A chemical understanding for the band convergence in thermoelectric CoSb₃ skutterudites: influence of electron population, local thermal expansion and bonding interactions

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Abstract

N-type skutterudites, such as Yb_xCo₄Sb₁₂, have recently been shown to exhibit high valley degeneracy with possible band convergence, explaining the excellent thermoelectric efficiency in these materials. Using a combined theoretical and experimental approach involving temperature-dependent synchrotron diffraction, molecular orbital diagrams and computational studies, the chemical nature of critical features in the band structure are highlighted. We identify how n-type doping on the filler site induces structural changes that are observed in both the diffraction data and computational results. Additionally, we show how chemical n-type doping slightly alters the electronic band structure moving the high valley degeneracy secondary conduction band closer to the primary conduction band and thus inducing band convergence.

1. Introduction

Engineering the electronic band structure of a material is an effective method for improving thermoelectric efficiency, as it increases the band degeneracy near the Fermi level, which is directly proportional to the quality factor of thermoelectric materials¹⁻⁴. For instance, in PbTe and SnTe materials the two valence bands converge at higher temperatures, which significantly increases the power factor and ultimately the zT . The convergence of these bands occurs because of an increasing off-centering displacement of Pb with temperature⁵, leading to a decreasing lone-pair s^2 dominated valence band⁶. The possibility of changing band convergence behavior through replacing Pb with non-lone-pair containing elements shows how important the local chemical bonding environment is in a thermoelectric material⁷⁻¹⁰. Further examples for the influence of crystal chemistry on the electronic bands and band convergence has been shown for chalcopyrites, Mg_2Sn and have even been predicted for Zintl phases^{2,11-14}. As the band convergence in these materials has shown, a materials band structure is deeply linked to the underlying nature of its chemical bonds. Therefore, changing bonding interactions is the most effective approach at engineering the band degeneracy of thermoelectric materials.

Skutterudite $CoSb_3$ is a well-known thermoelectric material, but only recently has it been shown that, when heavily doped¹⁵, it exhibits a complex Fermi surface with multiple valleys. Indeed, the extraordinary electronic properties of n -type thermoelectric $CoSb_3$ originates from the presence of a multi-valley secondary conduction band (CB_2) located between the Γ and N points, which is somewhat higher in energy compared to the primary, Γ -point conduction band (CB_1). For highly doped samples and at elevated temperatures ($\sim 700K$), CB_2 appears to contribute substantially to the thermoelectric performance possibly even converging with (having the same energy as) the primary conduction band at Γ .

Inspired by the underlying chemical reasons for band convergence in PbTe, in this study we aim to understand the observed band convergence in $CoSb_3$ from a chemical point of view. In this work, we use a combination of temperature dependent synchrotron diffraction and density functional theory calculations, in which the obtained structural data is used as an input for the theoretical calculations. The diffraction data reveals

differences in the coefficient of thermal expansion of local bonds within the structure (*local*-CTE). These structural parameters are employed in the calculations to assess changes in the band structure due to structural changes. These experimental and computational efforts identify the chemical nature of the primary (CB_1) and secondary (CB_2) conduction bands. We then show both experimentally and computationally how Yb doping changes the CoSb_3 structure beyond simple lattice expansion. Furthermore, a slight structure change observed with increasing Fermi level demonstrates a coupling of these conduction band states to the atom positions. It is also shown that this increase in Fermi level induces band convergence in CoSb_3 at room temperature and above. Here, we show that band convergence can be chemically induced through population of conduction band states not expected from a rigid band model.

2. Experimental and Computational Methods

The combined experimental and computational approach is described in detail below. Synthesis of the samples was performed using the method given by Tang *et al.*¹⁵

Powder Diffraction. X-ray powder diffraction was conducted at Argonne National Lab Advanced Photon Source (APS) on the designated powder diffraction beam line; 11-BM. Standard Debye-Scherrer geometry with a 1D detector was used for the experiment and the calibrated X-ray wavelength was 0.414208 Å. An $\text{Al}_2\text{O}_3/\text{Si}$ reference sample was used for alignment and an instrument parameter file was obtained using a LaB_6 standard (specifics about profile parameters are given below in the refinement section). Sample absorption was calculated using the ABSORB web utility¹⁷ (which uses the Cromer & Liberman algorithm to compute X-ray scattering cross sections¹⁸). After optimizing the absorption factor, quartz capillary diameters of 0.4 mm and 0.3 mm were used for powder samples of CoSb_3 and $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}$, respectively (no diluting media was necessary). The same anomalous scattering parameters, f' and f'' , used for the absorption calculation were also used in the Rietveld refinements. Room temperature scans of both samples were conducted using a high-speed sample spinner (~90 Hz). High temperature scans from 100 °C to 500 °C with 100 °C steps were conducted using the Cyberstar hot air blower with its corresponding sample spinner (~20Hz). A typical intensity for the

primary diffraction peak was ~300,000 counts for the 300 K scans and ~200,000 counts for the scans at elevated temperature, confirming the quality of the data.

