodate an external magnetic field, many-body interactions, impurities, and facilitates real space simulations.

The paper is organized as follows. In Sec. II, we discuss the configuration, crystal symmetry of Mg2X, and the displacement vectors used in our MOTB models. In Sec. III, the MOTB formalism is summarized. In Sec. IV and V, the Monte-Carlo search algorithm and details of the DFT calculations are given, respectively. The results are presented in Sec. VI and finally, the concluding remarks are summarized in Sec. VII.

II. CONFIGURATION OF Mg2X

Figure 1 displays the configuration of Mg2X with two different views. Figure 1(a) shows the top view of the structure whereas Fig. 1(b) is a three-dimensional perspective view. The structure is equivalent to the fluorite structure with the anions and cations swapped and is known as antifluorite. An antifluorite configuration can be generated with a face-centered cubic Bravais lattice and a simple-cubic lattice in the interstitial sites. The X atoms are located on the atom sites of the former lattice while the Mg atoms occupy the atom sites of the latter lattice. In what follows, for simplifying our notation, we have labeled the cation sublattice sites by A(A′) (two atoms per unit cell) and the anion sublattice site by B (one atom per unit cell). As seen in Fig. 1, the unit cell of Mg2X contains twelve atoms (8:4 ratio). To construct an accurate MOTB model, one needs to account for both the different atom types available in a composition and the distance and orientation of different atoms with respect to other atoms. Defining the tight-binding interaction vectors, we have summarized the nearest-neighbor interaction vectors δαβ among atoms located on the different sublattices of Mg2X in Table I. To further simplify our notation, we have defined α, β ∈ {A, A′, B}. Although, throughout the paper, we shall discuss the model constructed and results obtained by the nearest-neighbor interactions, we have constructed models incorporating both the nearest-neighbor and next nearest-neighbor interactions simultaneously. Our results revealed only a slight improvement and therefore we avoid presenting the models with the next nearest-neighbor interactions.

| α   | β   | (x, y, z)  | α   | β   | (x, y, z) |
|-----|-----|-----------|-----|-----|-----------|
| A   | A′  | a(±1, 0, 0)/2 | A   | B   | ±a(0, 1, 1)/2 |
| A′  | A   | a(0, ±1, 0)/2 | A′  | A   | ±a(1, 1, 1)/2 |
|     | a(0, 0, ±1)/2 | A   | B   | ±a(1, 0, 1)/2 |
| A   | B   | a(1, -1, 1)/4 | A′  | B   | ±a(1, -1, 1)/4 |
| A′  | a(-1, 1, 1)/4 | B   | A   | ±a(1, -1, 1)/4 |
|     | a(1, 1, 1)/4 |   |     | ±a(1, -1, -1)/4 |

TABLE I. Nearest-neighbor vectors δαβ among the sites of the sublattices A, A′, B. The lattice constant is denoted by a.
interaction is largest among electrons that occupy the outer electron shells and diminishes among electrons within inner electron shells. The interactions can be bonding or anti-bonding and therefore, the molecular orbitals that describe the physical properties of a material can be a combination of the original atomic orbitals. To construct a reliable model Hamiltonian that contains these pivotal aspects, the interaction among the electrons, occupying the outer electron shells, should be properly accounted for. In this case, the Hamiltonian can be expressed by

$$\hat{H} = \sum_{k, \mu, \nu, \sigma, \sigma'} \left\{ C_{\mu \nu, \sigma \sigma'}^{\alpha \beta} \delta_{\alpha \beta} \delta_{\mu \nu} \delta_{\sigma \sigma'} + \gamma_{\mu \nu, \sigma \sigma'}^{\alpha \beta} \right\} \delta_{\sigma \sigma'} + \eta_{\mu \nu, \sigma \sigma'}^{\alpha \beta} \right\} C_{\mu \nu, \sigma, \sigma'}^{\alpha \beta} + \text{h.c.},$$

where the on-site energy, hopping integrals among atoms, and spin-orbit interaction are denoted by $E$, $\gamma$, and $\eta$, respectively. The different atoms are marked by $\alpha, \beta$ whereas $\mu, \nu$ and $\sigma, \sigma'$ represent the electron orbitals and spin species, respectively, $C_{\mu \nu, \sigma \sigma'}^{\alpha \beta(1)}$ is the annihilation (creation) operator and $\delta_{ij}$ is the Kronecker delta function. By the inclusion of multi-orbital interactions among different atoms, electrons can occupy mixed and intermediate states with some finite probability. The multi-orbital nature of our tight-binding Hamiltonian is encoded into the hopping integrals as follows

$$\gamma_{\mu \nu}^{\alpha \beta}(k) = \sum_{\delta \in \delta_{\mu \nu}} t_{\mu \nu}^{\alpha \beta}(\delta) \exp(\text{i} k \cdot \delta),$$

in which $k$ is the momentum of a particular moving electron, $\delta$ is the displacement vector, and $t_{\mu \nu}^{\alpha \beta}(\delta)$ is the hopping integrals [33].

Because of stronger interactions in heavy elements, the spin-orbital mediated interactions play an important role and considerably change the properties of a material [34]. The intrinsic spin-orbit interaction in a crystal can generally be given by [34]

$$H_{SO} = \zeta(r) \hat{L} \cdot \hat{S},$$

$$\zeta(r) \propto \frac{1}{r} \frac{\partial V(r)}{\partial r},$$

where $\hat{L}$ and $\hat{S}$ are the total orbital and spin angular momentum operators, respectively, and $V(r)$ is the total crystal potential. In this model, $\zeta(r)$ depends both on position $r$ and the crystal potential, and therefore deals with the radial part $R_{n,l}(r)$ of the electron-orbital wave functions $\Psi_{n,l,m}$, which are dependent on quantum numbers $n$ and $l$ through

$$\Psi_{n,l,m} = R_{n,l}(r) Y_{l,m}(\theta, \phi).$$

Therefore, the spin-orbit coupled part of the Hamiltonian Eq. (1) in its component form can be expressed by

$$\eta_{\mu \nu, \sigma \sigma'} = \eta_{SO} \langle \hat{L} \cdot \hat{S} \rangle_{\mu \nu, \sigma \sigma'},$$

