Unraveling the origins of conduction band valley degeneracies in Mg$_2$Si$_{1-x}$Sn$_x$ thermoelectrics

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To better understand the thermoelectric efficiency of the Mg-based thermoelectrics, using hybrid density-functional theory, we study the microscopic origins of valley degeneracies in the conduction band of the solid solution Mg$_2$Si$_{1-x}$Sn$_x$, and its constituent components – namely, Mg$_2$Si and Mg$_2$Sn. In the solid solution of Mg$_2$Si$_{1-x}$Sn$_x$, the sublattices are expected to undergo either tensile or compressive strain in the light of Vegard’s law. Interestingly, we find both tensile strain of Mg$_2$Si and compressive strain of Mg$_2$Sn enhance the conduction band valley degeneracy. We suggest that the optimal sublattice strain as one of the origins of the enhanced Seebeck coefficient in the Mg$_2$Si$_{1-x}$Sn$_x$ system. In order to visualize the enhanced band valley degeneracy at elevated temperatures, the ground state eigenvalues and weights are projected by convolution functions that account for high temperature effects. Our results provide theoretical evidences for the role of sublattice strain in the band valley degeneracy observed in Mg$_2$Si$_{1-x}$Sn$_x$.

Recently, an interesting observation reported for Mg$_2$Si$_{1-x}$Sn$_x$ (MSS) solid solution compounds was explained on this basis.\cite{2} MSS alloys consist of Mg$_2$Si and Mg$_2$Sn, which are widely available, non-toxic, and cheap materials. MSSs share an optimal operational temperature range with PbTe thermoelectric materials (which is very efficient for power-generation at high temperatures), which makes it an attractive potential replacement material for PbTe composites when the toxicity of Pb, and the scarcity of Te, become an issue in conventional thermoelectric applications.

A significant enhancement in $ZT$ of MSSs by alloying an optimal proportion of Mg$_2$Si and Mg$_2$Sn has been reported.\cite{3,6} Initially, it was suggested that the relatively large effective mass of Mg$_2$Sn is responsible for increase in the derivative of the Seebeck coefficient, $S$, with lattice temperature $T$. Later, first-principles calculations in combination with experimental analyses suggested that the term $\frac{dn(E)}{dE}$ plays a prominent role in this alloy system,\cite{2} and attributed the enhancement to the so-called “convergence of conduction bands” by alloying. The observed enhancement was reproduced again with a different kind of dopant,\cite{7} and a recent experimental study confirmed that the Seebeck coefficient of MSS is improved by about 13–37% as compared to that of a highly optimized Mg$_2$Si.\cite{8}

Knowing the fundamental mechanism and principles behind this series of observations has significant implications, because it provides a straightforward means to optimize the electronic structure of materials simply by alloying isovalent anions. Previously, an enhancement of the $\frac{dn(E)}{dE}$ term has been

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reported for the PbTe system, where a “resonance level” in the observed density-of-states is established between the dopant and the semiconductor.\textsuperscript{1}

The band structures of Mg\textsubscript{2}Si and Mg\textsubscript{2}Sn have inherently a high level of degeneracy due to their crystalline lattice structures (as shown in Fig. 1). Pure Mg\textsubscript{2}Si alone produces a high level of degeneracy due to their crystalline lattice.\textsuperscript{10} On the other hand, Mg\textsubscript{2}Sn does not show great thermoelectric power since it undergoes a semiconductor-to-metal transition at high temperatures. However, when Sn is doped to replace Si, the efficiency almost doubles at an optimal composition range of Sn (x\textsubscript{Sn} = 0.5–0.7).

Considering the electronic band structure of MSS, it is suggested that the low-lying states of the conduction band are located close to each other, forming effectively degenerate levels in the solid solution at sufficiently high temperature.\textsuperscript{2} A Sb-doped MSS with x\textsubscript{Sn} = 0.6 led to ZT = 1.3 at T = 740 K, and a very similar performance was reproduced again with a Bi-doped MSS (x\textsubscript{Sn} = 0.6, with ZT = 1.4 at T = 800 K).\textsuperscript{7} Regardless of the choice of the dopants (Sb or Bi), the proportion of Sn present acted as a dominant factor in the enhancement of ZT.