Refinements. To examine structural changes of CoSb₃ with temperature and doping, Rietveld refinements were conducted on the temperature dependent, high-resolution, powder diffraction data of filled and unfilled CoSb₃. Refinements were conducted using the General Structure Analysis System (GSAS^{19,20}) for CoSb₃ in the Im $\bar{3}$ space group with Co atoms at (0.25, 0.25, 0.25), and Sb atoms at (0, *y*, *z*). In this representation, the filler atom is located at (0, 0, 0). Note that the origin in *Figure 1* is shifted to effectively show both Sb-Sb long and short bonds in one figure. LaB₆ powder was used to construct an instrument parameter file and a pseudo-Voigt peak profile was used (CW profile function 3 in GSAS). The peak profile parameters from this LaB₆ parameter file were fixed throughout the refinement procedure until the last refinement step in which all refinement parameters were unfixed and refined together. To account for peak anisotropy seen in the Yb_{0.3}Co₄Sb₁₂ sample, anisotropic peak broadening parameters were included through the γ -profile function (L11, L22, etc. parameters in GSAS) in these refinements. Refinements of Yb_{0.3}Co₄Sb₁₂ without the anisotropic profile parameters were also conducted and the same trends were concluded for structural changes with temperature and doping, however the peak positions were more accurately represented when anisotropic profile parameters were included and these results are reported here. In all diffraction histograms, the electron density on the Co site (0.25, 0.25, 0.25) was slightly larger relative to that on the Sb site (0, *y*, *z*). Several defect mechanisms were tested and statistically equivalent refinements were achieved for anti-site disorder of Sb on the Co site as well as Sb vacancies. As Sb vacancies would introduce electrons, and since the undoped samples are slightly n-type¹⁵, a slight Sb deficiency is assumed. To include Sb vacancies in the refinement, the Co occupancy was set to 100% and the Sb occupancy was refined along with the scaling parameter. Note that a high frequency sample spinner was used for the room temperature scans resulting in better counting statistics than the scans at elevated temperatures in which a lower frequency sample spinner was used. This is reflected in the refinement statistics, in which the room temperature refinements have a higher χ^2 due to better counting statistics. Refinement uncertainties are given in the

tabulated diffraction data in the Supporting Information and the experimental uncertainty of the lattice parameters of beam line 11-BM is 0.0001 Å.

Computational methods. Density-functional theory (DFT) calculations for both doped and undoped CoSb₃ were conducted to determine how changes in structure and Fermi level will affect the electronic band structure.

We performed all DFT calculations as implemented in the Vienna *ab initio* simulation package (VASP) code. The projector-augmented wave (PAW) method²¹ with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional were used for calculations on the primitive unit cell and the Yb-doped supercell²². The unit cell structure was fully relaxed with a plane wave cutoff energy of 550 eV with a Gamma centered 7x7x7 Monkhorst-Pack uniform *k*-point reciprocal space sampling. The 0.01 eV/Å Hellmann-Feynman forces were adopted for geometry optimization. The optimized lattice parameter is found to be 9.11 Å, which is consistent with the previous theoretical value of 9.115 Å using PBE²³, and the internal parameters $u=0.3333$, $v=0.1595$. The calculated direct band gap of CoSb₃ is 0.1665 eV, which agrees well with the gap of 0.17 eV reported earlier²⁴. Sofo *et al.* reported a slightly higher value of 0.22 eV²⁵. After our calculations of the fully relaxed CoSb₃ were validated with previous calculations and literature values, a systematic study on how crystal structure and doping effect the band structure was conducted.

The structural parameters of CoSb₃ and Yb_{0.3}Co₄Sb₁₂ from 300 to 800 K, as determined via synchrotron diffraction, were used to calculate band structures. In this way, a '0 K' calculation is conducted with structural parameters set to their values at a given temperature (300 to 800 K) and we refer to this, here, as the band structure at that specific temperature. This method neglects the contribution of lattice vibrations, meaning that the computations with temperature only probe the influence of structure change on the band structure. In reality, there is an additional contribution from lattice vibrations through electron-phonon interactions (e.g. see Figure 1 of Gibbs *et. al.*²⁶). The room temperature band gap of CoSb₃ calculated by this method is 0.1625 eV, which agrees with room temperature optical absorption measurements¹⁵.

