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Phys. Rev. Materials 2, 085401 — Published 2 August 2018
DOI: 10.1103/PhysRevMaterials.2.085401
Thermoelectric performance of materials with \( \text{Cu}Ch_4 \) \((Ch = S, Se)\) tetrahedra: similarities and differences among their low-dimensional electronic structure from first principles

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(Dated: July 12, 2018)

In this study, we perform a comparative theoretical study on the thermoelectric performance of materials with \( \text{Cu}Ch_4 \) \((Ch = S, Se)\) tetrahedra including famous thermoelectric materials Bi-CuSeO and tetrahedrite \( \text{Cu}_{12}\text{Sb}_4\text{S}_3 \), by means of first-principles calculations. By comparing these electronic band structures, we find that many of these materials possess a \( \text{Cu}-t_{2g} \) band structure consisting of the quasi-one-dimensional band dispersions and the isotropic (two-dimensional for layered compounds) band dispersion near the valence band edge. Therefore, the key factors for the thermoelectric performance are the anisotropy of the former band dispersion and the degeneracy of these two kinds of band dispersions. We also find that a large extension of the chalcogen orbitals often improve their thermoelectric performance by improving these two factors or by going beyond such a basic band structure through a large alternation of its shape. Such a large extension of the chalcogen orbitals might partially originate from the anisotropic \( \text{Cu}-Ch \) bond geometry of a tetrahedron. Our study reveals interesting similarities and differences of materials with \( \text{Cu}Ch_4 \), which provides important knowledge for future search of high-performance thermoelectric materials.

I. INTRODUCTION

Exploring high-performance thermoelectric materials is one of the most important tasks for solving the energy problem. The efficiency for the thermoelectric conversion is governed by the dimensionless figure of merit \( ZT = \sigma S^2 T / \kappa \), where \( \sigma \), \( S \), \( T \), and \( \kappa \) are the electrical conductivity, the Seebeck coefficient, the temperature, and the thermal conductivity, respectively. One promising and popular way to increase \( ZT \) is reducing the lattice thermal conductivity, e.g., by nanostructuring\(^1\)–\(^3\). Another way is to increase the power factor PF = \( \sigma S^2 \), a several kinds of the desirable band structures for which have been proposed such as a sharp peak of the density of states (DOS) near the Fermi level based on the Mott formula\(^4\), a pudding-mold-shaped band\(^5\), high degeneracy (band convergence) of the band edges (e.g. Ref. [6]), and low dimensionality\(^7\)–\(^11\). For example, a high-throughput search of thermoelectric materials was proposed using the Fermi surface complexity factor\(^12\), which becomes larger when the valley degeneracy becomes higher and the anisotropy of the effective mass becomes stronger. The entropy originating from the degeneracy of 3d electrons together with their strong degeneracy effects is also an intriguing source of a high thermopower\(^13\).

However, an ideal electronic structure is difficult to realize because of the high sensitivity of the power factor to the electronic band structure near its edge within few \( k_B T \sim \) an order of 10 or 100 meV. Therefore, theoretical investigation to control the band structure has usually been performed individually for a specific kind of materials, and so general observation for a wider group of materials has still been missing while it is rather important for searching a new material from the knowledge of existing compounds.

In this paper, we perform a comparative theoretical study on the thermoelectric performance of materials with \( \text{Cu}Ch_4 \) \((Ch = S, Se)\) tetrahedra, which can be found in famous thermoelectric materials such as BiCuSeO\(^{14}–\(^17\) and tetrahedrite \( \text{Cu}_{12}\text{Sb}_4\text{S}_3 \)\(^{18}–\(^25\) (see Fig. 1), by means of first-principles calculations. Through careful investigation into their electronic structure, we reveal several similarities and differences among them. Many of these materials have a valence band structure consisting of quasi-one-dimensional band dispersions with (nearly) two-fold degeneracy at their band edges, together with the rather isotropic (or two-dimensional for layered structures) band dispersion. Therefore, such a band structure can be basically characterized with the degeneracy of these three band edges\(^26\) and the anisotropy (quasi-one-dimensionality) of the band dispersion. An intriguing characteristic of the electronic structure of the \( \text{Cu}Ch_4 \) tetrahedra is that chalcogen atomic orbitals spreading into the void space in the crystal often enhance the thermoelectric performance by improving the two key factors mentioned above or by going beyond such a basic band structure through a large alternation of its shape. It is also characteristic that the band splitting induced by the spin-orbit coupling (SOC) in the non-centrosymmetric environment of the tetrahedron degrades the thermoelectric performance at low temperatures. Our observation will be important knowledge to search new high-performance thermoelectric materials including tetrahedra.

This paper is organized as follows. In Sec. II, we show the detail of the calculation methods we used in this study. Sections III A, III B, III C, III D, and III E present calculation results for \( \text{Sr}_2\text{SeCuChO}_3 \)\(^{27}–\(^28\), \( \beta\)-\( \text{BaCu}_2\text{S}_2 \)\(^{29}–\(^35\), BiCuSeO, \( \text{Cu}Ch \) with hypothetical zincblende and wurtzite structures, and \( \text{Cu}_{12}\text{Sb}_4\text{S}_3 \), respectively. In Sec. III A, we also present some general perspectives on materials with \( \text{Cu}Ch_4 \) tetrahedra. Some materials with \( \text{Cu}Ch_4 \) tetrahedra that are not investi-
gated in our study are briefly discussed in Sec. III F. Section IV is devoted to the summary of this study.

II. METHODS OF CALCULATIONS

First, we determined the crystal structures through structural optimization using the Perdew–Burke–Ernzerhof parameterization of the generalized gradient approximation (PBE-GGA) and the projector augmented wave method as implemented in the VASP code except BiCuSeO, for which we employed the experimental structure taken from Ref. [42]. Plane-wave cutoff energies for the structural optimization were 550 eV for Sr$_2$ScCuSeO$_3$ and 400 eV for other materials. The $k$-meshes used in the structural optimization were $10 \times 10 \times 4$ for Sr$_2$ScCuChO$_3$, $8 \times 8 \times 8$ for $\beta$-BaCu$_2$S$_2$ and Cu$_{12}$Sb$_4$S$_{13}$, and $16 \times 16 \times 16$ for other materials. For the structural optimization, we always included the SOC while the band structure calculation with and without SOC were both performed using those structures. For first-principles band structure calculation, we used PBE-GGA and the full-potential (linearized) augmented plane-wave method, as implemented in the Wien2k code. The $R_K^{\text{max}}$ parameter was set to 8.0.

After the first-principles band structure calculation, we extracted the Wannier functions from the calculated band structures using the WEnTHER and WANNIER90 codes. In this study, we took the following orbitals as the Wannier basis set: Cu-$d$, Ch-$p$, and O-$p$ orbitals for Sr$_2$ScCuChO$_3$, Cu-$d$ and Ch-$p$ orbitals for $\beta$-BaCu$_2$S$_2$ and CuCh with hypothetical zincblende and wurtzite structures, Cu-$d$ orbitals for Cu$_{12}$Sb$_4$S$_{13}$, and Cu-$s$, d, Se-$p$, and Bi-$p$ orbitals for BiCuSeO. For BiCuSeO, the outer and inner windows for Wannierization were set to $[-8:8]$ and $[-8:3]$ eV, respectively, where the valence band top was set to zero. For other materials, band structures with these Wannier basis are isolated (i.e., not entangled), so that there are no degrees of freedom to adjust the windows. We did not perform the maximal localization procedure for constructing the Wannier functions to prevent orbital mixing among the different spin components and to allow for a more intuitive understanding of the hopping parameters. While this issue is only related to calculations with SOC, we did not perform the maximal localization also for calculations without SOC in order to describe the electronic structure on the equal footing for both cases. We constructed the tight-binding model with the obtained hopping parameters among the Wannier functions and analyzed the transport properties using this model. For this purpose, we employed Boltzmann transport theory, where the transport coefficients $K_{\nu}$ are represented as follows:

$$K_{\nu} = \tau \int d\mathbf{k} \sum_n v_{n,k} \otimes v_{n,k} \left[ -\frac{\partial f_0}{\partial \epsilon_{n,k}} \right] (\epsilon_{n,k} - \mu(T))^\nu,$$

by using the Fermi–Dirac distribution function $f_0$, the chemical potential $\mu(T)$, the energy $\epsilon_{n,k}$ and the group velocity $v_{n,k}$ of the one-electron orbital on the $n$-th band at some $k$-point, and the relaxation time $\tau$, which was assumed to be constant ($\tau = 10^{-15}$ second) in this study. In reality, the relaxation time depends on many parameters such as temperature, $k$-point, band index, energy, and direction. A different band structure generally yields a different relaxation time, and several well-known characteristics such as the band degeneracy and low-dimensionality, which are considered to be favorable for high power factor, can shorten the relaxation time by the increased scattering rate such as by phonons and somewhat weaken their superiority. Nevertheless, our investigations into the band structures still offer an important knowledge for understanding the thermoelectric
performance of our target materials. In other words, our main objective in this study is to compare the shape of the band structure and discuss how to realize a favorable one in materials with CuCh$_4$ tetrahedra. Although the material dependence of $\tau$ is an important issue, it is beyond the scope of this study. Here, $\mu(T)$ was determined to provide a given carrier density against the temperature change for calculations with the fixed carrier density. The electrical conductivity $\sigma$ and the Seebeck coefficient $S$ are expressed as follows:

$$\sigma = e^2K_0, \quad S = \frac{1}{eT}K_0^{-1}K_1,$$

where $e$ ($>0$) is the elementary charge. The power factor $PF = \sigma S^2$ was calculated using the diagonal components of these tensors. For layered materials (Sr$_2$ScCuChO$_3$, $\beta$-BaCuS$_2$, and BiCuSeO), we only calculated the transport quantities along the $x$ direction, because the $y$ direction is equivalent to the $x$ direction and the conductivity along the $z$ direction is much smaller. Also for CuCh with the hypothetical zincblende structure and Cu$_3$Sb$_4$S$_{13}$, we only showed the transport quantities along the $x$ direction because of the isotropy, i.e., the $y$ and $z$ directions are equivalent to the $x$ direction. For CuCh with the hypothetical wurtzite structure, we showed the transport quantities along the $x$ and $z$ directions. To simulate the carrier doping, we adopted the rigid band approximation. In this study, we investigated the transport properties at $T = 300$ K unless noted otherwise. For transport calculations using the Boltzmann transport theory described above, we ignored the contribution from conduction bands to concentrate on the transport properties of the valence band structure. For evaluating the effective mass, we fitted a band dispersion with a parabola function within a normalized displacement in the Brillouin zone $\Delta k_i = \pi/20$ $(i = x, y, z)$ from the valence-band top.

III. RESULTS AND DISCUSSION

A. Sr$_2$ScCuChO$_3$ and general perspectives on materials with CuCh$_4$ tetrahedra

We first investigated the electronic structure of Sr$_2$ScCuChO$_3$ ($Ch = S, Se$) where CuCh$_4$ tetrahedra constitute a layered structure (CuCh layers) separated by insulating perovskite layers consisting of the Sr, Sc, and O atoms. These compounds are kinds of mixed-anion compounds$^{52}$. Because some of their analogous compounds are known to be p-type in experiments owing to Cu vacancies$^{53,54}$, we concentrated on the hole carrier doping (i.e., the valence band structure). Because the valence band structure near its edge is governed by the nearly isolated CuCh layers with high symmetry, Sr$_2$ScCuChO$_3$ can be regarded as a prototypical system to investigate basic properties existing in materials with CuCh$_4$ tetrahedra. Therefore, the main purpose of this subsection is to extract general perspectives on materials with CuCh$_4$ tetrahedra from analysis on Sr$_2$ScCuChO$_3$.

1. Band structure and its characteristics

Figure 2(a)(b) shows the band structure and (projected) DOS of Sr$_2$ScCuSO$_3$ calculated without SOC. Black broken and red solid lines in panel (a) represent the band structures obtained with the first-principles calculation and the tight-binding model of the Wannier functions, respectively. (c)-(f) Blow-up views of the first-principles band structures near the valence-band top for Sr$_2$ScCuChO$_3$ ($Ch = S, Se$) with and without SOC. (g) Schematic picture for the impact of SOC on the $d_{xz/yz}$ band dispersions near the valence-band top at the $\Gamma$ point.
shown with the black broken lines. We can see that the valence-band top mainly consists of the Cu states strongly hybridized with the S states. While we denote the valence band structures, e.g., as the ‘$d_{xz/yz}$ band’ in this paper also for other materials, we note that the chalcogen $p$-orbitals are always strongly hybridized with them, and so this notation is used just for simplicity. Because of the existence of the insulating layers, the conduction along the $z$ direction is almost prohibited at least near the valence-band top as inferred from the flat band dispersion along the $\Gamma$-$Z$ line shown in Fig. 2(a).

Blow-up views of the first-principles band structures near the valence-band top are shown in Fig. 2(c)–(f) for $Ch = S$, Se with and without SOC. For all these figures, the Cu-$d_{xz/yz}$ bands exist near the valence-band top of the $\Gamma$ point. A difference in the group velocity (or the effective mass) for these two band dispersions along the $\Gamma$-$X$ line corresponds to the anisotropy of the Cu-$d_{xz/yz}$ bands. In other words, along the $x$ direction, the Cu-$d_{xz}$ band should be more dispersive than the Cu-$d_{yz}$ band by the orbital anisotropy, and vice versa for the $y$ direction. This situation is schematically shown in the left half of Fig. 2(g). Therefore, the valence band structure near its edge can be regarded as quasi-one-dimensional one. Such a low-dimensionality is a key aspect for obtaining good thermoelectric performance because it increases the DOS near the band edge and therefore the $PE^{7-10}$. Note that, when one varies the effective mass of the isotropic band dispersion, an increase of the DOS lowers the group velocity and vice versa; such a trade-off relation makes it difficult to maximize the thermoelectric performance through band engineering. On the other hand, introducing the low-dimensionality increases the DOS without degrading the group velocity with respect to a specific direction, which is the reason why the low-dimensionality is regarded as one of the ideal band structures for the thermoelectric performance. A Cu-$d_{xz}$ band lies around 0.4 eV below the valence top for $Ch = S$ as shown in Fig. 2(c)–(d), while this energy distance is almost doubled for $Ch = Se$ as shown in Fig. 2(e)–(f). Note that the $t_{2g}$ orbitals correspond to the $d_{xz/yz}$ orbitals in the present coordinate. Here, a triple degeneracy of the $t_{2g}$ orbitals is lifted in the crystal field of this material, and so these orbitals should not be called the $t_{2g}$ orbitals in the strict sense of the term. However, for simplicity and convenience for comparing the band structures consisting of these orbitals in other materials with different crystal symmetries as we shall investigate, we simply call them the ‘$t_{2g}$’ orbitals in this paper.