To gain further insight into the experimental observations, a fundamental understanding of the electronic structure of these MSS composites is necessary, and there have been some recent studies in this direction. For instance, Tan et al.\textsuperscript{10} calculated the band structure of MSS using density-functional theory (DFT) for various compositions of MSS using ultra-soft pseudopotentials and a semi-local exchange–correlation functional (GGA-PW91). They found that the two bands with different effective masses were found to be very close in energy, forming an effectively degenerate level for x\textsubscript{Sn} = 0.625 in the MSS solid solution.

Using the semi-local generalized gradient approximation (GGA), the electronic structure of Mg\textsubscript{2}Sn is calculated to be metallic.\textsuperscript{11} This wrong electronic structure description and severe underestimation of the band gap as obtained by DFT-GGA is well known and expected. Given the known challenges in obtaining an accurate description of these narrow gap semiconductors at the semi-local treatment of the DFT exchange–correlation (\textit{xc}) functional, the study of these intricate band degeneracies may well require to go beyond this semi-local approximation. Thus, in this work, we go beyond the GGA and employ a hybrid DFT \textit{xc} functional which is known to significantly improve the description of the electronic band structures of complex materials.\textsuperscript{12}

Here, we report the electronic band structures projected by the orbital character, detailing individual contributions from the atomic orbitals. In previous studies, the contribution of the filled 4d state of Sn to the conduction edge of the band structure has not been discussed. In our projected band structure calculations, the presence of Sn 4d states are clearly demonstrated, and this observation coincides with a similar enhancement found in the Co–Si–Ge alloy, where changes in the Co 3d state was found to be closely correlated with an improved Seebeck coefficient of the n-type semiconductor.\textsuperscript{13} In addition, we address the possible origin of the “convergence of bands” in MSS solid solutions as suggested in ref. 2.

In addition, the relative electronic energy levels in the band structure may well be affected by applied geometric strain as shown in the PbTe–Se alloy.\textsuperscript{14} Vegard’s law suggests that the lattice parameter of the solid solution varies as a linear combination of the lattice parameters of the two constituent compounds. On this basis, the sublattice of Mg\textsubscript{2}Si is expected to experience tensile strain, while that of Mg\textsubscript{2}Sn will undergo compressive strain in the solid solution. Tensile and compressive strains in Mg\textsubscript{2}Si and Mg\textsubscript{2}Sn, respectively, are found to intensify the degree of conduction band valley degeneracy.

As mentioned above, the enhanced band valley degeneracy in the conduction band has been suggested to be responsible for the improvement, however, details of the electronic band structure, and the effect of geometric structural variation such as lattice expansion/compression are presently not understood. In this work, we focus on the origin of the effectively degenerate conduction bands of Mg\textsubscript{2}Si and Mg\textsubscript{2}Sn, presenting detailed information about the projected band structure.

II. Methodology and computational approach

We perform density-functional theory calculations as implemented in the Vienna ab-initio simulation package (VASP).\textsuperscript{15,16} The kinetic energy cutoff for the planewave basis set is 400 eV and the electron–ion interactions are represented using projector augmented wave (PAW) potentials.\textsuperscript{17,18} A \textit{k}-centered \textit{k}-point grid of 9 × 9 × 9 is used for geometric optimization. The total energy convergence criterion is 10^{-5} eV for electronic minimization steps, and 10^{-4} eV for ionic displacement steps.

Both Mg\textsubscript{2}Si and Mg\textsubscript{2}Sn crystalize in the \textit{Fm\textsubscript{3}m} fluorite crystal structure (as depicted in Fig. 1) The crystalline structures of Mg\textsubscript{2}Si and Mg\textsubscript{2}Sn are calculated using various DFT \textit{xc} functionals and compared to experimental results. In particular, the HSE06,\textsuperscript{12,19–21} PW91,\textsuperscript{22,23} PBE,\textsuperscript{24,25} PBEsol,\textsuperscript{26} PBE+D2,\textsuperscript{27} and PBE+D3,\textsuperscript{28} functionals have been tested. The calculated lattice parameter of the primitive unit cells of Mg\textsubscript{2}Si and Mg\textsubscript{2}Sn are compared to experimental values, as detailed in Table 1.