Here, all calculations of Yb-doped CoSb₃ were performed in a 2x2x2 supercell which contains 130 atoms. The chemical composition of this supercell is Yb_{0.25}Co₄Sb₁₂. The nominal composition of the doped CoSb₃ is Yb_{0.3}Co₄Sb₁₂ and the occupancy from refinements show that the Yb content is slightly lower than the nominal content, suggesting that this composition is close to that observed experimentally¹⁵. Again, the atomic positions were fixed to that measured from synchrotron diffraction. Typically, the atomic positions are relaxed in supercell calculations as the positions near an impurity atom will be different than the atomic positions away from one. Synchrotron diffraction and Rietveld analysis give a spatial average of the atomic positions. Because of this, fixing the atomic positions to the spatial average may be unphysical and skew the computational results. DFT calculations, where the lattice parameter was set and the ion-positions are relaxed, were conducted to ensure that the observed trends were not artifacts of the method in which the supercell calculations were conducted. Additionally, calculations in which the Fermi level was intentionally shifted were conducted to deduce how changing the carrier concentration will affect the band structure (summary provided in Supplemental Information) in addition to the calculations discussed in Section 3.2. This was achieved by manually increasing the number of electrons of CoSb₃, as well as conducting charged impurity calculations where Yb_i²⁺ was included and compared to the calculation with Yb_i⁰. A compensating background charge was included, in these, to prevent divergence of the total energy of the charged system.

The COHP were generated by transferring the PAW wave functions to properly chosen local basis with Local Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) code²⁷, and the band unfolding procedure for Yb-doped CoSb₃ supercell was performed using the BandUP code²⁸.

3. Results and Discussion

3.1 Temperature dependent structural changes in CoSb₃

Figure 1 shows a structural representation of a filled CoSb₃ skutterudite. For a more in-depth structural discussion, the reader is referred to a review by Uher²⁹. In brief, in CoSb₃ Sb forms polyanionic Sb₄ rings. Using a Zintl description, each Sb has a formal charge of

-1 forming two covalent bonds and giving the ring a formal charge of Sb_4^{4-} . The Sb_4 ring itself is not necessarily a square, having two longer and two shorter bonds of a rectangle. The remaining two Sb lone pairs coordinate to Co^{3+} to form CoSb_6 octahedra. These octahedra either share their vertices via one Sb atom or via one bond of the Sb_4 ring.

Figure 1: (a) Structural representation of Yb-filled CoSb_3 (shown with the origin shifted by $-\frac{1}{4}[111]$) with Co in blue, Sb atoms in gold, and Yb atoms (filler) in light blue. Sb forms Sb_4 rings that coordinate to Co. (b) Structural motif of CoSb_3 . Two octahedra share either one Sb or an edge of an Sb-Sb ring. Star labeled atoms represent the motif (b) in context within the structure (a).

The skutterudite structure can be completely defined by its lattice parameter, a , and the position of the Sb atom $(0, y, z)$. The different bond lengths illustrated in Figure 1a are then given as

$$d(\text{Co} - \text{Sb}) = a \left[\left(\frac{1}{4} \right)^2 + \left(y - \left(\frac{1}{4} \right) \right)^2 + \left(z - \left(\frac{1}{4} \right) \right)^2 \right]^{\frac{1}{2}}, \quad \text{Eq. 1}$$

$$d_1(\text{Sb} - \text{Sb}) = 2az, \quad \text{Eq. 2}$$

$$d_2(\text{Sb} - \text{Sb}) = a(1 - 2y), \quad \text{Eq. 3}$$

with d being the Co-Sb bond, d_1 the Sb-Sb short bond, and d_2 the Sb-Sb long bond²⁹. As mentioned above, the Sb_4 ring contains two bond lengths given by Eq. 2 and Eq. 3 and a fixed bond angle of 90° . When $d_2 = d_1$ the *Oftedal relation* of $y + z = 0.5$ is met (named

after the discoverer of the structure³⁰), the ring is a perfect square. In addition, the CoSb₆ octahedra do not exhibit perfect O_h symmetry either. All bond lengths are equal but the bond angles are distorted from 90°. One of the most defining characteristics of this structure is the large cage centered at (0,0,0). This interstitial site is commonly referred to as the filler site and can be used to for chemical doping. The solubility limit of doping atoms on this filler site can be a limiting factor when optimizing the chemical potential of thermoelectrics, and it was recently highlighted that this solubility limit is temperature and composition dependent^{31,32}. Interstitial doping atoms are weakly bonded to the cage structure and much effort has been devoted to understanding how lattice dynamics of this *rattling* atom affect the thermal properties of filled skutterudites^{33–35}.