To evaluate Eq. (5), it is more convenient to introduce the ladder SOI operators as follows

$$\hat{L} \cdot \hat{S} = \hat{L}_z \hat{S}_z + \frac{1}{2} (\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+),$$

$$\hat{L}_\pm = \hat{L}_x \pm i \hat{L}_y,$$

$$\hat{S}_\pm = \hat{S}_x \pm i \hat{S}_y.$$ 

Defining $n, l, m, s$ as the principal, azimuthal, magnetic, and spin quantum numbers, respectively, the quantum numbers are restricted by $l = \{0, 1, 2, ..., n - 1\}$, $m = \{-l, -l + 1, ..., l - 1, l\}$, and $s = \pm 1/2$. The operation of the angular and spin operators on a wave function at a state $\psi_{l,m,s}$ is summarized as follows

$$\hat{S}_z \psi_{l,m,s} = s \psi_{l,m,s},$$

$$\hat{L}_z \psi_{l,m,s} = m \psi_{l,m,s},$$

$$\hat{L}_\pm \psi_{l,m,s} = \sqrt{(l \pm m)(l \pm m + 1)} \psi_{l,m,s},$$

$$\hat{S}_\pm \psi_{l,m,\pm 1/2} = \psi_{l,m,\pm 1/2},$$

$$\hat{L}_z \hat{S}_\pm \psi_{l,m,s} = ms \psi_{l,m,s},$$

$$\hat{L}_\pm \hat{S}_\pm \psi_{l,m,\pm 1/2} = \frac{1}{2} \sqrt{(l - m)(l + m + 1)} \psi_{l,m,\mp 1/2}.$$ 

In the equations above, we have set $\hbar = 1$ to simplify the notation.

Since the inner shell electrons are strongly bonded to nuclei, one can consider them as frozen electrons and only account for the interaction among the valence shell electrons. Therefore, we have constructed several models, accounting for excited electrons up into the $d$ orbitals, i.e., $\{d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2}\}$. For example, in the smallest model where it describes five electronic bands around the Fermi level, we consider the interaction among $\{s, p_x, p_y, p_z\}$ orbitals. In the largest model, the interaction among $\{s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2}, s^*\}$ orbitals are considered and the model is able to describe eighteen electronic bands around the Fermi level. These interactions result in relatively large expressions for the hopping integrals that are given in Appendix A.

IV. MONTE-CARLO SEARCH FOR FINDING OPTIMIZED PARAMETERS TO THE MOTB MODELS

As described in the previous section and given in Appendix A, the MOTB models in the presence of SOI can contain tens of unknown parameters to be calibrated through comparison with a reference data set (in our case, the DFT data of the band structure is the reference). Therefore, one needs an efficient approach to find optimal and reliable parameter values to the MOTB models. One efficient approach is the simulated annealing (SA), which is a Monte-Carlo method for derivative-free
optimization, built on concepts from statistical physics [35]. The SA algorithm mimics the annealing process by first defining some cost function. Next, an initially high temperature $T$ is simulated by allowing the coordinates of the system to randomly fluctuate. Thermal equilibrium is gradually achieved by primarily allowing fluctuations with some probability of accepting fluctuations. In our optimization process, we have defined a cost function by

$$C(E) = \sqrt{\frac{1}{M} \sum_i w_i (E_i - E_i')^2},$$  \hspace{1cm} (8)

In Eq. (8), the sum runs both over all the data-points of the model and the corresponding reference data points $E_i'$. Depending on the problem, the weight distribution can be set to $w_i = 1$. Oftentimes, a nonuniform weight distribution, such as increased weights for bands closer to the Fermi energy, is appropriate for problems where the deviation among the data points and reference data points is considerably large and produces outliers. The acceptance criterion of a set of parameter values is used as follows

$$h(\Delta C) = \frac{1}{1 + \exp(\Delta C/T)} \approx \exp(-\Delta C/T).$$  \hspace{1cm} (9)

The variation of $C$ between two steps is shown by $\Delta C$. The cooling schedule for a given parameter $\alpha^i$ is

$$T(t) = T_0 \exp\left(-ct^{-d}\right),$$  \hspace{1cm} (10)

where $T_0$ is the initial temperature, $d$ is the dimension of parameter space, and $c$ is a tunable cooling constant. To incorporate the temperature scheduled, i.e., Eq. (10), the update to each parameter $\alpha^i$ is

$$\alpha^i_{t+1} = \alpha^i_t + y^i(B_i - A_i),$$  \hspace{1cm} (11)

are drawn from the distribution

$$y^i = \text{sgn}\left(u^i - \frac{1}{2}\right) T(t_i)[(1 + T(t_i)^{-1})^{2u^i - 1} - 1],$$  \hspace{1cm} (12)

where $\text{sgn}$ is the sign function, $T(t_i)$ is the temperature of parameter $\alpha^i$ at step $i$, and $U[0, 1]$ is the continuous uniform distribution between 0 and 1. Also, $B_i$ and $A_i$ are the upper and lower boundaries for the search space of parameter $\alpha^i$. The random generator (12) always produces a number in the range $[-1, 1]$. The full span of the search space for each parameter $B_i - A_i$ is not necessarily known, but may be approximated to bias the algorithm towards generating step sizes proportional to the relevant search space. The fluctuation in more sensitive parameter is large and causes significant changes to the cost function during the simulation. Therefore, one can find optimized values to the less sensitive parameter by a first round of the annealing process and next allow the more sensitive parameters to vary in a second annealing process. This re-annealing strategy was suggested by Ingber [36] where the less sensitive parameters are periodically re-annealed as follows

$$t \leftarrow t'_i = \max[0, \left( \frac{1}{c} \ln\left( \frac{T_0}{T(t_i)} \frac{s_i}{s_{\text{max}}} \right) \right]^d],$$

$$s_i = (B_i - A_i) \left( \frac{\partial C(\alpha)}{\partial \alpha} \right) \approx (B_i - A_i) C\left( \left[ \alpha^1, \ldots, \alpha^i + \delta \alpha, \ldots, \alpha^d \right] \right) - C(\alpha).$$  \hspace{1cm} (13)

Here, $s_i$ is the sensitivity of parameter $\alpha^i$, $s_{\text{max}}$ is the largest sensitivity, $\delta \alpha$ is a small increment in one parameter and $\alpha$ is the vector of parameters.

The required extensive search of the high-dimensional parameter space of our MOTB models using the Monte-Carlo algorithm is a slow process, especially when many different datasets are to be considered. To speed up our extensive search to find best optimized MOTB parameters, we have implemented a massively parallelized algorithm using graphical processing units (GPU).