Another important feature of the band structure is a non-negligible band splitting just near the valence-band top in Fig. 2(f), which is induced by SOC, while the Cu-$d_{xz/yz}$ dispersions are degenerate at the valence-band top if SOC is switched off as is expected from the crystal symmetry (i.e. the equivalence between the $x$ and $y$ directions). The effect of SOC is schematically shown in Fig. 2(g). Quasi-one-dimensional Cu-$d_{xz/yz}$ bands are hybridized each other by SOC, and then become two isotropic two-dimensional bands with a small gap. The size of this gap is around 30 and 90 meV for $Ch = S$ and Se, respectively. This band hybridization is pronounced only in the region near the $\Gamma$ point where the $d_{xz/yz}$ bands become close, which we can verify by comparing Fig. 2(e) and (f). Nevertheless, because of the valence-band-top structure is altered by SOC, the power factor is affected as we shall see later in this paper.

Table I presents the effective masses along the $x$ direction, $m^*_{xx}/m_e$, of the first and second highest valence bands for Sr$_2$ScCu$Ch$O$_4$ ($Ch = S$, Se). The anisotropy of the effective mass $\gamma$, which corresponds to the ratio of $m^*_{xx}$ for these two bands, is also shown for the band structure without SOC.

<table>
<thead>
<tr>
<th>$Ch$</th>
<th>w/o SOC</th>
<th>w/ SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>Highest valence band</td>
<td>2.94/0.97</td>
</tr>
<tr>
<td></td>
<td>Next highest valence band</td>
<td>0.47/0.71</td>
</tr>
<tr>
<td></td>
<td>Mass anisotropy $\gamma$</td>
<td>6.2</td>
</tr>
<tr>
<td>Se</td>
<td>Highest valence band</td>
<td>2.91/0.57</td>
</tr>
<tr>
<td></td>
<td>Next highest valence band</td>
<td>0.32/0.59</td>
</tr>
<tr>
<td></td>
<td>Mass anisotropy $\gamma$</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table I: The effective masses along the $x$ direction, $m^*_{xx}/m_e$, of the first and second highest valence bands for Sr$_2$ScCu$Ch$O$_4$ ($Ch = S$, Se). The anisotropy of the effective mass $\gamma$, which corresponds to the ratio of $m^*_{xx}$ for these two bands, is also shown for the band structure without SOC.

2. Transfer integrals and their roles

First, we analyzed microscopic origins that determine the valence band structure near the band edge of Sr$_2$ScCu$Ch$O$_4$. For this purpose, we investigated which transfer integrals in the tight-binding model for the Wannier functions contribute to the valence $t_{2g}$ band structure.

We begin with the definition of all the inequivalent nearest-neighbor transfer integrals between the Cu-$d_{xz/yz}$ and the $Ch$-$p$ orbitals: $t$, $t'$, and $t''$ as shown in Fig. 3(a). Figure 3(b)(d) and (c)(e) show possible hopping processes that might enhance or degrade the one-dimensionality of the $d_{xz/yz}$ bands, respectively, from a top view. Because the other hopping processes are also possible by considering many inequivalent $d$-$d$ and $p$-$p$ transfer integrals, the situation is not so simple. To obtain a clear insight, we hypothetically increased a spe-
specific portion of the transfer integrals by 10% in the tight-binding model of Sr$_2$ScCuSO$_4$, and evaluated how much the mass anisotropy $\gamma$ and the $d_{xz}$-$y^2$ level relative to the $d_{xz}$-$y^2$ level at the $\Gamma$ point changes, which is shown in Fig. 4(a). SOC was switched off here in order to calculate the mass anisotropy. The notation ‘in-plane’ and ‘out-of-plane’ for the $p$-$p$ transfer integrals means whether the $c$ ($z$) coordinates of the two S atoms between which the transfer integral is considered are the same or not.$^{55}$

By looking into Fig. 4(a), we first notice that $t''$ less affects both the anisotropy of the $d_{xz}$-$y^2$ bands and the $d_{xz}$-$y^2$ level shift. This is because the nearest-neighbor $d_{xz}$-$y^2$-$p_z$ hoppings become inactive at the $\Gamma$ point owing to the Bloch phase. We can see this situation in Fig. 3(d): when $k_x = 0$, the same Bloch phase of the $d_{xz}$ orbitals on two sites makes two $d_{xz}$-$p_z$ transfers cancel with each other. Therefore, on the $k_x = 0$ ($k_y = 0$) line, the $p_z$ orbitals are decoupled with the $d_{xz}$ ($d_{yz}$) orbitals.$^{56}$ In particular, the hopping process shown in Fig. 3(e), which requires the coupling of the $p_z$ orbital with both the $d_{xz}$($d_{yz}$) orbitals, is thus completely inactivated on the $\Gamma$-$X$ line where the mass anisotropy is evaluated. Whereas the hopping process shown in Fig. 3(d) begins to be activated when one moves from the $\Gamma$ point by increasing $k_x$, its effect seems very small in Fig. 4(a).

By comparing $t$ and $t'$ in Fig. 4(a), the anisotropy is much largely affected by $t'$. A possible explanation for it might be that $t$ contributes to two processes shown in Fig. 3(b)(c) that enhance and degrade the anisotropy, while $t'$ only contributes to the process shown in Fig. 3(c) that degrades the anisotropy. Therefore, it is desirable to reduce $t'$ for improving the one-dimensionality.

In Fig. 4(a), we can also see that, even if one increases all the $d$-$d$ direct hopping paths, its effect is small on the valence band structure near the $\Gamma$ point. On the other hand, $p$-$p$ hopping amplitudes have a large impact on the valence band structure. In particular, the in-plane $p_{x/y}$-$P_{x/y}$ hopping amplitudes play a very important role in enhancing the one-dimensionality of the $d_{xz}$-$y^2$ bands. Because there are hidden chains on the $Ch$ square lattices in the CuCh layer as shown in Fig. 4(b), it is natural to consider that one-dimensional character of the $d_{xz}$-$y^2$ bands is strongly assisted by the anisotropy of the $Ch$-$P_{x/y}$ orbitals, which have strong $\sigma$-bonds with respect to the $x/y$ directions, respectively. This mechanism has a remarkable resemblance with that in Bi$_2$Sr$_2$ superconductors, where some of the authors recently predicted that the PF can be drastically increased when the one-dimensionality of the $p$-states on the square lattice is further enhanced by atomic substitution$^{59,60}$. The situation
that the inter-chalcogen bonds play an important role for materials properties also reminds us of the intriguing roles of the chemical bonds between arsenic in iron-based superconductors\textsuperscript{61}. It was theoretically pointed out in SnSe that Sn-Sn hopping strongly enhances the one-dimensionality of the electronic structure and thus can further increase its power factor\textsuperscript{62}.

Discussion above teaches us which hopping amplitudes we should pay attention to when one tries to control the band structure of this material. We shall consider how the valence band structure changes by the substitution of the chalcogen atoms and the hypothetical variation of the Ch-Cu-Ch angle in Sections III A 3 and III A 4, respectively.

### 3. Ch = S vs. Se

In Table I, we can notice that the mass anisotropy $\gamma$ for Ch = Se, 9.0, is much larger than that for Ch = S, 6.2. As a matter of fact, the calculated peak value of the power factor, which we call PF\textsubscript{max} hereafter, is larger for Ch = Se than that for Ch = S; PF\textsubscript{max} are 1.40 and 1.55 $\mu$Wcm$^{-1}$K$^{-2}$ for Ch = S and Se, respectively, when SOC is switched off.

