Thermoelectric efficiency of anisotropic materials with an application in layered systems

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Abstract

Thermoelectric (TE) transport in anisotropic materials is investigated based on most general thermodynamical concepts. Currents and power conversion efficiency are studied in SnSe and SnS in different directions. The design of composites whose TE performance along different principles directions is the same is proposed. Although such features do not occur naturally, such man-made anisotropic materials can be constructed using bilayers achieving much broadened working conditions of TE conversion devices. Intricate relationships between the anisotropy and the direction of the electric and heat currents are revealed, which further help us understand how transport occurs in such composites.

1. Introduction

Thermoelectric (TE) materials are widely studied due to their ability to convert energy, as the Seebeck effect allows generating power generation from heat while the Peltier effect is used for achieving cooling from electricity [1]. Given the environmental benefits of thermoelectricity due to its solid state operation, TE materials are being pursued for many practical applications, such as power generation, cooling devices, and thermal management of microelements among others [2, 3]. However, wider applicability of TE devices is limited due to their low conversion efficiency, thus one of the main research directions of this field is to find efficient materials. First principles simulations together with experimental synthesis and characterization are used to design single-phase compositions with enhanced TE properties [2].

Macroscopic approaches based on composites and specially designed metamaterials have re-emerged recently for finding novel routes to manipulate and control thermal and electric flows [4–6]. Cloaks, rotators, and concentrators of thermal, electric, and TE transport have been proposed and some of these effects have been demonstrated in the laboratory [7–11]. Using selected design principles for these composites, pathways for independent control of coupled via the Seebeck effect thermal and electric flow have also been proposed [12]. Specifically, arranging layered materials whose components have properties chosen to follow in-series and in-parallel rules from circuit theory can be utilized to direct the thermoelectrically coupled electric and heat flows in predetermined separate directions.

Practical applications of TE phenomena rely on materials whose properties are designed based on the end goal of the device. Obtaining a functional device is based on our fundamental understanding of the microscopic electronic structure of the materials and macroscopic thermodynamic principles taking into account geometry, anisotropy, and inhomogeneity factors. Recently, it has been reported that anisotropic materials, such as SnSe, SnS, LaCuOSe, and Nb\textsubscript{2}Si\textsubscript{1−x}Te\textsubscript{4} among others possess properties highly dissimilar in different directions, which can be very attractive for TE energy conversion [13–16]. The anisotropic transport in many 2D materials have also gained recent interest as they offer additional benefits for thermoelectricity originating from their low dimensionality [17–19]. In the case of 3D system, for example, the multiple valence extrema and the ultralow conductivity are key features in achieving superior TE performance along the \textit{a}-axis of the layered orthorhombic of SnSe [14]. Electronic structure calculations have further elucidated the microscopic reasons for the outstanding transport properties for this material [13].
In this paper, we investigate TE transport in anisotropic materials from a macroscopic thermodynamic perspective. Specifically, the electric and heat currents are considered using the general theory of linearly coupled forces and fluxes within the main principles of thermodynamics. Although rarely studied these days, understanding how anisotropy affects the TE transport macroscopically is important especially for building devices. Taking SnSe and SnS as examples and using finite element methods, here we calculate the currents distribution and conversion efficiency as the sample is rotated so the transport does not happen along the preferred direction. Based on this knowledge, we propose designing a material with unique anisotropy: while the TE conversion efficiency is the same along two characteristic directions, their properties are markedly different. Note that such features are not possible in naturally occurring anisotropic materials, in which the TE conversion is more efficient along a specific direction (as is the case in SnSe and SnS, for example). We show that such a unique anisotropic metamaterial can be achieved by constructing bilayered composites. The advantage of such systems is that each layered component has its own transport properties, which can be highly dissimilar. Additionally, different orientations of the bilayers offer many possibilities of creating highly anisotropic and inhomogeneous conditions for TE transport. Our calculations based on a finite element method show how the electric and thermal flows evolve under various conditions giving further insight into the thermoelectricity in layered composites.