Figure 2: Exemplary refinement of (a) CoSb₃ and (b) Yb_{0.3}Co₄Sb₁₂ at 300 K with the corresponding profile residuals. The black circles are the experimental data, the red line is the calculated histogram, and the line below is the difference profile between the observed and calculated values. The insets show a zoomed in view on high angle reflections and the high quality fit of the refinement at the corresponding low d -spacing.

Thermal expansion effects. In this work, temperature dependent synchrotron X-ray diffraction has been performed to study the structural evolution of Yb filled and unfilled CoSb_3 at higher temperatures. Exemplary results obtained via Rietveld refinements of the synchrotron data for both CoSb_3 and $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}$ at 300 K can be found in *Figure 2*. The samples are all phase pure and good profile residuals can be obtained, indicating a high quality of the fit. All the relevant temperature dependent refinement data is tabulated in Table S1 and S2.

*Figure 3: Temperature dependent lattice parameter of CoSb_3 obtained from the Rietveld refinements, showing the positive thermal expansion of the unit cell. Introduction of the filler atom further increases the unit cell. For comparison, data for increasing amounts of Yb are shown from Tang *et al.*³². Literature data from Ohno *et al.*³⁶ show that the linear temperature dependence of a in CoSb_3 is maintained down to 10 K.*

Figure 3 shows the refined lattice parameter of CoSb_3 , which increases linearly with increasing temperature. Introduction of the filler atom further increases the lattice and corresponds well with the expectation of Vegard's law within a CoSb_3 system, in which an increasing Yb content increases the lattice parameter linearly³². *Figure 4* shows the changes of the structural motif with increasing temperature. The y and z positions of Sb change with temperature (see Supporting Information), resulting in an increasing octahedral angle shifting towards a more symmetric regular O_h symmetry (*Figure 4a*). While the octahedra become more symmetric (90° angle), the increasing temperature drives the Sb_4 ring away from a square towards a more rectangular arrangement (*Figure*

4b). In addition to the temperature effects, the filler atom itself changes these relations. Filling the structure partially with Yb increases the octahedral distortion and increases the $(y + z)$ relation towards a perfect square arrangement of the Sb_4 ring. Similar effects of substitution induced changing of bond angles have recently been reported in the YbZn_2Sb_2 Zintl phases³⁷.

Figure 4: Changes in the CoSb_6 octahedral angle (a) and the Octedal relation (b) with temperature. With increasing temperature, the structure shifts towards a more symmetric octahedron and away from a perfect square. Note that the doping with a filler atom leads to a distortion of the octahedral away from a symmetric 90° angle and a more square Sb_4 ring arrangement.

The atomic displacement parameters, $\langle u^2 \rangle$, obtained (Table S1 and S2) agree with what has been previously reported for CoSb_3 ³⁸, and other filled skutterudites³⁹. The Yb atom has significantly larger values for $\langle u^2 \rangle$ than the Co and Sb atoms, which has been cited as evidence of the rattling nature of the Yb atom on this cage site⁴⁰. The temperature dependence of $\langle u^2 \rangle$ gave an Einstein temperature for this localized mode of $\theta_E = 65(5)$ K, which is similar to Yb in $\text{YbFe}_4\text{Sb}_{12}$ ⁴¹.

Figure 5: Temperature dependence of the Co-Sb (c) and Sb-Sb bond lengths (a) and (b). Lines correspond to linear fits used to calculate the local thermal expansion coefficient α_{300K}^L . Literature values from Ohno *et al.*³⁶ are shown by triangles, showing the good fit of the data with literature values at room temperature and at 10K. While all bonds expand with increasing temperature in the undoped CoSb₃, the longer bond exhibits a larger slope and faster thermal expansion. Substitution with the filler atom increases the bond lengths as well. d) Temperature dependence of the octahedral volume, showing the linear thermal expansion of the CoSb₆ octahedra.