To understand this difference, we compared some transfer integrals as listed on Table II. By looking into the $d$-$p$ hopping amplitudes $|t|$, $|t'|$, and $|t''|$, it is hard to understand that the PF value is enhanced for Ch = Se. This is because a smaller $|t|$ in Ch = Se will worsen the one-dimensionality of the $d_{xz/yz}$ band dispersions as we have seen in Sec. III A 2. In addition, $|t'|$ is almost the same between Ch = S and Se, and a difference in $|t''|$ will have a small effect on the anisotropy of the electronic structure. On the other hand, it is rather plausible that the enhanced one-dimensionality in Ch = Se largely owes to the enhanced $p$-$p$ hopping amplitude, especially the in-plane $p_{x/y}-p_{x/y}$ ones, which were in Sec. III A 2 shown to be effective in increasing the anisotropy of the electronic structure. Because the Se orbitals spread in space more widely than the S orbitals do, it is natural that the $p$-$p$ hopping amplitudes become larger in Ch = Se than Ch = S. A decrease of the Ch-Cu-Ch angle $\theta$ from 113° to 108.2° might also play some role in increasing the in-plane $p_{x/y}-p_{x/y}$ hopping amplitudes, while it is a rather minor effect on the anisotropy as we shall see in the next section.

Whereas the anisotropy is enhanced for Ch = Se, stronger SOC can degrade the thermoelectric performance. As a matter of fact, PF\textsubscript{max} exhibits a sizable reduction for Ch = Se by introducing SOC while this effect is negligible for Ch = S, as shown in Fig. 3(a)–(d), where black solid lines show PF curves for the original Ch-Cu-Ch angle $\theta$. The effect of the SOC hybridization is quite pronounced in low temperatures such as $T = 100$ K as shown in Fig. 5(e)–(f), where the PF values calculated with and without SOC for Ch = S and Se, respectively. The PF curve for the original angle is shown with bold black lines in each panel. (e)(f) The same plots for Ch = Se and the original bond angle $\theta = 108.2^\circ$ using several temperatures obtained without and with SOC. The relaxation time $\tau = 10^{-12}$ second was used for all the panels.

![FIG. 5: Calculated PF values of Sr$_2$ScCuChO$_3$ with respect to the hole carrier number for (a) Ch = S without SOC, (b) Ch = S with SOC, (c) Ch = Se without SOC, and (d) Ch = Se with SOC, respectively. The Ch-Cu-Ch angle $\theta$ as defined in Fig. 3(a) is varied in the way described in Sec. III A 4, where the original angles are 113° and 108.2° for Ch = S and Se, respectively. The PF curve for the original angle is shown with bold black lines in each panel. (e)(f) The same plots for Ch = Se and the original bond angle $\theta = 108.2^\circ$ using several temperatures obtained without and with SOC. The relaxation time $\tau = 10^{-12}$ second was used for all the panels.](https://example.com/figure5.png)

TABLE II: Some model parameters extracted from the first-principles band structure calculation for Sr$_2$ScCuChO$_3$ (Ch = S, Se) without SOC. Definition of $t$, $t'$, and $t''$ are shown in Fig. 3(a). $t_{p,p,\sigma}$ is the transfer integrals between the Ch-$p$ orbitals with the same $\sigma$ coordinates and the neighboring $x$ coordinates. All in eV.

| Ch  | $|t|$ | $|t'|$ | $|t''|$ | $t_{p,p,\sigma}$ |
|-----|------|------|------|----------------|
| S   | 0.62 | 0.34 | 0.11 | 0.44           |
| Se  | 0.57 | 0.33 | 0.16 | 0.51           |
4. Hypothetical variation of the Ch-Cu-Ch angle

A CuCh monolayer has only two degrees of freedom in its structure: the Cu-Ch length and the Ch-Cu-Ch angle $\theta$ as defined in Fig. 3(a). Here, we hypothetically vary the Ch-Cu-Ch angle $\theta$ while fixing the Cu-Ch length for Sr$_2$ScCuSO$_4$. Concretely, the c coordinate of the Ch atoms and the lattice constant with respect to the a and b axes are changed with keeping the Cu-Ch length unchanged from the original structure, while other atomic coordinates and the lattice constant with respect to the c axis are fixed.

Figure 5(a)–(d) present the calculated PF with respect to the hole carrier number for $Ch = S$ without SOC, $Ch = S$ with SOC, $Ch = Se$ without SOC, and $Ch = Se$ with SOC, respectively. When one varies the Ch-Cu-Ch angle by few degrees from the original angles, we cannot see a large variation of the calculated PF. However, PF peaks become twice as high as the original value for all the cases by a large increase of the angle. This increase is induced by the degeneracy of the $d_{xz/yz}$ band edge with the $d_{xz/yz}$ band edge at the $\Gamma$ point. In Fig. 6(a)–(e), the valence band structures are shown for several S-Cu-S angles $\theta$. As is clearly seen, the $d_{xz/yz}$ level gets higher by increasing the Ch-Cu-Ch angle, and when the PF peak is the largest value in Fig. 5(a), say, when the Ch-Cu-Ch angle is $124^\circ$, the three band edges are almost degenerate at the valence band top as shown in Fig. 6(d). A further increase degrades the PF peak value as shown in Fig. 5(a). Corresponding to this observation, we can see that two PF peaks, e.g., $\theta = 122^\circ$ in Fig. 5(c), get together by increasing the Ch-Cu-Ch angle $\theta$.

To quantify the change of the band structures, we investigated the relation between the S-Cu-S angle and PF$_{\text{max}}$, $\Delta_{x^2-y^2}$ defined as the $d_{xz/yz}$ level relative to the $d_{xz/yz}$ level at the $\Gamma$ point, and the mass anisotropy $\gamma$ for Sr$_2$ScCuSO$_4$ without SOC. Figure 7(a)–(c) shows the plots, where both $\Delta_{x^2-y^2}$ and $\gamma$ increase by increasing the S-Cu-S angle. While PF$_{\text{max}}$ is not so sensitive to the enhancement of the mass anisotropy, $\Delta_{x^2-y^2} \sim 0$ yields the pronounced PF$_{\text{max}}$.

What is the microscopic origin of the change in the band structure? For a simple limiting case: $\theta = 180^\circ$, the CuCh layer becomes a square lattice where Cu and Ch atoms are alternatively aligned. In this case, we can expect that the $d_{xz/yz}$ orbital will be higher than that for the $d_{xz/yz}$ orbitals in that crystal field. Second, because of the two-dimensional conduction of the $d_{xz/yz}$ orbitals, the width of the $d_{xz/yz}$ band should be much larger than that for the $d_{xz/yz}$ bands, which is not necessarily the case when $\theta$ is much smaller than $180^\circ$ because of relatively small hopping amplitudes between the $d_{xz/yz}$ and $p$ orbitals owing to their different c coordinates. We also note that, for a small $\theta$, $d-d$ and $p-p$ hopping paths will also be activated. In our tight-binding models, the onsite energy difference between the $d_{xz/yz}$ and $d_{xz/yz}$ orbitals is 0.04 eV for $\theta = 113^\circ$ and 0.10 eV for $\theta = 124^\circ$ in Ch = S without SOC, a difference which is much smaller than the large difference in $\Delta_{x^2-y^2}$, around 0.45 eV. Therefore, the main origin of the change in $\Delta_{x^2-y^2}$ is not the onsite energies of the $t_{2g}$
orbitals, but the other model parameters. As a matter of fact, the $d_{x^2−y^2}$ band dispersion drastically changes by varying the bond angle $θ$ as shown in Fig. 6, which cannot be represented with a mere shift of the onsite energy. We do not go further details because the required change in $θ$ for the band degeneracy is prohibitively large: about 10° for $Ch = S$, and 20° for $Ch = Se$. While some atomic substitution, e.g., in the perovskite layer, might change the situation to some extent, we shall take another way: looking for other candidate materials with $CuCh_4$ tetrahedra from Section III B.

5. Impact of the $d_{xz/yz}$ degeneracy on the power factor

Before proceeding, we have a brief look at the effect of the $d_{xz/yz}$ degeneracy at their band edge on the power factor, which is another important aspect of general $t_2g$ systems, while we have so far concentrated on the anisotropy (one-dimensionality) of the $d_{xz/yz}$ bands and the degeneracy between the $d_{x^2−y^2}$ and $d_{xy}$ levels at the $Γ$ point.