We calculated the band structures of pure Mg\textsubscript{2}Si and Mg\textsubscript{2}Sn for varying degrees of lattice strain, in order to understand the
effect of the geometric lattice strain independent from other factors. Due to alloying, the Mg$_2$Si sublattice will experience tensile strain, while the Mg$_2$Sn sublattice will experience compressive strain.

To calculate electronic band structures of MSS solid solutions, we consider three representative alloy models. MSS alloys are known to form stable homogeneous alloys in the range of 0.55 $\leq$ $x$ $\leq$ 1.0, and the optimal range of $x$ is from 0.5 to 0.7 as reported from experimental measurements. To simulate these compositions, we use homogeneous solid solution models for $x = 0.5$ and 0.75, while an $x = 0.25$ model is used as a comparative case. A supercell which is eight times larger than the Mg$_2$Si primitive unit cell is created. There are 16 Mg atoms and 8 Si atoms in this (2$\times$2$\times$2) supercell of Mg$_2$Si.

In the Mg$_2$Si$_{0.5}$Sn$_{0.5}$ model, Si atoms at (0, 0, 0), (1/2, 0, 0), (0, 1/2, 0), (0, 0, 1/2) are substituted with Sn atoms, in order to model a representative homogeneous alloy. The Mg$_2$Si$_{0.5}$Sn$_{0.5}$ supercell has a geometric strain of +3.4% compared to pure Mg$_2$Si, and $-3.2\%$ compared to Mg$_2$Sn. In the Mg$_2$Si$_{0.25}$Sn$_{0.75}$ model, six Si atoms are substituted with Sn, leaving only two Si atoms (at the origin and at the center) unchanged. The supercell has a strain of $+5.1\%$ and $-1.6\%$, compared to pure Mg$_2$Si and Mg$_2$Sn, respectively. The Mg$_2$Si$_{0.75}$Sn$_{0.25}$ has only two Sn atoms, at the origin and at the center of the supercell. This supercell has a strain of $+1.7\%$ and $-4.8\%$ when compared to pure Mg$_2$Si and Mg$_2$Sn, accordingly. All lattice parameters of the alloy models are scaled according to Vegard’s law.

Thermoelectric materials operate at elevated temperatures, however, the calculated electronic structure conveys only the $T = 0$ K ground state property. A recent study reported explicit phonon-induced electronic structure calculations for Pb-based chalcogenides, and found that a high temperature (investigated up to about 600 K) introduces variations in the eigenvalues of the order of 0.1 eV. Noting that high operating temperatures can have a direct influence on the band degeneracies in these thermoelectric alloys, the explicit treatment of phonon–electron coupling has not been taken into account in this work. Instead, we approach this problem by modelling the temperature effect via a statistical treatment of temperature-broadened electron occupancies in our band structure calculations at specified temperatures.

According to Fermi–Dirac statistics, an elevated temperature results in a broadened distribution of electrons. To include the effect of temperature in our band structure calculations, we employ a Gaussian smearing function to approximate this broadening effect, and use a Gaussian normal distribution to represent weight in momentum–energy space. We then use a convolution between the two distribution functions to obtain a temperature-broadened projected electronic band structure.

