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Introduction to ($p \times n$)-Type Transverse Thermoelectrics

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<http://dx.doi.org/10.5772/intechopen.78718>

Abstract

This chapter will review ($p \times n$)-type transverse thermoelectrics (TTE). Starting with the device advantages of single-leg ($p \times n$)-type TTE's over other thermoelectric paradigms, the theory of ($p \times n$)-type TTE materials is given. Then, the figure of merit, transport equations, and thermoelectric tensors are derived for an anisotropic effective-mass model in bulk three-dimensional materials (3D), quasi-two-dimensional (2D), and quasi-one-dimensional (1D) materials. This chapter concludes with a discussion of the cooling power for transverse thermoelectrics in terms of universal heat flux and electric field scales. The importance of anisotropic ambipolar conductivity for ($p \times n$)-type TTEs highlights the need to explore noncubic, narrow-gap semiconductor or semimetallic candidate materials.

Keywords: transverse thermoelectrics, Seebeck tensor, transport equations, transverse thermoelectric figure of merit, transverse cooling power

1. Introduction

The paradigm of ($p \times n$)-type transverse thermoelectrics (TTE) [1–3] occurs in an anisotropic semiconductor or semimetal with p -type Seebeck response along one axis and n -type Seebeck orthogonal, whereby an appropriately applied electric current at an angle with respect to these axes can induce a *purely orthogonal* heat flow (the transverse Peltier effect), or conversely, an applied temperature gradient can generate a *purely orthogonal* electric field (the transverse Seebeck effect).

Transverse thermoelectric effects in general [4–6] require a broken symmetry to generate the necessary *off-diagonal* component in the Seebeck tensor. An off-diagonal component of the

Seebeck tensor S_{xy} describes, for example, an x -direction gradient in the electrochemical potential $\nabla_x V$ that results from a transverse y -direction temperature gradient $\nabla_y T$, expressed as

$$S_{xy} = -\frac{\nabla_x V}{\nabla_y T} \quad (1)$$

within the full tensor expression

$$\nabla_i V = -\sum_j S_{ij} \nabla_j T \quad (2)$$

where $i, j \in (x, y, z)$. The Kelvin relations show how the corresponding transverse Peltier coefficient is related to the transverse Seebeck coefficient:

$$\pi_{xy} = S_{xy} T \quad (3)$$

For standard thermoelectrics (called “longitudinal thermoelectrics” in the present context), the Seebeck tensor is typically assumed to be diagonal and isotropic, and intentionally doped to be unipolar (entirely n -type or p -type), with no off-diagonal terms. Although many materials found in standard thermoelectrics are anisotropic in their crystalline form, for optimal thermoelectric performance these crystals are typically crushed into a powder and sintered into a dense randomly oriented polycrystal with many grain boundaries to reduce thermal conductivity, resulting in a macroscopically isotropic Seebeck tensor. For example, even if the original crystals were to have a Seebeck tensor $\mathbf{S}_0$ that was anisotropic,

$$\mathbf{S}_0 = \begin{bmatrix} S_{xx} & 0 & 0 \\ 0 & S_{yy} & 0 \\ 0 & 0 & S_{zz} \end{bmatrix} \quad (4)$$

the resulting Seebeck tensor S_{snt} of the sintered polycrystal of randomly oriented grains becomes isotropic,

$$\mathbf{S}_{snt} = \begin{bmatrix} S_{tr} & 0 & 0 \\ 0 & S_{tr} & 0 \\ 0 & 0 & S_{tr} \end{bmatrix}. \quad (5)$$

If the thermal conductivity of the original crystal is approximately isotropic, or if the subsequent sintered material is dominated by grain boundary scattering, the diagonal components of the sintered Seebeck tensor can be approximated by the trace of the original anisotropic crystal, $S_{tr} = \frac{1}{3} \text{tr}(\mathbf{S}_0)$.

To generate off-diagonal terms, a transport symmetry must be broken. One way to do this is with a magnetic field, which *breaks time-reversal symmetry*. According to the Nernst-Ettingshausen effect (N-E) when a magnetic field is applied to a medium with ambipolar electron and hole conduction, an antisymmetric off-diagonal Seebeck response $S_{ij} = -S_{ji} = \alpha B$ is induced proportional to the

field strength B with N-E coefficient α and $i \neq j$. For a review of the Nernst-Ettingshausen effect, please see [4, 7] and references therein. A magnetic field-induced transverse thermoelectric effect has also been observed in unipolar materials, where a “spin voltage” is generated orthogonal to a temperature gradient, named spin Seebeck effect [8–11].