To quantify this effect, we performed a simple model calculation for the following four situations: (i) a single two-dimensional band dispersion:

$$
e_{2D}^{D}(k_x, k_y) = 2t_1 \cos k_x + 2t_2 \cos k_y, \quad (3)$$

(ii) a single three-dimensional band dispersion:

$$
e_{3D}^{D}(k_x, k_y, k_z) = 2t_1 \cos k_x + 2t_2 \cos k_y + 2t_2 \cos k_z, \quad (4)$$

(iii) degenerate two-dimensional band dispersions:

$$
e_{1}^{2D}(k_x, k_y) = 2t_1 \cos k_x + 2t_2 \cos k_y, \quad \ne_{2}^{2D}(k_x, k_y) = 2t_2 \cos k_x + 2t_1 \cos k_y, \quad (5)$$

and (iv) degenerate three-dimensional band dispersions,

$$
e_{1}^{3D}(k_x, k_y, k_z) = 2t_1 \cos k_x + 2t_2 \cos k_y + 2t_2 \cos k_z, \quad \ne_{2}^{3D}(k_x, k_y, k_z) = 2t_2 \cos k_x + 2t_1 \cos k_y + 2t_2 \cos k_z. \quad (6)$$

Note that a term ‘degenerate’ for the cases (iii) and (iv) is used to represent the degeneracy of the band edges of two dispersions at the $Γ$ point. We set $t_1 ≥ t_2 ≥ 0$. The mass anisotropy can be represented as $γ = t_1/t_2$. We shall denote $PF_{\text{max}}$ in each case (i)–(iv) as $PF_{\text{max}}^{2D}$, $PF_{\text{max}}^{3D}$, $PF_{\text{max}}^{2D, \text{degen}}$, and $PF_{\text{max}}^{3D, \text{degen}}$, respectively. The PF enhancement factor $α$ is defined as follows:

$$α_{2D} = \frac{PF_{\text{max}}^{2D, \text{degen}}}{PF_{\text{max}}^{2D}}, \quad α_{3D} = \frac{PF_{\text{max}}^{3D, \text{degen}}}{PF_{\text{max}}^{3D}}, \quad (7)$$

which quantify how much the degeneracy enhances $PF_{\text{max}}$ along the $x$ direction. All the results were obtained at the temperature $k_BT = 0.1t_1$.

$PF_{\text{max}}$ and $α$ with respect to the value of $t_2/t_1$ ($= γ^{-1}$) for each case are presented in Fig. 8(a) and (b), respectively. In these figures, we also show the following approximate relations, which are valid when $k_BT ≪ t_1, t_2$

\[γ ≈ \frac{t_2}{t_1} ≲ 1, \quad (8)\]

\[γ ≈ \frac{t_2}{t_1} ≳ 1, \quad (9)\]

\[γ ≈ \frac{t_2}{t_1} ≃ 1, \quad (10)\]

\[γ ≈ \frac{t_2}{t_1} ≈ 0, \quad (11)\]

The results are summarized in Figs. 8(a) and (b), which show the approximate relations Eqs. (8)–(11) for each case. (b) The PF enhancement factor $α$ defined in Eq. (7) as a function of $t_2/t_1$. A dotted horizontal line shows $α = 1$, on which PF is not enhanced by degeneracy. The other dotted line shows the approximate relation Eq. (12). (c) (d) Calculated PF as a function of the chemical potential relative to the valence band top, $μ$, normalized with $t_1$. Here, the results using $t_2 = 0.3t_1$ for the 2D and 3D band dispersions are shown in panels (c) and (d), respectively. The position of the van Hove singularity ($μ/t_1 = −1.2$) is shown with a broken line in each panel.
holds, by dotted lines:

\[
\begin{align*}
PF_{\text{max};xx}^{2D} & \simeq \sqrt{\gamma} PF_{\text{max};xx}^{2D,\text{iso}}, \\
PF_{\text{max};xx}^{2D,\text{degen}} & \simeq (\sqrt{\gamma} + \frac{1}{\sqrt{\gamma}}) PF_{\text{max};xx}^{2D,\text{iso}}, \\
PF_{\text{max};xx}^{3D} & \simeq \gamma PF_{\text{max};xx}^{3D,\text{iso}}, \\
PF_{\text{max};xx}^{3D,\text{degen}} & \simeq (\gamma + 1) PF_{\text{max};xx}^{3D,\text{iso}}, \\
\alpha_{2D} & \simeq \alpha_{3D} \simeq 1 + \frac{1}{\gamma},
\end{align*}
\]  

where 'iso' means the case of \( t_2 = t_1 \). These relations are proved in APPENDIX. Because the assumption required for these relations, \( k_B T \ll t_1, t_2 \), is satisfied for a large \( t_2/t_1 \) region in the plots shown in Fig. 8(a)–(b) since \( k_B T = 0.1 t_1 \), these relations are valid in that region.

In Fig. 8(a), PF is actually increased by low dimensionality. This tendency is verified by comparing \( PF_{\text{max};xx}^{2D} \) and \( PF_{\text{max};xx}^{3D} \) in the whole region of \( t_2/t_1 \), or seeing a sharp increase of PF for \( \gamma \to \infty (t_2/t_1 \to 0) \), which results in the one-dimensional band dispersion for all the four cases. This increase is due to a large DOS near the edge for the low-dimensional band dispersion.

Next, we turn our attention to the effect of degeneracy. As is clearly seen in Fig. 8(b), the PF enhancement factor \( \alpha \) is exactly two for \( \gamma = 1 \) (isotropic band dispersion), but decreases by increasing \( \gamma \), and finally goes to unity for \( \gamma = \infty \). The reason for this behavior is explained as follows. For \( \gamma = 1 \), two equivalent band dispersions are degenerate for the cases (iii) and (iv), which simply doubles the transport coefficients \( K_\nu \) compared with those for the cases (i) and (ii). Thus, \( PF \propto K_\nu^2/K_0 \) is also doubled, which means \( \alpha = 2 \). On the other hand, for the cases (iii) and (iv) with \( \gamma = 0 \), there are one-dimensional band dispersions with respect to the two different directions. In spite of the degeneracy at the band edge, each band dispersion can contribute to the transport only along the one direction. For example, in the case (iii), \( PF_{xx} \) is determined solely by \( \epsilon^{2D}_2(k_x, k_y) = 2t_1 \cos k_x \), and \( \epsilon^{2D}_2(k_x, k_y) = 2t_1 \cos k_y \) makes no contribution for it. Therefore, the degeneracy plays no role for PF enhancement: \( \alpha = 1 \).

In Fig. 8(b), we can also find that \( \alpha_{3D} \) goes down more rapidly than \( \alpha_{2D} \). To investigate this difference, PF as a function of the chemical potential relative to the valence band top, \( \tilde{\mu} \), for the 2D and 3D cases with \( t_2 = 0.3 t_1 \) are presented in Fig. 8(c) and (d), respectively. For the 2D band dispersion, both \( PF_{xx} \) and \( PF_{yy} \) in the case (i) have maximum near the band edge (\( \tilde{\mu} = 0 \)), and then \( PF_{xx}^{\text{degen}} \) in the case (iii) also has a peak there, where the peak value is approximately represented as a summation of \( PF_{xx} \) and \( PF_{yy} \) (see APPENDIX). On the other hand, for the 3D band dispersion, while \( PF_{yy} \) in the case (ii) becomes maximum near the band edge, \( PF_{xx} \) has a peak near the van Hove singularity at \( \tilde{\mu}/t_1 = -1.2 \). This is the origin of the small \( \alpha_{3D} \), in other words, weak enhancement of \( PF_{xx}^{\text{degen}} \). The difference originates from a sharp increase of DOS at the edge of the two-dimensional band dispersion, which is absent at the edge of the three-dimensional band dispersion. We note that (i) when one focuses on PF near the band edge, the enhancement is observed to some extent, and (ii) the existence of the van Hove singularity is not a universal issue for general systems. In addition, one often has to concentrate on the PF near the band edge in order to get a \( ZT \) peak because a deep chemical-potential usually yields an increase of the electronic thermal conductivity, which decreases \( ZT \). Because of these reasons, the difference between 2D and 3D shown in Fig. 8(b) is not so general.