2. Methods: theoretical model for anisotropic transport

Currently, isotropic homogeneous $p-$ and $n-$ materials are used to construct TE generators and coolers whose efficiency is directly related to the materials dependent figure of merit $ZT = S^2\sigma T / \kappa$, a dimensionless quantity in which $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity, and $T$ is the temperature [20]. The associated efficiency for a TE generator, for example, is found as:

$$\eta = \frac{T_h - T_c}{T_h + T_c} \frac{1}{1 + ZT},$$

where $T_h$ and $T_c$ are temperatures on the hot and cold sides, respectively, and $T = (T_h + T_c)/2$. Clearly, to obtain high $\eta$, the figure of merit $ZT$ must be large. These expressions for $ZT$ and $\eta$, however, are not appropriate if TE transport is considered in anisotropic and/or inhomogeneous materials [21, 22]. In such cases, in which transport properties are tensors with position dependent components, the efficiency must be considered numerically from more general considerations as analytical solutions are not possible.

The focus of our study are anisotropic homogeneous materials in 2D for which the electrical conductivity is a tensor $\bar{\sigma} = \begin{bmatrix} \sigma_{xx} & \sigma_{yx} \\ \sigma_{yx} & \sigma_{yy} \end{bmatrix}$ and the thermal conductivity, $\bar{\kappa}$, and Seebeck coefficient, $\bar{S}$, are of similar form. Unlike isotropic systems, in which TE transport is the same in all directions, the tensorial nature of $\bar{\sigma}$, $\bar{\kappa}$ and $\bar{S}$ will affect how the electric and thermal currents propagate in different directions in the anisotropic material. Our goal here is to understand how this happens in a given system from a macroscopic perspective. For this purpose, we consider a material being rotated at different angles $\theta$ by the $z$-axis under standard TE boundary conditions, as shown in figure 1. The rotation transforms the properties of the material according to $\bar{\sigma}' = A\bar{\sigma}A^T$, $\bar{\kappa}' = A\bar{\kappa}A^T$, and $\bar{S}' = A\bar{S}A^T$, where $A = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix}$. It is straightforward to find that:

$$\bar{\sigma}' = \begin{bmatrix} \frac{1}{2} (\sigma_{xx} + \sigma_{yy}) + \frac{1}{2} (\sigma_{xx} - \sigma_{yy}) \cos 2\theta - \frac{1}{2} (\sigma_{xy} + \sigma_{yx}) \sin 2\theta & \frac{1}{2} \sigma_{yx} \sin 2\theta + \frac{1}{2} \sigma_{xy} \sin 2\theta \\ -\frac{1}{2} (\sigma_{xx} - \sigma_{yy}) \sin 2\theta + \frac{1}{2} (\sigma_{xy} - \sigma_{yx}) \cos 2\theta & \frac{1}{2} (\sigma_{xx} - \sigma_{yy}) \cos 2\theta + \frac{1}{2} (\sigma_{xy} + \sigma_{yx}) \cos 2\theta \end{bmatrix}.$$  

(1)

Similar expressions can be obtained for $\bar{\kappa}'$ and $\bar{S}'$. Equation (1) shows that contributions from the diagonal terms $\sigma_{xx}$, $\sigma_{yy}$ can be found in $\sigma_{yy}'$, $\sigma_{xx}'$; the off-diagonal (Hall) conductivities also affect the diagonal components of $\bar{\sigma}'$. The admixture between these different contributions is controlled by the angle $\theta$.

Given the tensorial nature of the TE transport properties, the electric and thermal currents can be written using thermodynamics within Onsager’s theory establishing reciprocal relations between generalized currents generated by applied forces through linear coefficients [23, 24]. In the case of steady state with local equilibrium, the electric current density $\vec{J}$ and thermal current density $\vec{J}_Q$ can be expressed as:

$$\vec{J} = -\bar{\sigma} \cdot \nabla \mu_e - \bar{\sigma} \cdot \bar{S} \cdot \nabla T,$$

$$\vec{J}_Q = -\bar{\kappa} \cdot \nabla T + T \bar{S}^T \cdot \vec{J},$$  

(2)  

(3)
where $\nabla \mu_e$ is the gradient of the electrochemical potential $\mu_e = \mu_c + eV$ ($\mu_c$—chemical potential, $V$—electrical potential), $\nabla T$ is the temperature gradient, and $\tilde{S}^T$ is the transpose of the Seebeck tensor $\tilde{S}$. In addition to the above constitutive equations, the governing equations must also be satisfied,

$$\nabla \cdot \vec{J}_E = 0, \quad \nabla \cdot \vec{J}_N = 0,$$

(4)

where $\vec{J}_E = \vec{J}_Q + \mu_e \vec{J}_N$ is the total energy flux density and $\vec{J}_N$ is the particle current density. The first relation in equation (4) reflects charge conservation, while the second one stands for particle conservation. The second relation in equation (4), also written as $\nabla \cdot \vec{J}_Q = -\Sigma_{\text{ext}} \cdot \vec{f} = \vec{E} \cdot \vec{J}$, is a measure of the power density generated in the material ($\vec{E}$ is the electrical field). When $\tilde{S} = 0$ in (3,4), one recovers Ohm’s law and Fourier’s law for the uncoupled electric and thermal currents, respectively.