Local thermal expansion coefficients. The changing Sb positions clearly affect the *Oftedal relation*, therefore the local chemical bonds, especially the Sb-Sb bonds within the Sb₄ ring, must be changing as well. Figure 5 shows the temperature dependent evolution of the different bond lengths; the Co-Sb bond and the short and long Sb-Sb bonds, d_1 and d_2 , respectively. At room temperature, the results correspond well with the structural data by Ohno *et al.*³⁶ While all bond lengths increase with temperature, as expected due to thermal expansion, differences in the slopes between the different bonds can be detected. In addition, differences in the bond lengths of the substituted samples

can be seen as well. To assess these differences, the coefficient of thermal expansion (CTE) is calculated for each bond separately and is treated as a linear expansion coefficient defined as

$$\alpha_{300K}^L = \frac{\Delta l}{\Delta T} \frac{1}{l_{300K}}, \quad \text{Eq. 4}$$

where Δl is the change in length, ΔT is the change in temperature, and l_{300K} is the length at 300 K. For a better understanding of the changes we will define α_{300K}^L for bond lengths as a *local*-CTE and the evolution of the lattice parameter as CTE. Temperature dependence ($\Delta l/\Delta T$) of the obtained structural parameters were successfully fit, giving α_{300K}^L through Eq. 4 and are shown in *Figure 5*. The values for the CTE and the *local*-CTE are tabulated in *Table 1*. The obtained values of the thermal expansion coefficients of the unit cell correspond well with other literature values. For instance, Rogl *et al.*⁴² measured a CTE of CoSb_3 to be $9.1 \times 10^{-6} \text{ K}^{-1}$ via dilatometer measurements agreeing with our value in *Table 1*.

Table 1: Linear thermal expansion coefficients of the Sb-Sb, Co-Sb and Yb-Sb bonds in unfilled and filled skutterudite (normalized to the bond lengths at 300 K).

Structural parameter	$\alpha_{300K}^L (10^{-6} \text{ K}^{-1})$	
	CoSb_3	$\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}$
Lattice parameter, a	9.9	10.5
Sb-Sb long (d_2)	15.6	15.9
Sb-Sb short (d_1)	8.6	12.6
Co-Sb (d)	9.2	9.1
Yb-Sb	-	8.6

Figure 5 and *Table 1* show that the *local*-CTE (α_{300K}^L) of the long Sb-Sb bond in CoSb_3 is significantly larger than that of the Co-Sb and the short Sb-Sb bond. In other words, with increasing temperature the long Sb-Sb bond (d_2) expands much faster than the other two bonds. This faster increase of bond length of d_2 and the corresponding

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3 slower increase of the short Sb-Sb bond (d_I) leads to the observed behavior of a structural
4 shift towards a more rectangular Sb₄ ring.
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7 Upon doping of CoSb₃ with Yb, the α_{300K}^L of the Sb-Sb short bond increases by nearly
8 50% while the α_{300K}^L for the Co-Sb and the Sb-Sb long bond remains essentially
9 unchanged (*Figure 5a*). In addition, the length of the short Sb-Sb bond is significantly
10 increased upon doping, while the length of Co-Sb bond is only slightly increased and that
11 of the long Sb-Sb bond remains unchanged (see *Figure 5*). The size of the filler atom and
12 the resulting change in lattice parameter cannot account for the different changes of the
13 local bonding nature, as a typical Vegard behavior is supposed to change the lattice and
14 the atomic positions in a similar manner. These data clearly show the qualitative
15 differences in the chemical nature of the two Sb-Sb bonds in CoSb₃. Differences of these
16 two chemical bonds has already been reported by Ohno *et al.*³⁶ using the maximum
17 entropy method to reveal differences in the electron density between the Sb-Sb long and
18 Sb-Sb short bonds. The electron density between the short bond was larger (by about
19 30%) than that between the long bond. This agrees well with the data presented here; less
20 electron density results in a weaker bond, which should have a larger thermal expansion
21 coefficient than a bond with more electron density between the atoms. In addition,
22 calculations via density functional theory on the CoSb₃ lattice under strain showed that
23 the Sb-Sb long bond was the first to break under a shear stress, which also support these
24 experimental results²³. From these structural data one may speculate the reason for the
25 differences in the *local*-CTE behavior between the doped and undoped CoSb₃. The filler
26 atom leads to an elongation of the short Sb-Sb bond and hence less bonding interaction
27 and lower bond order⁴⁷ for the Sb-Sb bond (see *Figure 5*) and with it a much faster
28 thermal expansion similar to the long Sb-Sb bond.
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31 The differences in the bonds local thermal expansion coefficients as well as the
32 differently affected bond length after substitution with the filler atom are somewhat
33 unexpected results. To provide an explanation, we will consider the inherent bonding
34 interactions using a molecular orbital theory approach and the changes in the electronic
35 band structure are examined via density functional theory.
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3.2 Band structure of doped and undoped CoSb₃

A chemical understanding of the electronic band structure. As recently shown for Zintl compounds⁴³, a combined approach using molecular orbital (MO) diagrams and density function theory can help gain a better understanding of the underlying chemical nature of the bands and how changes in structure and Fermi level may affect the bonding and electronic band situation. To interpret the observed thermal expansion behavior, we first attempt to understand the bonding qualitatively using a molecular orbital approach to determine the character of the valence and conduction bands. We then compare these conclusions to Crystal Orbital Hamilton Population (COHP) and density of states calculations.