Here, we come back to our first-principles calculation, which yields \( \gamma = 6.2 \) and 9.0 for \( Ch = S \) and Se in \( Sr_2ScCuChO_3 \), respectively. Because of such a large anisotropy and the observation made in this subsection, we can conclude that the degeneracy of the \( d_{xz}/yz \) band edges is not so effective to enhance the power factor, while the degeneracy between the \( d_{xy} \) and \( d_{x^2−y^2} \) band edges can drastically increase the power factor. In general, degeneracy of the band dispersions with strong anisotropy with respect to the orthogonal directions cannot increase the power factor so much.

### B. \( \beta-BaCu_2S_2 \)

From now on, we investigate the electronic structure of other materials with CuCh\_4 tetrahedra. The first target is \( \beta-BaCu_2S_2 \) with separated CuS layers similarly to \( Sr_2ScCuSO_3 \). Figure 9(a) presents the first-principles (black broken lines) and tight-binding (red solid lines) band structures of \( \beta-BaCu_2S_2 \) calculated with SOC. Blow-up views of the first-principles band structures near the valence-band top calculated without and with SOC are shown in Fig. 9(b) and (c), respectively. In spite of the similarity of the crystal structure to that of \( Sr_2ScCuSO_3 \), a remarkable difference in the band structure is a nearly degenerate \( d_{xy} \) band edge at the \( \Gamma \) point in \( \beta-BaCu_2S_2 \). This degeneracy can be seen more easily in Fig. 9(d), where the tight-binding band structure calculated without SOC is shown with the \( d_{xy} \) orbital weight by color. An arrow in the figure denotes the \( d_{xy} \) band edge at the \( \Gamma \) point. To investigate the effect of the band degeneracy on the power factor, in Fig. 9(e), we also present the tight-binding band structure without an inclusion of the \( t_2 \) hopping between the \( S-p_z \) orbitals, which is defined in Fig. 9(f). As is clearly seen in Fig. 9(e), the \( d_{xy} \) band edge is lowered by the hypothetical removal of the \( t_2 \) hopping, while the \( d_{xy} \) band structures are not changed so much. By comparing the power factors obtained from these two conditions, we can evaluate the effect of the \( d_{xy} \) band degeneracy on the thermoelectric performance. We note that the Cu-\( d_{xy} \) orbitals strongly hybridize with the \( S-p_z \) orbitals, as seen in a sharp band dispersion of the \( d_{xy} \) band along the \( \Gamma-Z \) line, while the hybridization of the \( S-p_z \) and Cu-\( d_{xz/yz} \) orbitals are prohibited at the \( \Gamma \) point as

\[
\begin{align*}
PF_{\text{max};xx}^{2D} & \simeq \sqrt{\gamma} PF_{\text{max};xx}^{2D,\text{iso}}, \\
PF_{\text{max};xx}^{2D,\text{degen}} & \simeq (\sqrt{\gamma} + \frac{1}{\sqrt{\gamma}}) PF_{\text{max};xx}^{2D,\text{iso}}, \\
PF_{\text{max};xx}^{3D} & \simeq \gamma PF_{\text{max};xx}^{3D,\text{iso}}, \\
PF_{\text{max};xx}^{3D,\text{degen}} & \simeq (\gamma + 1) PF_{\text{max};xx}^{3D,\text{iso}}, \\
\alpha_{2D} & \simeq \alpha_{3D} \simeq 1 + \frac{1}{\gamma},
\end{align*}
\]
FIG. 9: (a) Band structure of $\beta$-BaCu$_2$S$_2$ calculated with SOC. Black broken and red solid lines represent the band structures obtained with the first-principles calculation and the tight-binding model of the Wannier functions, respectively. Blow-up views of the first-principles band structures near the valence-band top calculated (b) without and (c) with SOC. (d) Tight-binding band structure calculated without SOC, where the black broken and red solid lines present those obtained with the first-principles and tight-binding model calculations, respectively. The blow-up view of the $t_z$ band with a sharp dispersion along the $Z$-$\Gamma$-$(k_x, k_y, k_z)=(2\pi/a, 0, 0)$ line is shown. (e) The same as panel (d) but the $t_z$ hopping is hypothetically removed from our tight-binding model. (f) Definition of the $t_z$ hopping between the $S$-$p_z$ orbitals.

we have seen for Sr$_2$ScCuSO$_3$. Such an inter-layer hopping is almost absent in Sr$_2$ScCuSO$_3$.

Figure 10 shows the calculated PF for several conditions: a regular calculation and one without $t_z$, with and without SOC. It is natural that the SOC plays a negligible role on the power factor. However, against our expectation, PF$_{\text{max}}$ is not enhanced by the degeneracy of the band edge. A possible reason for it is the sizable anisotropy, i.e. quasi-one-dimensionality, of all the $t_{2g}$ orbitals. For example, the $d_{x^2-y^2}$ bands are very heavy along the $z$ direction, and the $d_{x^2-y^2}$ is much heavier along the $x$ and $y$ directions than the $z$ direction. Therefore, the power factor along the $x$ direction is not so much improved by the $d_{x^2-y^2}$ band with a sharp dispersion along the $z$ direction, as discussed in Sec. III A 5. Note that this characteristics is not inherent to the compounds with the same or similar structures. As a matter of fact, the $d_{x^2-y^2}$ bands have a sizable dispersion along the $z$ direction for other materials such as Mg$_3$Sb$_2$, and in that case, the degeneracy becomes a good measure for evaluating its power factor as shown in Ref. [26]. The higher value of the calculated PF of $\beta$-BaCu$_2$S$_2$ than that of Sr$_2$ScCuSO$_3$ might be due to a large difference of the band width: the band structures for the former compound exhibits a much sharper dispersion as presented in Figs. 2(c) and 9(d).

C. BiCuSeO

BiCuSeO is the most famous thermoelectric materials with CuCh layers, but its electronic structure is rather exceptional. In previous studies, it is shown that the Bi atoms play a crucial role not only in reducing its lattice thermal conductivity, but also in changing the shape of its band structure drastically.

Figure 11(a) shows band structures calculated with SOC, where the black broken and red solid lines present those obtained with the first-principles and tight-binding model calculations, respectively. The blow-up view of the band structure calculated using the tight-binding model is presented in Fig. 11(b), where the Bi orbital weight is shown by color. As is clearly seen, the Bi states are strongly hybridized with the valence-band edge near the $\Gamma$ point. As a result, a peculiar shape of the band structure is realized here. If one hypothetically eliminates the Bi orbitals contribution from the band structure, the valence band structures shown in Fig. 11(c)–(d) are very similar to that for Sr$_2$ScCuChO$_3$.

Calculated PF is shown in Fig. 12, where we also show PF with a hypothetical removal of the Bi orbitals contribution from our tight-binding model. The calculation results with and without SOC are plotted. Here, we neglected the conduction bands in transport calculations.