<table>
<thead>
<tr>
<th>xc</th>
<th>Mg$_2$Si</th>
<th>Mg$_2$Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>4.440 (−1.73)</td>
<td>4.742 (−0.80)</td>
</tr>
<tr>
<td>PW91</td>
<td>4.434 (−1.86)</td>
<td>4.738 (−0.88)</td>
</tr>
<tr>
<td>HSE06</td>
<td>4.419 (−2.20)</td>
<td>4.721 (−1.24)</td>
</tr>
<tr>
<td>PBEsol</td>
<td>4.419 (−2.20)</td>
<td>4.710 (−1.47)</td>
</tr>
<tr>
<td>PBE+D2</td>
<td>4.404 (−2.53)</td>
<td>4.720 (−1.26)</td>
</tr>
<tr>
<td>PBE+D3</td>
<td>4.397 (−2.68)</td>
<td>4.707 (−1.53)</td>
</tr>
<tr>
<td>Expt.</td>
<td>4.518$^a$</td>
<td>4.780$^b$</td>
</tr>
</tbody>
</table>

$^a$ Ref. 32. $^b$ Ref. 33.

Fig. 2 The projected band structure (atom species indicated in brackets) of Mg$_2$Si and Mg$_2$Sn as calculated using the HSE06 xc functional. Circles are used for conduction bands, squares for valence bands. $E_g$ is the indirect band gap between the $\Gamma$ and $X$ points. The size of the symbols indicates the magnitude of the weight of the orbital character at each $k$-point. The results capture the Sn 4d states in the low-lying heavy band.
Specifically, once the ground state projected band structures are obtained, the additional calculations are performed in two steps. Firstly, the band occupancy is projected onto a normal distribution along the energy axis (eqn (2)). Here, the product of the Boltzmann constant and absolute temperature \((k_B T)\) is used as a broadening parameter \(\sigma\). Secondly, the calculated distribution is convoluted with a Gaussian smearing function (eqn (3)). The final projection (eqn (4)) is cast upon the energy axis at each \(k\)-point, showing temperature-dependent broadening of the band occupancy.

\[
\Phi = \frac{\exp\left(\frac{E^2}{2\sigma^2}\right)}{\sigma\sqrt{2\pi}} \quad (2)
\]

\[
f\left(\frac{E - \mu}{k_B T}\right) = \frac{1}{2}\left(1 - \text{erf}\left(\frac{E - \mu}{k_B T}\right)\right) \quad (3)
\]

\[
w(E,T) = \omega f \odot \Phi. \quad (4)
\]

Here \(\Phi\) denotes the projection of individual weight upon the energy \((E)\) axis, \(f\left(\frac{E - \mu}{k_B T}\right)\) shows the Gaussian smearing function, where \(\mu\) denotes the eigenvalue, and finally, a convoluted-weighted projection, \(w\), is defined by the convolution of the Gaussian smearing and Gaussian distribution functions, multiplied by the calculated weight \(\omega\).

In our finite temperature approach, the broadening parameter \(k_B T\) is about 0.07 eV at 800 K in accordance with...
the variance range of the explicit phonon-induced band structure calculations.30

III. Results and discussion

The calculated lattice parameters of Mg2Si and Mg2Sn are listed in Table 1. The PBE functional exhibits good agreement with experiment (within 2%). The HSE06 shows a very similar result to the PBEsol for Mg2Si, and performs slightly better for Mg2Sn. The HSE06 functional is not frequently used for geometric optimization calculations, due to the significant computational cost which varies exponentially with increasing size of the system. The HSE06 functional describes the atomic geometry as well as the widely used efficient functionals in Table 1.

A common approach to calculate the electronic structure of materials with a complex geometry is to first determine the ground state geometry with computationally cheaper (semi-)local functionals, and then to perform the more costly (albeit more accurate) band structure calculations at the determined geometry. This approach avoids significant computational cost and affords a more accurate description of certain material properties (e.g. more accurate band gaps). However, since the geometry found from the first step is not necessarily the equilibrium structure of the higher level functionals (though maybe very close), material properties that depend sensitively on the atomic structure may not be described as accurately as they could be. For instance, the lattice parameter of Mg2Si calculated by the PBE is 4.440 Å, but HSE06 yields a 0.5% smaller value. Thus, if we calculate the electronic structure from the two-step approach as described above, the results obtained by the HSE06 calculation will retain a 0.5% compressive strain effectively. When geometric strain is considered an important factor to the property under investigation, as is in this study, it becomes pivotal to calculate both the lattice geometry and the electronic structure optimized under the same xc functional.