The constitutive and governing equations (1)–(4) describe completely the thermodynamic transport in a given system, where the TE effects are captured via the Seebeck coefficient. It is the presence of $\tilde{S}$ that plays a key role in energy conversion based on TE phenomena. From general considerations, the efficiency for power generation, for example, is given as $\eta = \frac{\text{dissipated power}}{\text{input heat}}$. Specifically, one finds:

$$\eta = \frac{\int \left( \nabla \cdot \vec{J}_Q \right) d^2x}{\int \left( T\tilde{S}^T \cdot \vec{f} - \tilde{\kappa} \cdot \nabla T \right) \cdot dL_h},$$

(5)

where the integration in the nominator is over the surface of the 2D material to obtain the generated power in the sample that is being measured. The input heat in the denominator is found as a linear integral at the hot site of the sample that is being measured. Note that equations (2)–(5) are valid without making any assumptions for the transport properties of the system, where the thermoelectrically coupled transport takes place. In the case of homogenous isotropic materials, the power generation efficiency in standard TE modules can be reduced to an expression governed by the internal figure of merit $ZT$ of the material [20], as discussed earlier. Nevertheless, equation (5) is beneficial in terms of finding pathways for optimization and control of TE conversion in any media regardless of its anisotropy or inhomogeneity.

3. Results and discussions: transport in anisotropic materials

Anisotropic materials have shown promising results for TE applications, which have generated great interest in pursuing systems with one preferred direction of optimal TE transport. Materials, such as SnSe and SnS, have very low thermal conductivity along the a-axis of their orthorhombic crystal structure and as a result, $ZT > 2$ at $T \sim 900$ K has been reported [13, 14]. In addition to these single-phase studies, polycrystalline
Figure 2. TE efficiencies for (a) SnSe and (b) SnS as a function of the incoming current density. Electric (black arrows) and heat (red arrows) current distributions for (c) SnSe and (d) SnS for two rotation angles. The background color scheme for the temperature distribution is indicated as $T(K)$ color bar. A schematic representation for the crystal structure of both materials together with the lattice vectors and axis are shown between the top two panels.

Table 1. Calculated transport properties at two temperatures of SnSe and SnS at $10^{19} \text{ cm}^{-3}$ for p-doping as reported in [13]. The electronic thermal conductivity is estimated using Wiedemann–Franz law $\frac{\kappa_e}{\sigma} = LT(L = 2.44 \times 10^{-8} \text{W K}^{-2} \text{Ω}^{-1})$. The $x, y$-axis are taken along the $a, b$ lattice vectors (see figure 1).

| Material | $T$ (K) | $\kappa_{xx}$ ($\kappa_a^b$) | $\kappa_{yy}$ ($\kappa_b$) | $\kappa_{ce,xx}$ ($\kappa_{xx}^c$) | $\kappa_{ce,yy}$ ($\kappa_{yy}^c$) | $\sigma_{xx}(\sigma^a)$ | $\sigma_{yy}(\sigma^b)$ | $S_{xx}(S^a)$ | $S_{yy}(S^b)$ |
|----------|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|
| SnSe     | 300    | 0.900           | 2.000           | 0.037           | 0.184           | 5010            | 25 120          | 270            | 310            |
|          | 750    | 0.400           | 0.750           | 0.014           | 0.058           | 790             | 3160           | 400            | 420            |
| SnS      | 300    | 0.900           | 2.350           | 0.012           | 0.092           | 1580            | 12 590          | 400            | 300            |
|          | 750    | 0.500           | 0.900           | 0.003           | 0.018           | 180             | 1000           | 560            | 500            |

compactions have also been investigated in the laboratory [25, 26]. In this paper, we focus on the TE transport and performance on a single phase crystal rotated about its $c$-axis. Even though we expect that the energy conversion would be worse as compared to when the transport takes place along its most optimal $a$-direction, we believe it is important to see how the currents distribution and efficiency evolve as a function of the rotation angle since this direction has not been explored previously.