FIG. 10: Calculated PF of $\beta$-BaCu$_2$S$_2$ for several conditions: a regular calculation and one without $t_z$, with and without SOC. These results are shown using red thick solid (regular calculation without SOC), red thin solid (regular calculation with SOC), blue thick broken (without $t_z$ and without SOC), and blue thin broken lies (without $t_z$ and with SOC), respectively. The relaxation time $\tau=10^{-15}$ second was used.
FIG. 11: (a) Band structures of BiCuSeO calculated with SOC, where the black broken and red solid lines present the first-principles band structure and that obtained by using the tight-binding model consisting of the Wannier functions, respectively. (b) Blow-up view of the band structure calculated using the tight-binding model, where the Bi orbital weight is shown by color. (c) The same band structure calculated with a hypothetical removal of the Bi orbitals contribution. (d) The same plot as panel (c) but calculated without SOC.

FIG. 12: Calculated PF of BiCuSeO for several conditions: a regular calculation and one without the contribution of the Bi orbitals (denoted as ‘w/o Bi’), with and without SOC. These results are shown using red thick solid (regular calculation without SOC), red thin solid (regular calculation with SOC), blue thick broken (without Bi and without SOC), and blue thin broken lines (without Bi and with SOC), respectively. The relaxation time $\tau = 10^{-15}$ second was used.

because GGA is known to underestimate the band gap. Because the experimental direct band gap is about 0.8 eV$^{64}$, we can safely neglect the conduction bands in evaluating PF at 300 K$^{69}$. In Fig. 12, we can verify that the Bi hybridization drastically increases PF$_{max}$ by a factor of three when calculation includes SOC. As seen in Fig. 11(b), the valence-band deformation can yield a large valley degeneracy, the Fermi surface for which was shown in Ref. [67]. This is the origin of the large enhancement of PF while the band dispersion along the $\Gamma$-Z line suggests rather isotropic electronic structure (i.e. no longer flat along the $\Gamma$-Z line), as pointed out by previous studies (e.g. Refs. [65, 67]). On the other hand, the power factor without the Bi hybridization is rather similar to those obtained for Sr$_2$ScCuCh$_3$. In fact, the mass anisotropy $\gamma$ for the band structure shown in Fig. 11(d) is around 4.2, which is not a large value. Therefore, Bi hybridization with the valence-band top is crucial in BiCuSeO to enhance its PF.

D. Zincblende and wurtzite CuCh

We have so far focused on the two-dimensional CuCh layered structures, but how about the three-dimensional network of copper and chalcogen atoms? Zincblende and wurtzite are the most fundamental crystal structures consisting of tetrahedra. Because of such an importance, we investigated zincblende and wurtzite CuCh although they are hypothetical materials. While zincblende and wurtzite CuCh exist as insulators, we adopted CuCh$_3$ as our target to make a fair comparison between these electronic structure and those in other materials with CuCh$_4$.
FIG. 13: First-principles band structures of (a) zincblende CuS, (b) zincblende CuSe, (c) wurtzite CuS, and (d) wurtzite CuSe, respectively, calculated with SOC.

The first-principles band structures of CuS and CuSe have been calculated with SOC. The band structure near the valence top should be called Cu-

The calculated PF with respect to the hole carrier number is shown in Fig. 14. The zero hole carrier number corresponds to the insulating state where all the bands shown in Fig. 13 are filled.
deteriorates them for relatively heavy atoms.

E. \textit{Cu}_2\textit{Sb}_4\textit{S}_13 (tetrahedrite)

Tetrahedrite \textit{Cu}_{12}\textit{Sb}_4\textit{S}_13 has a complex crystal structure as shown in Fig. 1(f), which contains \textit{CuS}_4 tetrahedra together with \textit{CuS}_3 triangles. Here, we considered the crystal structure with a space group \textit{I}4\overline{3}m\textsuperscript{70}. While the lower symmetry phase was reported in low temperature below 88 K by experiments\textsuperscript{71}, we concentrate on the cubic phase to investigate its thermoelectric performance. Figure 15(a) presents the first-principles (black broken lines) and tight-binding (red solid lines) band structures for \textit{Cu}_{12}\textit{Sb}_4\textit{S}_13. We note that the stoichiometric \textit{Cu}_{12}\textit{Sb}_4\textit{S}_13 is metallic. Blow-up views of the first-principles band structures are shown in Fig. 15(b)–(c) without and with SOC, respectively. By looking into the \textit{k}-path between the \textit{H} \((k_x, k_y, k_z) = (2\pi/a, 0, 0)\) and \textit{Γ} points in Fig. 15(b), we can see that there are three quasi-one-dimensional band dispersions and one isotropic band dispersion, the latter of which lies in the valence-band top as indicated by an arrow. Note that there is a two-fold degeneracy for the band dispersion with the heavy effective mass of the quasi-one-dimensional band dispersions along the H-Γ line, in a similar manner to the band dispersions of the zincblende \textit{CuCh} along the L-Γ line. SOC makes the relative energy level of the isotropic band compared with the quasi-one-dimensional bands higher by around 30 meV.

The calculated PF is shown in Fig. 15(d)–(e), with respect to the hole carrier number and the chemical potential, respectively. The zero hole carrier number in Fig. 15(d) corresponds to the insulating state where all the bands shown with the red solid lines in Fig. 15(a) are filled. The obtained PF is not small in spite of the weak anisotropy compared with layered structures in the sense that electrons are mobile along the \textit{z} direction. A good hint to understand this behavior is a chemical potential corresponding to \textit{PF}_\text{max} around 60 or 70 meV, which is shown with blue broken lines in Fig. 15(b)–(c). This is a bit far from the band edge, and so a relatively small splitting between the quasi-one-dimensional and isotropic band dispersions at the \textit{Γ} point might not cause a sizable reduction in PF. In addition, we can also notice that another valley around \textit{Γ} point possibly contributes to PF\textsuperscript{25}. While the basic characteristics of the band structure are similar to that for other materials with \textit{CuCh}_4 tetrahedra, this interesting multiple degeneracy for these complex band structures seems to contribute to enhance PF in this material.

F. Other materials with \textit{CuCh}_4 tetrahedra

One of the other important examples of materials with \textit{CuCh}_4 tetrahedra is \textit{Cu}_2\textit{Ch}, which is known to exhibit a high \textit{ZT}\textsuperscript{72–74} such as 1.5 at 1000 K for \textit{Cu}_2–\textit{Se}\textsuperscript{74}. While we do not investigate this class of material owing to the theoretical complexity including a large sensitivity of its band structure to the calculation methods\textsuperscript{75}, we here point out that its valence band structure near the band edge (e.g. see Ref. [75]) looks similar to that of the hypothetical zincblende \textit{CuCh} shown in our paper because of the similarity in the crystal structure.

IV. CONCLUSION

In this study, we have performed the comparative study on the thermoelectric performance of the materials with \textit{CuCh}_4 tetrahedra. We have found that their electronic band structure is characterized as degenerate low-dimensional electronic structure of the \textit{Cu}-\textit{t}_2g states. In particular, for the materials with the separate \textit{CuCh} layers, the \textit{Cu}-\textit{t}_2g bands are further classified as the quasi-one-dimensional \textit{Cu}-\textit{d}_{xz/yz} and the two-dimensional \textit{Cu}-\textit{d}_{x^2−y^2} states, the degeneracy of which can be crucial to improve their thermoelectric performance while it is sometimes not effective as in \textit{β}-\textit{BaCuS}_2, where the \textit{Cu}-\textit{d}_{z^2} band with a large out-of-plane group velocity and a small in-plane group velocity does not enhance the in-plane power factor. By looking into the important hopping paths for determining the low dimensionality shown in Fig. 3(b)–(c) and 4(b), we can say that the \textit{CuCh} layer can be regarded as a kind of the square lattice both for the \textit{d}-\textit{p} and \textit{p}-\textit{p} networks.