The projected band structures of Mg2Si and Mg2Sn are shown in Fig. 2. Both compounds exhibit an indirect band gap between the conduction band minimum (CBM) at the X point and the valence band maximum (VBM) at the Γ point. The band gap of Mg2Si is 0.49 eV as calculated using the HSE06 functional. A GW calculation gave 0.45 eV,34 and a spin–orbit coupled all-electron calculation with PBEsol gave 0.39 eV.35 Though it is unseen from the graph, the Mg 3s states have an inherent degeneracy of two since a primitive unit cell has two Mg atoms in symmetrically equivalent positions.

The narrow band gap and conduction band degeneracy make Mg2Si alone an attractive thermoelectric material, yielding a ZT value of 0.75 at 750 K, when doped with 0.15% Bi.9 The compound Mg2Sn has a narrower band gap of 0.13 eV (as calculated using the HSE06 functional), which explains why Mg2Sn displays relatively lower thermoelectric power at high temperature compared to Mg2Si. In both Mg2Si and Mg2Sn, the CBM at the X point has inherently high degeneracy, not only due to the crystalline symmetry, but also due to the closely located eigenvalues of Mg 3s, Si 3s, Sn 5s and Sn 4d states, which at high temperature may become effectively degenerate. For an optimal composition of the Sn dopant, the degeneracy of the conduction bands at the X point in Mg2Si1−xSnx solid solutions can be maximized, resulting in greater enhancement of the band valley degeneracy.

The closely positioned conduction bands are distinguished in terms of their effective masses. A theoretical study of Mg2Si1−xSnx showed that the heavy and light bands converge to form effectively degenerate states for x = 0.625, with a calculated lattice parameter of 6.64 Å, which is roughly 4.5%
expanded relative to that of Mg$_2$Si, and 2.4% compressed relative to that of Mg$_2$Sn, coinciding with the prediction by Vegard’s law (6.63 Å).

For Mg$_2$Si, the heavier conduction band consists mainly of Mg 3s character, while the lighter band shows Si 3s character. Interestingly, Mg$_2$Sn shows the presence of Sn 4d states in the heavy band. The role of the delocalized d states in enhancing the thermoelectric transport efficiency is still under active debate.$^{1,11,36}$ In the present study, the heavy d band of Sn takes on an important role as well. The Sn 4d states hybridize with Mg 3s states in the conduction band, thereby further intensifying the band valley degeneracy in the CBM.

Turning to the effect of geometric lattice strain, we find that the varying lattice parameters significantly affects the position of the heavy and light bands (see Fig. 3 and 4). In particular, the projected band structures clearly show that geometrical strain may affect the light and heavy bands so that they overlap to form effectively degenerate levels. Mg$_2$Si shows an overlap for a 5% expanded structure, and Mg$_2$Sn shows an overlap for a 1–3% compressed structure. This behavior has been reported previously for both Mg$_2$Si and Mg$_2$Ge,$^{37}$ and here, we account for this behavior in Mg$_2$Sn for the first time. If we use Vegard’s law to calculate the lattice parameter for $x = 0.6$ in the Mg$_{1-x}$Si$_x$Sn$_x$ solid solution from experimental data of Liu et al.$^6,7$ the calculated lattice parameters also correspond to the optimal range of geometric lattice strain. These results therefore show that the increased degeneracy of the conduction bands is closely related to the degree of strain.

We now address the band structures of our solid solution models of Mg$_{2-x}$Si$_x$Sn$_x$, as shown in Fig. 5. In a homogeneous solid solution of Mg$_{2-x}$Si$_x$Sn$_x$, both Si and Sn sub-lattices experience expansive and compressive strain, respectively. Therefore it is also important to investigate the electronic structure of these MSS solid solutions to determine the accurate position of degenerate levels with the HSE06 functional, having the varying degree of lattice strain in mind.