SnSe and SnS are found in the Pnma orthorhombic phase with a lattice structure given in figure 2. First principles simulations [13] show that there is remarkable anisotropy in the thermal conductivity $\kappa_b > \kappa_c > \kappa_a$ and electrical conductivity $\sigma_c > \sigma_a > \sigma_b$. As a result, the figure of merit is largest along the $a$-axis and smallest along the $c$-axis. In our calculations, we utilize the temperature dependent transport properties for these two materials obtained by first principles simulations. In table 1, we summarize the conductivity, thermal conductivity, and Seebeck coefficient for the $a = x; b = y$ axes only, since the rotation of the sample is along the $c = z$ axis. Our calculations are performed using finite element methods as implemented in the COMSOL MULTIPHYSICS package [27]. The governing and constitutive equations (2)–(4) are solved for a 2D square material with dimensions $10 \text{ cm} \times 10 \text{ cm}$ for the length and width. The cold and hot sites are kept at $300 \text{ K}$ and $750 \text{ K}$, respectively.

Instead of focusing on the material dependent figure of merit (as done by others [13, 14, 25, 26]), we aim at solving the general equation (5) for the TE efficiency. This is quite beneficial as it gives a more realistic representation of how to optimize $\eta$ by taking into account Joule’s heating and understanding the role of external load in the device. In figures 2(a) and (b) the TE conversion efficiency is shown as a function of the external current load for different orientations of the SnSe and SnS samples. For each angle, there is an external current for which $\eta$ is maximized. This optimum $J_{in}$ value and the maximum $\eta$ increase as the sample for each material rotates from $\theta = 0$ to $\theta = \frac{\pi}{2}$, which simply follows the transition from a smaller ZT...
along the $y = b$-axis to the larger ZT along the $x = a$ axis. We note that as $\theta$ approaches the preferred direction at $\theta = \frac{\pi}{2}$, $J_{\text{max}}$ and the corresponding current density $J_{\text{in}}$ increase. Most bell-like curves are encompassed by the red curve corresponding to $\theta = \frac{\pi}{2}$. The exception are smaller angles such that $\sigma_{\text{max}}$ for SnSe occurs at larger of the red curve for both materials. Furthermore, comparing the results for both SnSe and SnS, the current densities are not strictly along the $T$, while $\kappa_{\text{max}} = 382.2 \, \mu V \, K^{-1}$ for SnS.

For example, $\eta_{\text{max}} = 0.06$ occurs at $J_{\text{in}} \approx 4.67 \, A \, cm^{-2}$ for SnS, while $\eta_{\text{max}} = 0.09$ occurs at $J_{\text{in}} = 9.95 \, A \, cm^{-2}$ for SnSe at $\theta = \frac{\pi}{2}$.

In figures 2(c) and (d) the electric and heat current density temperature distributions are also shown for two representative rotation angles. For $\theta \neq 0, \frac{\pi}{2}$, the current densities are not strictly along the $x$-axis, but they acquire components in the $y$-directions as well. This is due to the contribution from the off-diagonal components in $\hat{\tau}, \hat{\kappa}, \hat{S}$ tensors as given in equation (1). Note that even though there are no Hall transport properties in SnSe and SnS crystal lattice, there are off-diagonal contributions due to the rotation itself diverting some of the transport making it two-dimensional. As a result, the efficiency of the sample decreases, as seen in figures 1(a) and (b).

SnSe and SnS are representative examples of naturally occurring materials that support anisotropic transport due to the different components in the tensors of their properties. In all such materials, the figure of merit and consequently the TE conversion efficiency are better along a certain principal direction ($x, y$ or $z$ axis) compared to the others. Here we propose a different possibility of an anisotropic material, which can have the same ZT and $\eta$ along the $x$ and $y$ axes, for example, but different properties. This is a special type of an anisotropic material, in which $\sigma_{xx} \neq \sigma_{yy}, \kappa_{xx} \neq \kappa_{yy}, S_{xx} \neq S_{yy}$ but their values are such that $ZT_{xx} = ZT_{yy}$.