One of the interesting characteristics of \textit{CuCh}_4 tetrahedra is the chalcogen orbitals extended in the void region, which enables relatively distant transfer of electrons. It sometimes forms the hidden chains in layered compounds, which strongly enhances the one-dimensionality of the \textit{d}_{xz/yz} band dispersion, and sometimes induces a strong inter-layer coupling, which alters the valence band structure of \textit{BiCuSeO} and \textit{β}-\textit{BaCuS}_2 and then largely improves the thermoelectric performance for \textit{BiCuSeO}. In other words, the important aspects of the band structures of materials with \textit{CuCh}_4 tetrahedra often originate from the existence of the extended chalcogen orbitals, which sometimes makes the blocking layer rather crucial for thermoelectric performance. In fact, while the \textit{t}_2g band degeneracy looks important for enhancing the power factor of \textit{Sr}_2\textit{ScCuChO}_3, it is not the case for \textit{β}-\textit{BaCuS}_2. In addition, the electronic structure of the \textit{CuSe} layer is largely altered by the \textit{BiO} layer in \textit{BiCuSeO}. Controlling the blocking layer can bring a large modification of the electronic structure in materials with \textit{CuCh} layers.

The large extension of the chalcogen orbitals partially owes to the anisotropic \textit{Cu-Ch} bond geometry of a tetrahedron. This situation reminds us of the concept of a lone-pair electron\textsuperscript{76–78}, which extends into the void space partially by the anisotropic environment. While a crucial role of lone-pair electrons on the structural instability in realizing the low thermal conductivity has been pointed out for several (thermoelectric) materials\textsuperscript{76–78}, it is in-
FIG. 15: (a) Band structures of Cu$_{12}$Sb$_4$S$_{13}$ obtained with SOC, where the black broken and red solid lines present the first-principles calculations and tight-binding models consisting of the Wannier functions, respectively. Blow-up view of the first-principles band structures calculated (b) without and (c) with SOC. The calculated PF (d) with respect to the hole carrier number and (e) with respect to the chemical potential. In panels (d)–(e), Calculation results obtained with and without SOC are shown using thin broken and thick solid lines, respectively. The zero hole carrier number in panel (d) corresponds to the insulating state where all the bands shown with the red solid lines in panel (a) are filled. Chemical potentials that maximize PF in panel (e) are shown in panels (b)–(c) with blue broken lines. The relaxation time $\tau = 10^{-15}$ second was used for panels (d)–(e).

Interesting that the extended electronic states (but not the lone-pair electrons) can also enhance the power factor by altering the electronic band structure. In BiCuSeO, the origin of the alternation of the valence band structure might be interpreted as an interplay of the lone-pair electrons of the Bi atoms and the extended Se orbitals.

Another characteristic of the tetrahedron is the large band splitting by SOC, which might be because of the lack of the inversion symmetry of a tetrahedron. While the power factor is not so much degraded by SOC for Se at room temperature, much higher temperature will be desirable to make the SOC band splitting less deteriorate the power factor by large temperature broadening for materials with heavier atoms such as Te.

Several observation made in this study will be important knowledge not only for designing new thermoelectric materials with Cu$\text{Ch}_4$ tetrahedra but also for investigating the interesting and complicated roles of the extended electronic states on the transport properties of electrons and phonons.

Acknowledgments

We appreciate fruitful discussion with Hiraku Ogino, Koichiro Suekuni, Kunihiro Kihou, and Chul-Ho Lee. This study was supported by JSPS KAKENHI (Grant Nos. JP17H05481 and JP17K14108) and JST CREST (Grant No. JPMJCR16Q6), Japan.

APPENDIX: Powerfactor for degenerate anisotropic bands

In this section, we assume that $k_BT/t_1$ is always fixed. First, we consider the single-band problem with anisotropy. If the band dispersion is given as Eq. (3), the transport coefficients along the $x$ direction read

$$K_{2D,xx}[\mu] = \tau \int dk \ (4t_1^2 \sin^2 k_x)g_{\nu}(2t_1 \cos k_x + 2t_2 \cos k_y - \mu),$$

where

$$g_{\nu}(E) \equiv -\frac{\partial f_0}{\partial E}(\frac{E}{k_B T}) E^\nu.$$  

As described in the main text, the anisotropy $\gamma$ is defined as $\gamma = t_1/t_2$. Suppose that the temperature is sufficiently smaller than $t_1$ and $t_2$ (i.e. $k_BT \ll t_1, t_2$), the transport coefficients are approximately related to those for the isotropic case ($t_2 = t_1$), $K_{2D,iso}^{2D}$, as follows:

$$K_{2D,xx}^{2D,iso}[\mu] \approx \sqrt{\gamma}K_{2D,iso}^{2D}[\mu + 2(t_2 - t_1)],$$

by using $\cos k_y \approx 1 - k_y^2/2$ near the $\Gamma$ point and a transformation $\tilde{k}_y = k_y/\sqrt{\gamma}$. Thus, PF$_{\text{max}}$, which is the maxi-
num value of the power factor with respect to the chemical potential, satisfies
\[
PF^{2D,xx}_{\text{max}} \simeq \sqrt{PF^{2D,\text{iso}}_{\text{max}}}, \quad (16)
\]
In the same manner, we can obtain
\[
PF^{2D,yy}_{\text{max}} \simeq \frac{1}{2} PF^{2D,\text{iso}}_{\text{max}}, \quad (17)
\]
by using \(4t_2^2 \sin^2 k_y \simeq (4t_2^2 \sin^2 k_y)/\gamma\). For the three-dimensional band dispersion, Eq. (4), we can obtain
\[
PF^{3D,xx}_{\text{max}} \simeq \gamma PF^{3D,\text{iso}}_{\text{max}}; \quad (18)
\]
\[
PF^{3D,yy}_{\text{max}} = PF^{3D,zz}_{\text{max}} \simeq PF^{3D,\text{iso}}_{\text{max}}; \quad (19)
\]
Next, we move on to the problem with degenerate two-dimensional anisotropic bands: Eq. (5). Based on the discussion above, we can immediately represent the transport coefficients with degeneracy \(K^{2D, \text{degen}}_{xx,\nu}\) as follows:
\[
K^{2D, \text{degen}}_{xx,\nu}[\mu] \simeq (\sqrt{\gamma} + \frac{1}{\sqrt{\gamma}})K^{2D, \text{iso}}_{xx,\nu}[\mu + 2(t_2 - t_1)], \quad (20)
\]
which yields Eq. (9). As for the three-dimensional band dispersions, Eq. (6), the similar relation, Eq. (11), clearly holds. Therefore, the PF enhancement factors \(\alpha\) defined in Eq. (7) obeys Eq. (12): \(\alpha_{2D} \simeq \alpha_{3D} \simeq 1 + \gamma^{-1}\). For example, the isotropic band dispersion \((\gamma = 1)\) yields a doubled power factor by the two-fold degeneracy. The relations shown in APPENDIX hold only when the assumption we used, i.e., \(k_BT \ll t_1, t_2\), is valid. Therefore, the \(t_2 \to 0\) limit that corresponds to \(\gamma \to 0\) is out of the range for application.

The same consequence is obtained even if one takes other distant $d_{xz/yz}-p_x$ hopping amplitudes into account. This is guaranteed by the mirror symmetry.

Hidden chains on the $Ch$ square lattice discussed here is named after the hidden ladder in the Ruddlesden–Popper compounds, which was recently pointed out to be realized by orbital anisotropy of the $d_{xz/yz}$ orbitals in the bilayer (or trilayer) square lattice and lead to a possible occurrence of high-temperature superconductivity.\(^{58}\)


We verified that the first-principles band structure calculated with the mBJ potential, which is known to give a reasonable band gap, also exhibits a strong hybridization of the Bi states with the valence bands. This trend was also reported in several literatures using various methodologies.\(^{64–68}\)