Figure 6: In all panels, blue corresponds to contributions from Co and orange to contributions from Sb. a) Molecular orbital diagrams of the CoSb₆ octahedron and the Sb₄ ring. Atomic orbitals are not shown for the Sb₄ ring. The octahedral crystal field splitting is visible and gives, in combination with the bonding, anti-bonding separation of the Sb-Sb bonds the band gap. b) Crystal Orbital Hamilton Population (COHP) calculated from the DFT data shown in Figure 7a, showing the bonding nature of the Sb-Sb bonds in the valence bands and Sb-Sb anti-bonding states in the conduction band. The Co-Sb bonds in the valence band are predominantly non-bonding (t_{2g}) in nature, whereas the conduction band has anti-bonding Co-Sb contributions. c) Schematic DOS estimated from MO diagrams in (a). d) Partial, atom projected DOS calculated from DFT data shown in Figure 7a.

Figure 6a shows the molecular orbitals for a CoSb₆ octahedron in which the Sb lone pairs of the Sb₄ ring coordinate to Co³⁺ forming an octahedral crystal field. The molecular orbital shows the octahedral crystal field splitting between the t_{2g} and e_g

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3 orbitals. Co^{3+} exhibits six d -electrons (d^6 configuration) and therefore, the filled non-
4 bonding t_{2g} orbitals express themselves as heavy states in the density of states of the
5 valence band.⁴³ The filled deeper energy levels (a_{1g} , t_{1u} and e_g) in the valence band are of
6 bonding nature and the empty anti-bonding states form the conduction band, with e_g^*
7 representing the conduction band minimum⁴⁴. *Figure 6b* shows the COHP of the different
8 bonds and confirms the nature of low lying bonding Co-Sb states, the non-bonding t_{2g}
9 closer to the valence band maximum and anti-bonding states at the conduction band edge.
10 *Figure 6a* shows the molecular orbital diagram of a hypothetical Sb^{-1} – Sb^{-1} 4-member ring
11 in D_{4h} symmetry (square arrangement), with the electronic configuration of a Sb with two
12 bonds, *i.e.* valence of -1 using Zintl valence counting.
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21 This molecular orbital diagram represents an oversimplification of the real electronic
22 arrangement; for one the Sb_4 ring is rectangular and therefore D_{2h} symmetry and also a
23 rigorous description of the molecular orbitals of the Sb_4^{4-} unit would need to account for
24 all 4 states/atom not only the two shown here. For simplicity, we have chosen this single
25 Sb-Sb bond in which the symmetry of the square and the corresponding electronic energy
26 levels⁴⁵, as well as the electron count for Sb^{-1} with two bonds and two lone pairs
27 incorporated. A deeper discussion regarding the contribution of the polyanionic ring to
28 the skutterudite band structure, as well as a full tight-binding calculation, can be found in
29 reference⁴⁶. For a more in depth discussion on the bands and energetic configurations in
30 solids with square arrangements, the reader is referred to Tremel and Hoffmann⁴⁵. While
31 the difference in symmetry between D_{4h} to D_{2h} will shift (and potentially split) the energy
32 levels, the qualitative nature of the bonding states in the valence and anti-bonding states
33 in the conduction band will be unaltered as can be seen in the COHP. In brief, the Sb-Sb
34 bonding arrangement will result in bands with square-ring bonding character at the top of
35 the valence band and bands with square-ring anti-bonding character near, but not exactly
36 at, the bottom of the conduction band.
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49 While the s and p_z orbitals of Sb^{-1} can mix with the s , p_z , d_{z^2} and $d_{x^2-y^2}$ of the metal at
50 the Γ point (*i.e.* the lone pairs coordinate to Co to form CoSb_6 octahedra) the bonding
51 orbitals of the Sb_4 ring cannot significantly mix with the CoSb_6 octahedron as they do not
52 have the correct topology with the Co $3d$ -orbitals in the D_{3d} point group^{45,46}. In other
53 words, at the Γ point we can neglect the interaction of the Sb_4^{4-} ring molecular orbitals
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with the CoSb_6 octahedron and the electronic structure of Sb_4^{4-} will superimpose on top of this CoSb_6 molecular orbital diagram. The bonding states of the Sb_4 ring are at a similar energy level as the t_{2g} nonbonding orbitals of Co character requiring DFT calculations to place them in the correct order. This makes the valence band edge of CoSb_3 primarily Sb-Sb bonding character. The Sb_4 anti-bonding states are located slightly above the e_g^* anti-bonding states of Co character, as confirmed by the calculated partial density of states (*Figure 6d*). Following this, we conclude that the primary conduction band CB_Γ can be attributed to the Co-Sb anti-bonding states, as has previously been established by Luo *et al.*⁴⁴. The secondary conduction band, CB_2 , could then be of Sb-Sb anti-bonding character.