Let us consider a hypothetical anisotropic material with the transport properties given in figure 3. Maintaining $T_c = 300$ K and $T_h = 750$ K, we find that $ZT_{c,xx} = ZT_{c,yy} = 0.54$ and $ZT_{h,xx} = ZT_{h,yy} = 1.35$, however, $\sigma_{xx}, \kappa_{xx}, S_{xx}$ correspond to a metallic-like, while $\sigma_{yy}, \kappa_{yy}, S_{yy}$ correspond to a semiconducting type of transport. The results for simulating equation (5) are shown in figure 3(a). As $\theta$ changes from $0$ to $\pi/2$,
there is a non-monotonous behavior of the maximum value of $\eta$ as it goes from $\eta_{\text{max}} = 0.13$ ($\theta = 0$) to $\eta_{\text{max}} = 0.10$ ($\theta = \pi/4$) to 0.13 ($\theta = \pi/2$) again. There are also large variations in the external current density for which certain efficiency can be reached. Also, there are now many different possible configurations to achieve particular efficiency. For example, from figure 3(a), $\eta_{\text{max}} = 0.13$ can be obtained at $J_{\text{in}} = 5.4$ A cm$^{-2}$ ($\theta = \pi/2$) or $J_{\text{in}} = 22.5$ A cm$^{-2}$ ($\theta = 0$) depending on the sample orientation. Also, if one just looks at one particular efficiency such as $\eta = 0.10$, it can be obtained at many possible configurations, for instances, $J_{\text{in}} = 3.5$ A cm$^{-2}$ or $J_{\text{in}} = 10$ A cm$^{-2}$ ($\theta = \pi/2$), $J_{\text{in}} = 9.75$ A cm$^{-2}$ or $J_{\text{in}} = 21.12$ A cm$^{-2}$ ($\theta = \pi/6$).

We note that it is not possible to surpass $\eta_{\text{max}} = 0.13$ for this anisotropic material corresponding to the $x$ and $y$ axes for which ZT is largest. However, by rotating the sample the possibilities for achieving lower value efficiencies are increased. This broadens significantly the working conditions for a device operation as current densities with large variations of magnitude can be used to obtain particular $\eta$. This may have important practical applications for making devices more diverse and multifunctional. Nevertheless, a naturally occurring material with such anisotropic features is not available. We propose that, such a system can be designed using bilayered composites with carefully chosen natural materials for which the conductivity, thermal conductivity and Seebeck coefficient follow basic rules from circuit theory.

Here we take a composite made of two alternating layers of isotropic materials labeled as $A, B$. The layers can be arranged with an angle of inclination corresponding to the sample rotation angle $\theta$, as shown in figure 1(c). The properties of the isotropic materials are taken to follow in-series and in-parallel circuit elements, such that:

$$\sigma_{xx} = \sigma_A + \sigma_B \frac{2\sigma_A \sigma_B}{\sigma_A + \sigma_B}, \quad \sigma_{yy} = \frac{2\sigma_A \sigma_B}{\sigma_A + \sigma_B} \frac{\sigma_{xx} \sigma_{yy}}{\sigma_{xx} \sigma_{yy} + \sigma_{yy} \sigma_{xx}}, \quad \sigma_{xx} \sigma_{yy} = \frac{2\sigma_A \sigma_B}{\sigma_A + \sigma_B} \frac{\sigma_{xx} \sigma_{yy}}{2} \approx \frac{\kappa_A + \kappa_B}{2}, \quad \kappa_{yy} = \frac{2\kappa_A \kappa_B}{\kappa_A + \kappa_B}. \quad (6)$$

The above equations can be solved for the properties of the $A$ and $B$ materials,

$$\sigma_{A,B} = \sigma_{xx} \pm \sqrt{\sigma_{xx} (\sigma_{xx} - \sigma_{yy})}, \quad (7)$$

$$\kappa_{A,B} = \kappa_{xx} \pm \sqrt{\kappa_{xx} (\kappa_{xx} - \kappa_{yy})}, \quad (8)$$

$$S_{A,B} = \frac{\sigma_{A,B} \sqrt{\sigma_{A,B} (\sigma_{A,B} - \sigma_{yy})}}{\sqrt{\sigma_{A,B} (\sigma_{A,B} - \sigma_{yy})}}, \quad (9)$$

where (+) corresponds to $A$ and (−) corresponds to $B$ material.