V. FIRST-PRINCIPLES DENSITY FUNCTIONAL THEORY CALCULATIONS

The density functional calculations are performed using the GPAW package. [37] We have required the gradient-corrected functional approximation and PBE is used for the exchange-correlation energy. The $k$ space is grid by the Monkhorst-Pack scheme and a relatively large value of the grid density is used, i.e., 8.0 $k$-points per 1/$\text{Å}$. The cut-off for the kinetic energy of the plane
The lattice constant of Mg$_2$X from experiment and DFT predictions.

| Compound | Experiment | DFT |
|----------|------------|-----|
| Mg$_2$Si | 6.340      | 6.362 |
| Mg$_2$Ge | 6.385      | 6.426 |
| Mg$_2$Sn | 6.765      | 6.807 |
| Mg$_2$Pb | 6.836      | 6.908 |

TABLE II. The lattice constant of Mg$_2$X from experiment and DFT predictions.

waves is set to 800 eV. The width of the Fermi-Dirac distribution is set to 0.01 eV. In what follows, the DFT calculations are performed in the presence of SOI.

To simulate the strained configurations, we introduce a strain tensor with components $\varepsilon_{ij}$ in which the indices run over real space coordinations, i.e., $ij \in x, y, z$. The strained unit cell and therefore updated locations of the different atoms can be described by the new vectors $a = \varepsilon_{xx}a_0$, $b = \varepsilon_{yy}b_0$, and $c = \varepsilon_{zz}c_0$. The unstrained vectors are $a_0$, $b_0$, and $c_0$. In what follows, we restrict our simulations to a low-strain regime, i.e., $\pm 10\%$ to make sure no structural transition occurs upon inserting strain into the unit cell. Note that $\pm 10\%$ of strain corresponds to $10\%$ of tensile and compressive strain, respectively. Throughout the paper, we consider uniform strain in all directions.

As the X elements in Mg$_2$X possess differing atomic numbers, their radii differ considerably. Therefore, one can expect that the lattice constant in these compositions vary significantly. In order to find the energetically stable lattice constant for each composition, we have performed DFT calculations and plotted the formation energy of these compounds as a function of lattice constant. The optimized parameter values of the five-band TB model are given in Appendix C. Our five-band TB model is able to describe the low-energy properties of the compounds Mg$_2$X, e.g., through projection of the total band structure onto different orbitals. Figure 3 exhibits the band structure of Mg$_2$X(X = Si, Ge, Sn, Pb). In all cases, the Fermi level is shifted to zero energy. The dashed red curves are obtained through DFT whereas the solid blue curves are the results of our five-band TB model. Column-wise, the element X changes as X = Si, Ge, Sn, Pb from left to right, respectively. Row-wise, Fig. 3 shows how strain affects the band structure at $\varepsilon = -10\%, 0\%, +10\%$ from top to bottom, respectively. The band structure is plotted along the high-symmetry path $\Gamma X W L K X$ in k-space. As seen, our five-band TB model reproduces the band structures in a good agreement to the DFT results. Specifically, the three valence bands produced by the five-band TB model deviate only slightly from those of DFT. The two conduction bands, however, have larger deviations from those of DFT although at the $\Gamma$ point we yet see good agreement between the model prediction and DFT. The main reason for the larger deviation of the conduction bands originates from the exclusion of higher excited states in our five-band TB model. In fact, an excited mode over the Fermi level is a complicated hybridization of several excited states. However, in the five-band TB model, we have considered the contribution of five orbitals only, namely the 3$s$ orbitals of Mg and the $\{p_x, p_y, p_z\}$ orbitals of the X elements. Therefore, in order to obtain more accurate predictions for the conduction bands using the MOTB method, one needs to take more of the excited orbitals into account. To confirm this, we have considered the $\{3s, 3p\}$ orbitals of Mg and $\{s, p, d, s'\}$ orbitals of X, constructed an eighteen-band TB model, and calibrated the model to the DFT band structures. The results revealed almost perfect reproduction of the band structures obtained by DFT, close to the Fermi level. A representative band structure from the eighteen-band TB model is shown in Fig. 7 of Appendix B. As seen, most of the band features and details of DFT are now reproduced with the larger TB model. In the following, the s orbital of Mg and the p orbitals of X is equivalent to the 3$s$ orbital of Mg, and 3$p$ orbitals of Si, 4$p$ orbitals of Ge, 5$p$ orbitals of Sn, and 6$p$ orbitals of Pb, respectively.

B. The contribution of $s$ and $p$ orbitals

The optimized parameter values of the five-band TB model for $\varepsilon = 0\%, \pm 10\%$ are given in Appendix C. Our five-band TB model is able to describe the low-energy properties of the compounds Mg$_2$X, e.g., through projection of the total band structure onto different orbitals. Figure 4 illustrates the projection of the total band struc-
First, the figures illustrate that the contribution of the s orbitals is generally less favorable (appears at larger positive energy gaps) than those occupying the p valence bands. Therefore, in a compound MgX, the p orbital of Mg is largest to the conduction bands whereas the s orbital of Mg and the p orbitals of X contribute slightly to the total valence band as well, but much less significant than the s orbital of Mg and p orbitals of X. It is well understood that the excited particles are basically governed by the conduction bands. Hence, Fig. 4 reveals the fact that when the two elements Mg and X are brought together in the antifluorite configuration shown in Fig. 1, Mg tends to transfer its two s electrons to the p orbitals of X. Therefore, in the MgX (X = Si, Ge, Sn, Pb) compounds considered here, Mg plays a cation role whereas X turns into an anion and create Mg$^{2+}$X$^{4-}$, which is consistent with the electronegativity scale.

Second, Fig. 3 shows that the main contribution to the valence band structure and accordingly, the main physical properties of MgX at equilibrium originate from the p orbitals of the X atoms. Thus, to account for SOI in our five-band TB model, one can simply include the spin-orbit mediated interactions among the p particles only.

A compressive strain on the order of $\varepsilon = -10\%$, shown in the leftmost panels of Fig. 4, weakens the contribution of the s orbital of Mg (Fig. 4(a1)) and causes a dominant contribution of the p orbitals of X to the valence bands. Subject to $\varepsilon = -10\%$ of strain, the contribution of the p orbitals of X to the conduction bands is negligible while the s orbital of Mg governs the conduction bands. The application of $\varepsilon = +10\%$ tensile strain, however, has an exact reversed effect and causes more contribution of the s orbital of Mg and p orbitals of X to the valence and conduction bands, respectively. These features can be fully understood by noting the fact that compressive and tensile strains result in stronger and weaker coupling of the orbitals, respectively. Therefore, in the presence of $\varepsilon = -10\%$ strain, the s orbital of Mg acquires stronger contribution to the conduction bands and becomes energetically less favorable (appears at larger positive ener-
FIG. 4. The projection of the total band structure onto the \{s, p_x, p_y, p_z\} orbitals. The applied uniform strain to the system is \(\varepsilon = -10\%, 0\%, +10\%\) in panels with (a), (b), and (c) labels, respectively. The panels with index ‘1’ show the contribution of the 3s orbital of Mg whereas the panels with indices ‘2’, ‘3’, and ‘4’ display the contribution of the 4p_x, 4p_y, 4p_z orbitals of Ge, respectively.