Band convergence with n-type doping. Using the structural data of Section 3.1, the electronic band structures were calculated and the results at 300 K are given in *Figure 7*. Results at higher temperatures are shown in *Figure S3* and reveal how lattice expansion influences the band structure (neglecting lattice vibrations and the electron-phonon interaction). The band structure shows a direct band gap at the Γ point and an additional secondary conduction band (CB_2) at higher energies. The extraordinary thermoelectric properties of n-type filled CoSb_3 have recently been attributed to contributions from this secondary conduction band. At higher temperatures and when n-type doped, carrier transport seems to occur in both bands, resulting in a higher valley degeneracy and higher thermopower¹⁵. An understanding of the chemical nature of the bands and how they change with temperature and chemical doping are of critical importance when optimizing n-type CoSb_3 . To elucidate the effect of the doping on the CoSb_3 band structure, DFT calculations were conducted on supercell structures with Yb atoms included on the filler site representing a composition of $\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12}$.

Because the calculations were conducted on supercell structures the Brillouin zone size was reduced, resulting in a folding of the bands. To compare these band structures to that of undoped CoSb_3 (primitive cell), the band structures were unfolded and are shown in *Figure 7b* (effective primitive cell band structure). The two conduction bands become closer in energy with Yb doping as observed in *Figure 7*, where by aligning energy scales at the bottom of CB_Γ , a decrease in the energy of the band offset ($\text{CB}_2 - \text{CB}_\Gamma$) is shown. This band convergence was also observed in the calculations of Shi *et al.*¹⁶ in which a

different, higher conduction band (at Γ in the supercell), was highlighted as opposed to the CB_2 discussed here. It can also be seen that the Fermi level is increased to just above the CB_2 minimum, confirming the contribution of this band to electrical transport in n -type doped $CoSb_3$. The band between the Γ and P point also moves quickly upon the addition of filler atoms,¹⁶ which is associated with the movement of the CB_2 and addition of Yb.

Figure 7: a) Calculated band structure of undoped $CoSb_3$ at 300 K with the relevant band extrema labeled. The valence band maximum and conduction band minimum are at the Γ point (3-fold degenerate), making $CoSb_3$ a direct band gap semiconductor. At higher energies, there is a second conduction band with 12 carrier pockets (CB_2). b) Effective primitive cell band structure of Yb-doped $CoSb_3$ calculated using a supercell (with fixed structural parameters). Dashed lines and color-coded arrows are guides to the eye, showing that in the doped structure the conduction bands are shifted compared to the undoped $E(k)$. The scale bar represents the weighting function.

In these calculations, the introduction of Yb on the filler cage site can influence the band structure in several ways. When introduced, the Yb atom will simultaneously change the potential field set by the nuclei of the lattice (lattice potential effect) and increase the number of electrons in the system (carrier density effect). Therefore, to truly know the origin of band convergence, one needs to determine which of these effects is most responsible for the changes in band structure observed from Figure 7a to Figure 7b, namely the decrease of $(CB_2 - CB_\Gamma)$. To achieve this, an additional calculation was

conducted on CoSb₃ with additional electrons introduced to simulate the electrons donated with Yb doping, but without the associated change in the lattice potential field.

The result of this calculation is shown in *Table 2*, and reveals that a decrease in ($CB_2 - CB_F$), an increase in E_g , and a slight increase of the Sb-Sb short bond all occur when the Fermi level is increased. Charged impurity calculations of Yb_{0.25}Co₄Sb₁₂ with Yb_i²⁺ on the interstitial site, simulating a removal of the conduction electrons donated by Yb, show similar trends. In *Table 2* CoSb₃: doped refers to the addition of four electrons (per 2x2x2 supercell) and Yb_{0.25}Co₄Sb₁₂: doped refers to Yb_i⁰ as the interstitial defect, undoped refers to Yb_i²⁺. The position-relaxed calculations show that upon doping with Yb, Sb-Sb short and Co-Sb bonds increase while the Sb-Sb long bond is essentially unchanged, agreeing with the diffraction data (see *Figure 5*). Through this analysis, we suggest that the filler atom changes the local structure leading to changes in bonding interactions resulting in what may have been unexpected trends in bond lengths and *local*-CTE, as discussed above. Additionally, the slight change in crystal structure with increased E_f demonstrates a coupling of it with these electronic states.