Considering the temperature-broadened electronic band structure of Mg$_{Si_{0.25}}$Sn$_{0.75}$ in Fig. 5, there exist multiple adjacent low-lying bands around the CBM. This can be explained in terms of the geometric strain. The lattice parameter of the solid solution model is about 5.1% larger than pure Mg$_2$Si, and is about 1.6% smaller than pure Mg$_2$Sn; where the low lying bands of the pure bulk models showed enhancement of the band valley degeneracy in previous results.

The formation of the solid solution at this value of $x$ yields the optimal ranges of sublattice strain, where the band valley becomes maximally degenerate. Comparing the separation between the low-lying bands around the CBM to those for Mg$_{2-x}$Si$_x$Sn$_x$, it can be seen that for the latter structure, these bands are relatively rather far apart. This is because the lattice strain imposed by forming this solid solution deviates from the optimal ranges found for the pure

![Fig. 6](image-url) Upper plots: the finite-temperature induced projected band structure (atom species indicated) for various concentrations with finite temperature $T = 800$ K. With $x = 0.75$ in Mg$_{Si_{0.25}}$Sn$_{0.75}$ solid solutions, the degree of effectively degenerate states' at the conduction band valley is greatest (indicated by the arrow). Lower plots: line profiles along the energy axis (at the point). The orbital characters of Sn are shown in the inset.
compounds. On the other hand, when the geometric strain falls within the optimal range, the low-lying bands are close to each other and form effectively degenerate levels.

Based on the calculated results, we attempt to explain the chemical and physical origins of the enhanced degeneracy in the conduction bands of MgSi1−xSnx (MSS) alloys. We first discriminate the distinct contributions from Si and Sn from the projected electronic band structures (see Fig. 6). In both MSS solid solution models, Sn persistently contributes to both heavy and light low-lying bands, while Si contributes less to the second low-lying bands. This leads us to believe that the chemical composition of the solid solution can be closely correlated with its enhanced band valley degeneracy.

Besides this chemical origin, the conduction band states of the MSS alloys are also found to be significantly affected by the geometric strain of the sublattices. Compared to the constituent parent compounds MgSi and MgSn, the MgSi1−xSnx solid solution has an optimal range of sublattice strain, where the conduction band states of pure constituents exhibit conductive band valley degeneracies, as well (as discussed in Fig. 3 and 4). With about +5.1% expansive strain compared to pure MgSi, and with ~1.6% compressive strain compared to pure MgSn, the xsn = 0.75 alloy shows the most pronounced conduction band valley degeneracy.

In addition to the geometric origin, we find the delocalized Sn 4d and 5s states significantly contribute to the enhanced band valley degeneracy (see inset of xSn = 0.75 results in Fig. 6). We suggest X-ray absorption spectroscopy (XAS) can be a useful tool to investigate the supposedly increasing Sn 4d–Sn 5s hybridization with respect to the increasing proportion of Sn of the Mg2Si1−xSnx solid solution.

IV. Summary and conclusion

The Mg-based alloy is an excellent example where electronic band structure engineering leads to substantial strengthening of the performance. To conclude, we investigated the electronic structures of alloy models (x = 0.25, 0.50, and 0.75) as well as those of the constituent pure bulk materials (MgSi and MgSn). We found that going beyond semi-local DFT (e.g. using the hybrid HSE06 functional) was necessary to accurately describe the band gap of both MgSn and its alloys. From the finite-temperature projected electronic band structures of these Mg-based alloys, we were able to elucidate and provide compelling evidence for the chemical and geometric origin of the observed conduction band valley degeneracy, and the significance of the Sn 4d states in the conduction band of the MgSi1−xSnx alloy system. Finally, our findings contribute to an ongoing discussion about the electronic structure of MSS, using hybrid DFT temperature-broadened, orbital-projected band structure calculations. The enhanced thermoelectric character of the MSS solid solutions suggests a novel means to further improve the thermoelectric performance through electronic band structure engineering, and could well play a paramount role in the future discovery and design of novel and efficient thermoelectric materials for real devices.

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References