gies when comparing the conduction bands of Fig. 4(a_1) to Fig. 4(b_1)). Whereas the contribution of the p orbitals of X to the total band structure is more localized on the valence bands. This can be confirmed when comparing Figs. 4(a_2, a_3, a_4) with Figs. 4(b_2, b_3, b_4) where the p orbitals of X become energetically more favorable (appear at larger negative energies). In contrast, when subject to +10% of tensile strain, the Mg and X atoms are slightly decoupled and therefore the entire system tends to acquire properties closer to isolated atomic species. This is clearly seen in Figs. 4(c) that not only the contribution of the s orbital of Mg to the valance bands is strengthened but the conduction bands also acquire smaller positive energies. Likewise, the p orbitals of X acquire smaller negative energies. The results of our five-band TB model for the orbital contributions in unstrained Mg_2X are in agreement with those concluded from DFT. \[15, 41, 42\]

C. Strength of spin-orbit interaction

As pointed out earlier, the MOTB model allows us to estimate the strength of SOI in the Mg_2X compounds. Utilizing our five-band TB model, we have summarized the strength of SOI, \(\eta_{SO}\), for X = Si, Ge, Sn, Pb and strain values from \(\varepsilon = -10\%\) to \(\varepsilon = +10\%\) by a step of 2% in Table III. To obtain the results of \(\eta_{SO}\) in Table III, we have confined our model to a small interval around the \(\Gamma\) point. This confinement results in a perfect fit to the DFT band structure and more accurate estimation of \(\eta_{SO}\). Also, we have summarized the values of \(\eta_{SO}\) by fitting the five-band TB model to the entire Brillouin zone in Appendix C. Nevertheless, the physical trends and conclusions made remain the same. We have shown the values of \(\eta_{SO}\), obtained through the confined five-band TB model, as a function of X = Si, Ge, Sn, Pb for \(\varepsilon = 0\%, \pm 10\%\) by dots in Fig. 5. As seen, the strength of SOI follows a significant and systematic enhancement by increasing the atomic number \(z\) of X. We tested several functions, including exponential and polynomial ones, to determine the functionality of \(\eta_{SO}\) to \(z\) and \(\varepsilon\). Our results suggested a second order polynomial as a function of \(z\) with a least deviation from the original data points.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{X} & \textbf{Si(14)} & \textbf{Ge(32)} & \textbf{Sn(50)} & \textbf{Pb(82)} \\
\hline
\textbf{\(\eta_{SO}\) (eV)} & 0 & 1 & 2 & 3 \\
\hline
\end{tabular}
\caption{Values of \(\eta_{SO}\) for X = Si, Ge, Sn, Pb.}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5}
\caption{The strength of spin-orbit interaction as a function of the atomic number of the elements X = Si, Ge, Sn, Pb. The maximum compressive and tensile strain values are applied to the system, i.e., \(\varepsilon = \mp 10\%\) and compared with the cases without any strain, i.e., \(\varepsilon = 0\%\).}
\end{figure}
various physical properties of Mg important ingredients to be accounted for when analyzing and exerting strain point into the fundamentally im-
terminate the thermoelectric power of a material. There-
ter quantities determine the Seebeck coefficient, charge conduc-
mainly from the interaction of the
found in Fig. 4. It clearly affirms that SOI originates
properly predict the variation of SOI in Mg
1meV. Therefore, Eqs. (14) and
2
ε
1
1
B
2
1
2
ε
ε
so that the coefficients can be described by

\eta_{SO}(\varepsilon, z) = A(\varepsilon)z^2 + B(\varepsilon)z + C(\varepsilon). \quad (14)

Further investigations found that the coefficients of the
describe polynomial function possess linear functionalities with re-
where the constant values are

\begin{align}
A(\varepsilon) &= A_1\varepsilon + A_2, \\
B(\varepsilon) &= B_1\varepsilon + B_2, \\
C(\varepsilon) &= C_1\varepsilon + C_2, 
\end{align} \quad (15)

in which the constant values are

\begin{align}
A_1 &= -0.3\text{meV}, \\
A_2 &= 0.5\text{meV}, \\
B_1 &= 8.0\text{meV}, \\
B_2 &= -15.4\text{meV}, \\
C_1 &= -79.7\text{meV}, \\
C_2 &= 168.1\text{meV}.
\end{align}

Therefore, Eqs. (14) and (15) determine the dependence of the strength of SOI to the atomic number of X and strain \(\varepsilon\). To illustrate the efficiency of this model, we have plotted \(\eta_{SO}(\varepsilon, z)\) as a function of \(z\) and three values of strain by dashed lines in Fig. 5. We see that the obtained equation (14) can properly predict the variation of SOI in Mg\(_2\)X subject to strain. Figure 5 and Table III demonstrate that compressive and tensile strains enhance and suppress \(\eta_{SO}\), respectively. This is in full agreement with the contri-
the values of the band splittings

\begin{align}
s_1 &= \frac{1}{2}g_{1SO}^2, \\
s_2 &= \frac{1}{2}g_{2SO}^2, \\
s_3 &= \frac{1}{2}g_{3SO}^2
\end{align}

acquires nonzero values when applying \(\varepsilon > 5\%\) of tensile strain to Mg\(_2\)Ge. The splitting increases in Mg\(_2\)Sn and Mg\(_2\)Pb and appears even at compressive strains. This is in contrast to \(g_{2SO}^2\), which is nonzero for all compounds and enhances (suppresses) in the presence of compressive (tensile) strain similar to the strength of SOI. Note that the values of the band splittings \(g_{1SO}^2\) are different from the strength of SOI, \(\eta_{SO}\).

D. The contribution of \(\sigma\) and \(\pi\) bondings

The five-band TB model further provides insightful in-
for Mg\(_2\)X compounds. We have extracted the behavior of the \(\sigma\) bondings and \(\pi\) bonding energies from our model and plotted them as a function of strain for different X in Fig. 6. Also, the exact values of the bonding parameters are given in Appendix C. The \(\sigma\) bondings among s-s orbitals, p-p orbitals, and s-p orbitals are shown by \(\sigma_{ss}\), \(\sigma_{pp}\), and \(\sigma_{sp}\), respectively, while the \(\pi\) bonding among the p-p orbitals is denoted by \(\pi_{pp}\). The results in Fig. 6(b) reveal that the \(\pi_{pp}\) bonding is negligible compared with the \(\sigma\) bonding shown in Figs. 6(a), 6(c), and 6(d). The largest variation upon strain belongs to \(\sigma_{pp}\) and compres-
sive strain enhances \(\sigma_{pp}\). Also, Figs. 6(c) and 6(d) show that \(\sigma_{sp}\) and \(\sigma_{pp}\) are the dominating bondings in Mg\(_2\)X.