We consider a system composed of $N = 10$ $A, B$ bilayers, which can be constructed with different inclination angles. Their properties are chosen according to equations (7)–(9), where $\sigma_{xx(yy)}, \kappa_{xx(yy)}, S_{xx(yy)}$ are the components of the original anisotropic material. For the given values, specified earlier, we find that $\sigma_A \approx 341400$ S m$^{-1}$, $\kappa_A \approx 4.7$ $\mu$V K$^{-1}$, $\sigma_B \approx 0.77$ W (m K)$^{-1}$ and $\kappa_B \approx 5857$ S m$^{-1}$, $S_B \approx 380$ $\mu$V K$^{-1}$, $\kappa_B \approx 0.05$ W (m K)$^{-1}$. In figure 3(b), we show numerical results for the efficiency as calculated using equations (1)–(3) for the composite material with inclination angle for the bilayers corresponding to the angle of rotation. Note that the boundary conditions between the individual layers are treated within the finite element method simulations, such that the temperature, electric and heat currents are required to be continuous across each such boundary. We find that the overall efficiency is somewhat reduced; for example, $\eta_{\text{max}} \approx 0.13$ ($\theta = 0, \pi/2$) for the original material, while $\eta \approx 0.11$ for the bilayered material. Nevertheless, the overall characteristic behavior of figures 3(a) and (b) is very similar. The currents distribution with temperature is also shown in figure 3(c). Although, $I_{A}, I_{Q}$ follow the same pattern, there is more disruption in the direction of the currents inside the inclined composite as expected from the interlayer boundaries. Despite this, the temperature distribution is similar, which is related to the similar $\eta$ vs $J$ behavior discussed earlier.

4. Conclusions

Anisotropic materials have properties with tensorial nature, and as a result, the transport can be markedly different from the one along the principal directions of their lattice structures. In the context of thermoelectricity, several materials have displayed a very small thermal conductivity along a particular direction, which is quite beneficial for energy conversion with enhanced efficiency. The TE transport and
associated conversion efficiency, however, are rarely studied from a thermodynamic perspective when transport occurs in some general direction in an anisotropic material. Here this problem is considered for heat to electrical power generation from a most general point of view for which the constitutive and fundamental equations are written in the framework of thermodynamics.

By taking SnS and SnSe as examples, the TE efficiency optimization as a function of the input current of the external load of a TE device is investigated. As expected, the best \( \eta \) is found when transport occurs along the direction for which ZT is maximum (corresponds to smallest \( \kappa \)). Rotating the sample decreases \( \eta_{\text{max}} \) and shifts it to smaller values of \( I_{\text{in}} \) due to the off-diagonal components of the transport properties tensors, which divert some of the transport to transverse directions. Nevertheless, there are now more diverse working conditions, such that the optimized maximum efficiency can be achieved by more than one \( I_{\text{in}} \) simply by changing \( \theta \).

Naturally occurring anisotropic materials have different components in \( \hat{\sigma}, \hat{\kappa}, \hat{S} \) and the figure of merit corresponding to various crystal axes is always different. In fact, there is always one preferred direction for TE conversion due to its largest ZT. Here we bring the attention to a hypothetical anisotropic material, which can have different components in \( \hat{\sigma}, \hat{\kappa}, \hat{S} \), but ZT is the same along two crystal axes, for example. For the case studied here, we show that the maximum conversancy \( \eta_{\text{max}} = 0.132 \) now occurs for two values of \( I_{\text{in}} \) (\( I_{\text{in}} = 5.4 \text{ A cm}^{-2} (\theta = \pi/2) \) or \( I_{\text{in}} = 22.5 \text{ A cm}^{-2} (\theta = 0) \) figure 3(a)). There is also a non-monotonic behavior of \( \eta_{\text{max}} \) as \( \theta \) changes between 0 and \( \pi/2 \). We note that even though \( \eta_{\text{max}} < 0.13 \) for \( \theta \neq 0, \pi/2 \), the working conditions for \( I_{\text{in}} \) of the external load are broadened significantly. This can be quite advantageous for practical devices with enhanced functionalities. The performance of such a hypothetical material, which requires extreme properties, can be approximately achieved by a composite constructed by inclined bilayers made of isotropic metals, semiconductors, or insulators. Systematic data for various compositions are now available in the literature, thus it is possible to find suitable systems for this purpose. For example, the A layers for the case considered in figure 3(b) can be made from doped skutterudites, such as CoSb \(_3\) [28], while the B layers can be made from appropriate quaternary chalcogenides or their doped derivatives [29]. Nevertheless, finding the most suitable material is a matter of materials science and goes beyond the scope of this paper.

We note that the purpose of our paper is to broaden the understanding of TE transport in anisotropic materials and give design strategies for diversifying conversion efficiency optimization in terms of different working conditions. Composites may be promising for the problem of enhancing the figure of merit beyond the one of a single phased material; however, it may be necessary to consider quantum mechanical effects that are beyond classical thermodynamics. Such studies are beyond the scope of this paper.

**Data availability statement**

The data that support the findings of this study are available upon reasonable request from the authors.

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