While the addition of Yb leads to the observed structural changes and with it changes in the band structure, the increasing Fermi level due to a donation of electrons into the conduction band and occupation of anti-bonding states (see *Figure 6*) further lowers the secondary energy gap ($CB_2 - CB_F$). These results suggest that band convergence in n-type CoSb₃ can be induced by increasing the *carrier density*, and therefore should happen with all types of n-type dopants (e.g. other rare earth fillers, alkaline earth and alkali metal fillers, as well as Te or Ni doping).

Tang *et al.*¹⁵ constructed a three-band model within the rigid band approximation, with a band offset of ($CB_2 - CB_F$) = 0.8 eV, which is between the values we obtained for CoSb₃ and Yb_{0.25}Co₄Sb₁₂. This model successfully predicted the experimentally observed change in density of states effective mass (obtained via Seebeck measurements). The change in ($CB_2 - CB_F$) observed here is a higher order effect that would not alter the qualitative conclusions of Tang.

Simply stated, Yb doping induces structural changes and increases carrier density populating anti-bonding states both of which affect the electronic band structure. This mechanism for obtaining band convergence is different than other approaches in

thermoelectric materials, such as changing band dispersion in $\text{PbTe}^{2,7,9,10}$, and has not been observed before.

Table 2: DFT calculations with different Fermi levels, and computational parameters. Similar changes in the band structure and structural parameters are observed with ‘doping’ regardless of computational method. * Indicates that this calculation is shown in Figure 7. † Indicates that the values are average bond distances within the supercell.

Description				Band structure		Structural parameters		
Composition	doped/ undoped	<i>a</i>	positions	E_g (eV)	$CB_2 - CB_\Gamma$ (eV)	Sb-Sb short (Å)	Sb-Sb long (Å)	Co-Sb (Å)
CoSb_3^*	undoped	fixed	fixed	0.163	0.089	2.854	2.983	2.527
CoSb_3	doped	fixed	fixed	0.215	0.077	2.854	2.983	2.527
CoSb_3	undoped	fixed	relaxed	0.242	0.105	2.882	3.014	2.518
CoSb_3	doped	fixed	relaxed	0.292	0.093	2.884	3.013	2.518
$\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12}^*$	doped	fixed	fixed	0.191	0.050	2.866	2.984	2.533
$\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12}$	undoped	fixed	relaxed	0.221	0.088	2.898 [†]	3.012 [†]	2.524 [†]
$\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12}$	doped	fixed	relaxed	0.272	0.075	2.900 [†]	3.012 [†]	2.523 [†]

4. Conclusion

The thermal expansion behavior of bonds (*local*-CTE) within Yb-filled and unfilled CoSb_3 has been studied with temperature-dependent synchrotron diffraction, revealing a difference in the chemical nature of the Sb-Sb long and short bonds. Specifically, the Sb-Sb long bond is found to have a significantly larger thermal expansion than the Sb-Sb short, and Co-Sb bonds. By combining these structural results with systematic density functional theory calculations and molecular orbital diagrams, the chemical nature of band structure features was determined. It was identified that upon n-type doping, the charge carriers introduced populate anti-bonding states and change the electronic structure, leading to band convergence at room temperature in electron doped CoSb_3 . Computational results on Yb-doped CoSb_3 agree with diffraction data showing that occupying the filler site changes the local structure in addition to simple lattice expansion. This work shows that the introduction of charge carriers, from presumably any n-type dopant, can influence the electronic structure and lead to band convergence.

We show the importance of combining accurate structure determination with systematic density functional theory calculations to understand band convergence and

structural changes in thermoelectric materials. This combined approach is a powerful tool that can provide new strategies and approaches in optimizing energy materials.

ASSOCIATED CONTENT

Supporting Information

Tables of the refined temperature dependent structural parameters and refinement statistics, obtained from Rietveld refinements against synchrotron diffraction data, their corresponding diffraction pattern as well as the resulting calculated band structures at different temperatures can be found here. Furthermore, comparisons of bond lengths calculated with the Yb dopant with and without electrons added, as well a comparison of calculated band offsets are given. The temperature dependence of the band gap and band offset is given as well as information about the thermal expansion behavior and Einstein temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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