VII. CONCLUSIONS

We have developed multi-orbital tight-binding (MOTB) model Hamiltonians to study the electronic

\begin{align}
\eta_{SO}(\varepsilon, z) &= A(\varepsilon)z^2 + B(\varepsilon)z + C(\varepsilon), \\
\eta_{SO}(\varepsilon, z) &= A(\varepsilon)z^2 + B(\varepsilon)z + C(\varepsilon).
\end{align} \quad (14)

Further investigations found that the coefficients of the polynomial function possess linear functionalities with respect to strain \(\varepsilon\) so that the coefficients can be described by

\begin{align}
A(\varepsilon) &= A_1\varepsilon + A_2, \\
B(\varepsilon) &= B_1\varepsilon + B_2, \\
C(\varepsilon) &= C_1\varepsilon + C_2, 
\end{align} \quad (15)

in which the constant values are

\begin{align}
A_1 &= -0.3\text{meV}, \\
A_2 &= 0.5\text{meV}, \\
B_1 &= 8.0\text{meV}, \\
B_2 &= -15.4\text{meV}, \\
C_1 &= -79.7\text{meV}, \\
C_2 &= 168.1\text{meV}.
\end{align}

Therefore, Eqs. (14) and (15) determine the dependence of the strength of SOI to the atomic number of X and strain \(\varepsilon\). To illustrate the efficiency of this model, we have plotted \(\eta_{SO}(\varepsilon, z)\) as a function of \(z\) and three values of strain by dashed lines in Fig. 5. We see that the obtained equation (14) can properly predict the variation of SOI in Mg\(_2\)X subject to strain. Figure 5 and Table III demonstrate that compressive and tensile strains enhance and suppress \(\eta_{SO}\), respectively. This is in full agreement with the contribution of the \(p\) orbitals of X to the total band structure found in Fig. 4. It clearly affirms that SOI originates mainly from the interaction of the \(p\) orbitals of X. According to the findings of thermoelectric effects reported in the literature and discussed earlier in Introduction, the delicate splitting and aspects of the band structure highly influence the Seebeck coefficient, charge conductance, and phonon scattering. The latter quantities determine the thermoelectric power of a material. Therefore, our results of the band structure upon changing X and exerting strain point into the fundamentally im-
portant ingredients to be accounted for when analyzing various physical properties of Mg\(_2\)X.

properties of Mg\(_2\)X(X = Si, Ge, Sn, Pb) with the antiflu-
orite structure subject to uniform strain. Our models
TABLE III. The strength of SOI, $\eta_{SO}$, and band splittings $g_{1,SO}^1$ and $g_{4,SO}^4$ at the $\Gamma$ point in the Mg$_2$X (X = Si, Ge, Sn, Pb) compounds subject to strain $\varepsilon \in [-10\%, +10\%]$.

| Compound | $\eta_{SO}$ (meV) | $g_{1,SO}^1$ (meV) | $g_{4,SO}^4$ (meV) |
|----------|--------------------|--------------------|--------------------|
| Mg$_2$Si  | 25.4               | 24.7               | 23.6               |
| Mg$_2$Ge  | 149.1              | 144.8              | 141.0              |
| Mg$_2$Sn  | 408.7              | 394.3              | 379.9              |
| Mg$_2$Pb  | 1519.0             | 1475.9             | 1425.5             |

The band splitting between 1$\text{st}$ and 2$\text{nd}$ valence bands at the $\Gamma$ point $g_{1,SO}^1$ (meV) for Mg$_2$X compounds.

| Compound | $g_{1,SO}^1$ (meV) | $g_{4,SO}^4$ (meV) |
|----------|--------------------|--------------------|
| Mg$_2$Si  | 0.0                | 0.0                |
| Mg$_2$Ge  | 226.2              | 219.8              |
| Mg$_2$Sn  | 622.8              | 600.8              |
| Mg$_2$Pb  | 2334.5             | 2247.0             |

The band splitting between 1$\text{st}$ and 3$\text{rd}$ valence bands at the $\Gamma$ point $g_{4,SO}^4$ (meV) for Mg$_2$X compounds.

| Compound | $g_{1,SO}^1$ (meV) | $g_{4,SO}^4$ (meV) |
|----------|--------------------|--------------------|
| Mg$_2$Si  | 37.5               | 36.4               |
| Mg$_2$Ge  | 226.2              | 219.8              |
| Mg$_2$Sn  | 622.8              | 600.8              |
| Mg$_2$Pb  | 2334.5             | 2247.0             |

are calibrated to the band structure of DFT using a massively parallelized Monte-Carlo search algorithm. The investigations demonstrated that a five-band TB model, accounting for the $s$ orbital of Mg and $\{p_x, p_y, p_z\}$ orbitals of X, occupying their outer electron shells, can sufficiently describe the electronic characteristics of Mg$_2$X close to the Fermi level. We find that the Mg atoms tend to transfer their electrons, occupying the $s$ orbital, to the $p$ orbitals of the X atoms and create Mg$_2^{-2}$X$^{+4}$. This phenomenon is clearly seen in the projected band structure where the $s$ orbital of Mg is largest on the conduction bands, supporting excited states, whereas the contribution of the $p$ orbitals of X is largest on the valence bands with energies lower than the Fermi level. The application of compressive strain causes further localization of the contribution of the $s$ orbital of Mg to the conduction bands at higher energies above the Fermi level and the $p$ orbitals of X to the valence bands at lower energies below the Fermi level. The tensile strain, however, has a reversed effect and weakens the contributions of the $s$ orbital of Mg and the $p$ orbitals of X to the conduction bands and valence bands, respectively. The analysis of the projected band structures shows that the spin-orbit interaction (SOI) in Mg$_2$X originates from the $p$ orbitals of X. Extracting the strength of SOI $\eta_{SO}$ through the five-band TB model, we have obtained a function for predicting $\eta_{SO}$ in the presence of strain and against the atomic number of X. The five-band TB model reveals that the main bonding contributions in the Mg$_2$X compounds are $|\sigma_{sp}| > |\sigma_{pp}| > |\sigma_{ss}|$, and the $\pi$ bonding is negligible. When applying strain, the largest variation belongs to $\sigma_{pp}$.

We have found that both X and strain can effectively control the band gap of Mg$_2$X, turning a semiconductor into metal and vice versa, and efficiently manipulate the band splitting of the valence bands at the $\Gamma$ point. These findings point into controllable electronic properties, quantum transport, and thermoelectric effects in these materials. Our five-band TB model can be generalized and utilized to study large-scale Mg$_2$X-based compounds both in molecular dynamics simulations and quantum transport studies with more accuracy compared to those of single-band parabolic models available in the literature.

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Appendix A: Hopping integrals and SOI matrix elements for the eighteen-band TB model

In this Appendix, we present the components of the largest MOTB model constructed. This model includes $\{s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2}, s^*\}$ orbitals and describes eighteen electronic bands around the Fermi level. To construct smaller models, similar to the five-band TB model presented in the main text, one simply needs to
remove the associated interactions in the eighteen-band TB model. The basis set for the largest TB model is given by

$$
\Psi_{18} = \left( C_{s\sigma}^{A}, C_{p_{x}\sigma}^{A}, C_{p_{y}\sigma}^{A}, C_{p_{z}\sigma}^{A}, C_{s_{\sigma}}^{A}, C_{p_{x}\sigma}^{A'}, C_{p_{y}\sigma}^{A'}, C_{p_{z}\sigma}^{A'}, C_{s_{\sigma}}^{B}, C_{p_{x}\sigma}^{B}, C_{p_{y}\sigma}^{B}, C_{p_{z}\sigma}^{B}, C_{d_{x\sigma}}^{B}, C_{d_{y\sigma}}^{B}, C_{d_{z\sigma}}^{B}, C_{d_{x^{-2}\sigma}}^{B}, C_{d_{y^{-2}\sigma}}^{B}, C_{s_{\sigma}}^{B'} \right)^{T}.
$$

(A1)

The basis set used in the five-band model is instead

$$
\Psi_{5} = \left( C_{s\sigma}^{A}, C_{s\sigma}^{A'}, C_{p_{x}\sigma}^{B}, C_{p_{y}\sigma}^{B}, C_{p_{z}\sigma}^{B} \right)^{T}.
$$

(A2)

In the following, we have summarized the various interactions and hopping integrals in matrices that arise in our largest MOTB model:

$$
\gamma(k) = \begin{pmatrix}
\mu \\
A_{s} & A_{p} & A'_{s} & A'_{p} & B_{s} & B_{p} & B_{d} & B^{*}
\end{pmatrix}
\begin{pmatrix}
\gamma_{sp}(k)[12 \times 12]
\end{pmatrix},
$$

(A3)

$$
\gamma_{sp}(k) = \begin{pmatrix}
\mu \\
A_{s} & A_{x} & A_{y} & A_{z} & A'_{s} & A'_{x} & A'_{y} & A'_{z} & B_{s} & B_{px} & B_{py} & B_{pz}
\end{pmatrix}
\begin{pmatrix}
\gamma_{ss}^{AA} & \gamma_{sp}^{AA} & \gamma_{sp}^{AA'} & \gamma_{ss}^{AA'} & \gamma_{sp}^{AA'} & \gamma_{ss}^{AA'} & \gamma_{sp}^{AA'} & \gamma_{sp}^{AA'} & \gamma_{ss}^{AA'} & \gamma_{sp}^{AA'} & \gamma_{sp}^{AA'} & \gamma_{sp}^{AA'}
\end{pmatrix}. \quad (A4)
$$

The interaction parameters defined in Eqs. (A3) and (A4) are given by

$$
\gamma_{ss}^{AA'} = \gamma_{ss}^{A'A} = 2\sigma_{ss}^{AA} \left( \cos \frac{k_{x}}{2} + \cos \frac{k_{y}}{2} + \cos \frac{k_{z}}{2} \right),
$$

(A5)

$$
\gamma_{ss}^{AA} = \gamma_{ss}^{A'A'} = 4\sigma_{ss}^{AA} \left( \cos \frac{k_{x}}{2} \cos \frac{k_{y}}{2} + \cos \frac{k_{x}}{2} \cos \frac{k_{z}}{2} + \cos \frac{k_{y}}{2} \cos \frac{k_{z}}{2} \right),
$$

(A6)

$$
\gamma_{ss}^{BB} = 4\sigma_{ss}^{BB} \left( \cos \frac{k_{x}}{2} \cos \frac{k_{y}}{2} + \cos \frac{k_{x}}{2} \cos \frac{k_{z}}{2} + \cos \frac{k_{y}}{2} \cos \frac{k_{z}}{2} \right).
$$

(A7)
\[ \gamma_{ss}^{AB} = (\gamma_{ss}^{A'B'})^* = 4\sigma_{ss}^{AB} \left( \cos \frac{k_x}{4} \cos \frac{k_y}{4} \cos \frac{k_z}{4} - i \sin \frac{k_x}{4} \sin \frac{k_y}{4} \sin \frac{k_z}{4} \right), \]  

(A8)

\[ \frac{\gamma_{pp}^{BB}}{2} = t^{p\sigma_{pp}}(\delta_1^+) \cos \left( \frac{k_y}{2} + \frac{k_z}{2} \right) + t^{p\sigma_{pi}}(\delta_1^+) \cos \left( \frac{k_y}{2} - \frac{k_z}{2} \right) + t^{p\sigma_{pi}}(\delta_3^+) \cos \left( \frac{k_y}{2} + \frac{k_z}{2} \right) + t^{p\sigma_{pi}}(\delta_3^+) \cos \left( \frac{k_y}{2} - \frac{k_z}{2} \right), \]  

(A9)

where

\[
\begin{align*}
  t^{p\sigma_{pi}}(\delta_1^+) &= \begin{pmatrix} \pi_{pp}^A & 0 & 0 \\ 0 & p_+ & p_- \\ 0 & p_- & p_+ \end{pmatrix}, \\
  t^{p\sigma_{pi}}(\delta_2^+) &= \begin{pmatrix} p_+ & 0 & p_- \\ 0 & \pi_{pp}^{} & 0 \\ -p_0 & 0 & p_+ \end{pmatrix}, \\
  t^{p\sigma_{pi}}(\delta_3^+) &= \begin{pmatrix} p_+ & 0 & p_- \\ 0 & \pi_{pp}^{} & 0 \\ -p_0 & 0 & p_+ \end{pmatrix}, \\
  t^{p\sigma_{pi}}(\delta_4^+) &= \begin{pmatrix} \pi_{pp}^{} & 0 & 0 \\ 0 & p_+ & p_- \\ 0 & p_- & p_+ \end{pmatrix}.
\end{align*}
\]  

(A10)

Here, \( p_{\pm} \equiv (\sigma_{pp}^B \pm \pi_{pp}^B)/2 \) where \( \sigma_{pp}^B \) and \( \pi_{pp}^B \) represent the \( \sigma \) and \( \pi \) bonds for the \( p \) orbitals of the A atoms. The elements \( t^{p\sigma_{pi}}(\delta)[i,j] \) of (A10) represent the coupling between orbitals \( p_i \) and \( p_j \) in the direction \( \delta \). The equivalent expressions for the A elements are obtained as

\[ \frac{\gamma_{pp}^{AA'}}{2} = \frac{\gamma_{pp}^{A'A}}{2} = \begin{pmatrix} \sigma_{pp}^A & 0 & 0 \\ 0 & \pi_{pp}^A & 0 \\ 0 & 0 & \pi_{pp}^A \end{pmatrix} \left( \begin{array}{lll} k_x & 0 & 0 \\ 0 & k_y & 0 \\ 0 & 0 & k_z \end{array} \right) \left( \begin{array}{lll} k_x & 0 & 0 \\ 0 & k_y & 0 \\ 0 & 0 & k_z \end{array} \right) \left( \begin{array}{lll} k_x & 0 & 0 \\ 0 & k_y & 0 \\ 0 & 0 & k_z \end{array} \right) \]  

(A11)

\[ \gamma_{pp}^{AA'} = \gamma_{pp}^{A'A} = \gamma_{pp}^{BB'} = \gamma_{pp}^{A'B'} \left[ \sigma_{pp}^A \leftarrow \tilde{\sigma}_{pp}^A, \ \pi_{pp}^A \leftarrow \tilde{\pi}_{pp}^A \right]. \]  

(A12)

\[ \gamma_{pp}^{AB} = 2\sqrt{2i} \sigma_{sp}^{BB} \left( \sin \frac{k_x}{2} \left( \cos \frac{k_y}{2} + \cos \frac{k_z}{2} \right), \sin \frac{k_y}{2} \left( \cos \frac{k_x}{2} + \cos \frac{k_z}{2} \right), \sin \frac{k_z}{2} \left( \cos \frac{k_x}{2} + \cos \frac{k_y}{2} \right) \right), \]  

(A14)
\[ \gamma_{sp}^\text{AB} = -(\gamma_{sp}^\text{BA})^* = \frac{4\sigma_p^{\text{AB}}}{\sqrt{3}} \begin{pmatrix} \cos \frac{k_x}{4} \sin \frac{k_y}{4} \sin \frac{k_z}{4} - i \sin \frac{k_x}{4} \cos \frac{k_y}{4} \cos \frac{k_z}{4} \\ \cos \frac{k_y}{4} \sin \frac{k_x}{4} \cos \frac{k_z}{4} - i \sin \frac{k_y}{4} \cos \frac{k_x}{4} \sin \frac{k_z}{4} \\ \sin \frac{k_x}{4} \sin \frac{k_y}{4} \cos \frac{k_z}{4} - i \cos \frac{k_x}{4} \sin \frac{k_y}{4} \cos \frac{k_z}{4} \end{pmatrix}, \]

(A17)

The interaction of the \(d\) orbitals with those of \(s, p, d\) are summarized as follows.

\[ \gamma_{dd} = \sum_{\delta \in \delta_{\text{dd}}} 2t_{dd}(\delta) \cos(k \cdot \delta), \]

(A19)

\[ t_{dd}(\delta) = \begin{pmatrix} 3l^2m^2 & 3lm^2n & \frac{3}{2}lm(l^2 - m^2) & \sqrt{3}lm[n^2 - \frac{1}{2}(l^2 + m^2)] \\ 3m^2n^2 & 3ln^2m & \frac{3}{2}mn(l^2 - m^2) & \sqrt{3}mn[n^2 - \frac{1}{2}(l^2 + m^2)] \\ 3l^2n^2 & \frac{3}{2}nl(l^2 - m^2) & \sqrt{3}nl[n^2 - \frac{1}{2}(l^2 + m^2)] & [n^2 - \frac{1}{2}(l^2 + m^2)]^2 \\ T & \frac{3}{2}(l^2 - m^2)^2 & \sqrt{3}(l^2 - m^2)[n^2 - \frac{1}{2}(l^2 + m^2)] & \end{pmatrix} \sigma_{dd} \]

\[ + \begin{pmatrix} l^2 + m^2 - 4l^2m^2 & ln(1 - 4m^2) & mn(1 - 4l^2) & 2lm(m^2 - l^2) \\ m^2 + n^2 - 4m^2n^2 & lm(1 - 4n^2) & -mn[1 + 2(l^2 - m^2)] & \sqrt{3}mn(l^2 + m^2 - n^2) \\ l^2 + n^2 - 4l^2n^2 & nl[1 - 2(l^2 - m^2)] & \sqrt{3}ln(l^2 + m^2 - n^2) & 3n^2(l^2 + m^2) \\ T & \frac{3}{2}(l^2 - m^2)^2 & \sqrt{3}n^2(m^2 - l^2) & \end{pmatrix} \pi_{dd}, \]

(A20)

in which \(\sigma_{dd}, \pi_{dd}\) and \(\delta_{dd}\) are the hopping parameters, and \(T\) denotes the transpose of the upper-triangular matrix. \(\delta_{BB}^\text{AB}\) is the half of the BB vectors presented in Table I with a positive sign. Also, \(\{l, m, n\}\) are respectively the \(x, y\) and \(z\) components of the direction of \(\delta\).

\[ \gamma_{pd}^\text{BB} = \sum_{\delta \in \delta_{\text{pd}}} 2it_{pd}(\delta) \sin(k \cdot \delta), \]

(A21)

where \(t_{pd}(\delta)\) is the \(p-d\) interaction matrix given by

\[ t_{pd}(\delta) = \begin{pmatrix} \sqrt{3}lm & \sqrt{3}mn & \frac{3}{2}l(n^2 - \frac{1}{2}(l^2 + m^2)) \\ \sqrt{3}ln^2 & \sqrt{3}lmn & \frac{3}{2}l(m^2 - l^2) \\ \sqrt{3}mn^2 & \sqrt{3}lnm & \frac{3}{2}n(l^2 - m^2) \end{pmatrix} \sigma_{pd} \]

\[ + \begin{pmatrix} m(1 - 2l^2) & -2lnm & n(1 - 2l^2) & l(1 - l^2 + m^2) & -\sqrt{3}ln^2 \\ l(1 - 2m^2) & m(1 - 2m^2) & -2lnm & -m(1 + l^2 - m^2) & -\sqrt{3}mn^2 \\ -2lnm & m(1 - 2n^2) & l(1 - n^2) & -n(l^2 + m^2) & \sqrt{3}nl(l^2 + m^2) \end{pmatrix} \pi_{pd}. \]

(A22)

For the \(\gamma_{pd}^\text{AB}\) interaction, no significant simplifications are available, and it is most convenient to use Eq. (2) directly,

\[ \gamma_{pd}^\text{AB} = \sum_{\delta \in \delta_{\text{AB}}} t_{pd}(\delta) \exp(ik \cdot \delta), \]

(A23)
FIG. 7. The band structure of Mg\textsubscript{2}Ge along the high-symmetry path ΓXWLΓKX. The strain is set to zero and the Fermi level is shifted to \( E = 0 \). The solid curves belong to the eighteen-band TB model whereas the dashed curves are obtained by DFT.

Finally, the interaction between the \( s \) and \( d \) orbitals can be expressed by

\[
\gamma_{ss}^{BB} = \sum_{\delta \in \delta^+} 2t_{sd}(\delta) \cos(k \cdot \delta),
\]  

(A24)

\[
l_{sd}^{BB}(\delta) = \sigma_{sd}^{BB} \left( \sqrt{3}lm, \sqrt{3}mn, \sqrt{3}ln, \frac{\sqrt{3}}{2} (l^2 - m^2), \frac{1}{2} (l^2 + m^2) \right),
\]  

(A25)

and \( \gamma_{sd}^{AB} \) is found to be

\[
\gamma_{sd}^{AB} = (\gamma_{sd}^{B'})^* = \frac{\sigma_{sd}^{AB}}{\sigma_{sp}^{AB}} \left( \gamma_{sp}^{AB}, \gamma_{sp}^{AB}, \gamma_{sp}^{AB}, 0, 0 \right).
\]  

(A26)

A virtual \( s^* \) orbital may be introduced into the formulations to represent the 4s/5s/6s/7s orbitals of Si/Ge/Sn/Pb in order to obtain better fittings with less deviations with respect to the DFT band structure. The interaction integrals, corresponding to \( s^* \), can be calculated using

\[
\gamma_{s^*}^{BB} = \frac{\sigma_{s^*p}^{BB}}{\sigma_{s^*s}^{BB}} \gamma_{s^*s}^{BB}, \quad \gamma_{s^*s^*}^{BB} = \frac{\sigma_{s^*s^*}^{BB}}{\sigma_{ss}^{BB}} \gamma_{ss}^{BB}, \quad \alpha = \{A, A', B\}, \mu = \{s, p, d\}.
\]  

(A27)

Also, we may summarize the \( p \) orbital matrix elements for the SOI operator \( \eta_{uv,\sigma\sigma'} \) as

\[
\eta_{p,p,\sigma\sigma'} = \frac{\eta_{SO}}{2} \begin{pmatrix}
p_{x\uparrow} & p_{x\downarrow} & p_{y\uparrow} & p_{y\downarrow} & p_{z\uparrow} & p_{z\downarrow} \\
p_{x\uparrow} & 0 & 0 & -i & 0 & 1 \\
p_{x\downarrow} & 0 & 0 & i & -1 & 0 \\
p_{y\uparrow} & i & 0 & 0 & 0 & -i \\
p_{y\downarrow} & 0 & -i & 0 & 0 & 0 \\
p_{z\uparrow} & 0 & 0 & i & 0 & 0 \\
p_{z\downarrow} & 1 & i & 0 & 0 & 0
\end{pmatrix}.
\]  

(A28)

Appendix B: The total band structure using the eighteen-band TB model

As pointed out in the main text, the deviation of the conduction bands in our five-band TB model originates from the truncation of the more complete basis set given by Eq. (A1). A full conduction band is a complicated hybridization of different excited orbitals such as the \( d \) orbitals in Mg\textsubscript{2}X. To show how the inclusion of higher excited states in
our TB models can improve the fitting of conduction bands in the five-band TB model, we have employed the largest
MOTB model we constructed, i.e., the eighteen-band TB model, and plotted its results in Fig. 7. We have considered
a representative case where strain is set to zero and X = Ge. The dashed red curves are the DFT band structure
whereas the solid blue curves are the band structure from our eighteen-band TB model. Compared to Fig. 3(b2),
we clearly see that the conduction bands are now greatly improved and more delicate features are captured by
the eighteen-band TB model. The same improvement is accessible through the eighteen-band TB model when applied to
the cases shown in Fig. 3.

Appendix C: Optimized parameters to the five-band TB model

Table C summarizes the optimized bonding parameter values obtained for the five-band TB model, presented in
the main text, to describe Mg$_2$X (X = Si, Ge, Sn, Pb). We have included the obtained parameter values when strain
is $\varepsilon = 0\%$, $\pm 10\%$. The presented bonding parameter values, on-site energies, and spin-orbit coupling strength $\sigma_{\text{SO}}$ in
Table C reproduce the band structure within the entire Brillouin zone.

| type | strain | AA $\sigma_{ss}$ (eV) $\bar{\sigma}_{ss}$ (eV) $\sigma_{pp}$ (eV) $\pi_{pp}$ (eV) $\sigma_{sp}$ (eV) | on-site $E_{As}$ (eV) $E_{Bp}$ (eV) $\sigma_{SO}$ (eV) |
|------|--------|-----------------------------|-----------------------------|
| Si   | $\varepsilon = -10\%$ | 0.0400 0.1036 0.6370 0.0002 0.6559 | 1.9654 -2.6307 0.0190 |
| Ge   | $\varepsilon = 0$ | 0.0793 0.1092 0.6251 0.0039 0.7674 | 2.0422 -2.6611 0.1234 |
| Sn   | $\varepsilon = 0$ | 0.0327 0.0955 0.6451 0.0147 0.6695 | 1.5619 -2.8796 0.3059 |
| Pb   | $\varepsilon = +10\%$ | -0.0955 0.0932 0.5718 0.0344 0.9046 | 0.9047 -3.0787 1.0731 |
| Si   | $\varepsilon = 0$ | -0.0759 0.0660 0.4952 0.0052 0.6642 | 1.3375 -2.2480 0.0190 |
| Ge   | $\varepsilon = 0$ | -0.1499 0.0587 0.4362 0.0233 0.8279 | 1.0853 -2.1530 0.1220 |
| Sn   | $\varepsilon = 0$ | -0.0762 0.0678 0.4430 0.0281 0.7744 | 0.8680 -2.1290 0.2836 |
| Pb   | $\varepsilon = +10\%$ | -0.1913 0.0479 0.3936 0.0451 0.8707 | 0.4543 -2.0863 0.9174 |

Table IV. Hopping parameters, on-site energies, and spin-orbit coupling strength for the five-band TB model.

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