Similarly, *structural asymmetry* can cause nonzero off-diagonal Seebeck terms, provided the asymmetry is maintained at a macroscopic scale. For example, sintering of randomly oriented polycrystals is disallowed, but in certain cases, twinned polycrystals with common c -axis alignment might still manifest the necessary anisotropy. If the diagonal Seebeck tensor elements S_{ii} and S_{jj} in Eq. (4) are not equal, a simple rotation $\mathbf{R}$ can induce symmetric nonzero off-diagonal terms $S_{ij} = +S_{ji}$ for $i \neq j$. With appropriate choice of the rotation tensor $\mathbf{R}$, the off-diagonal terms become

$$S_{ij} = - \sum_k R_{ik}^{-1} S_{kk} R_{kj} \quad (6)$$

Note that a *purely* p - or n -type *unipolar* material can never generate *purely* orthogonal Seebeck response—any transverse Seebeck will always be accompanied by a finite longitudinal Seebeck response. Such unipolar transverse Seebeck effects have been observed and studied, for example, in Refs. [12–16].

A more interesting structural asymmetry is one that includes an ambipolar Seebeck tensor, whereby the diagonalized Seebeck tensor elements S_{xx} , S_{yy} , and S_{zz} in Eq. (3) have at least one p -type $S > 0$ along one direction and at least one n -type $S < 0$ along another direction, as illustrated in **Figure 1**.

In such a material, there *does* exist a rotation $\mathbf{R}$ such that the Seebeck response is *purely orthogonal*, such that an applied thermal gradient can induce a purely orthogonal electric field, or equivalently,

$$\nabla T \cdot \nabla V = 0 \quad (7)$$

where ∇V is determined from ∇T via Eq. (2). A well-documented example of such a transverse thermoelectric is the composite multilayered transverse thermoelectric [4–6, 17, 21, 22] (see **Figure 3**), whereby a sequence of macroscopic alternating n - (typically metallic or semi-metallic) and p -type (semiconducting) layers create the necessary structural asymmetry. Orthogonal to the layers, electrical and thermal resistance is in series from adjacent p - to n -layers, whereas parallel to the layers, the electrical and thermal conduction is in parallel.

The most recent addition to the lexicon of transverse thermoelectric phenomena is single crystals that themselves possess orthogonal p - and n -type Seebeck components, and which the authors have dubbed “ $(p \times n)$ -type” [1, 2]. The cause of such ambipolar behavior is fundamentally different from that of the composite multilayered materials, since the $(p \times n)$ -type materials are bulk crystals, and thus both the electrical and thermal conductions are in parallel in *all* directions. Although this may seem like a trivial distinction, the consequences are profound. Once a bulk crystal is solely responsible for the ambipolar Seebeck tensor, this material can be scaled to arbitrary size—large or small—allowing one to envision both sheets

Figure 1. The $(p \times n)$ -type thermoelectrics have p -type dominant conduction and Seebeck coefficient along the a -axis, where holes are the main charge carriers to transport (blue dashed lines), and n -type-dominant conduction and Seebeck coefficient along the orthogonal b -axis, where electrons are the main charge carriers to transport (orange dashed lines). The $(p \times n)$ -type character is notated by the blue and orange crossed arrow symbol at the upper right. The movement of electrons (orange arrows) and holes (blue arrows) in orthogonal directions results in net charge current J_x to the right and net particle or heat flow Q_y up. The carrier transport shown in this figure can be driven either by drift due to an electric field along the $+x$ direction or by diffusion due to a temperature gradient along the $-y$ direction. As shown at the bottom left corner of this figure, the rotation angle between x - y transport coordinate system and a - b crystal axis coordinate system is θ .

of active cooling layers as well as microscale cooling applications for integrated thermal management. Furthermore, because such ambipolar materials operate close to the intrinsic limit with minimal doping, there is no danger of dopant freeze-out; thus, these materials can be expected to achieve transverse thermoelectric performance at arbitrarily low temperatures, provided that the band gap is of order the operation temperature. Finally, the $(p \times n)$ -type materials continue to have the same structural advantage of all transverse phenomena, namely that they can be implemented as single-leg devices, allowing for improved cooling differentials in tapered structures [19] as well as geometric implementation in other unconventional geometries that standard thermoelectrics cannot achieve.

Because the underlying phenomenology of these $(p \times n)$ -type transverse thermoelectrics materials has only recently been introduced, their band characteristics are just now being explored theoretically and experimentally. Section 2 reviews intuition behind how $(p \times n)$ -type materials function in simple devices, while Section 3 reviews the key band-theoretical equations for generating the necessary ambipolar Seebeck tensor in bulk materials from a simple effective mass model for 3D bulk semiconductors. Because quasi-2D and quasi-1D materials represent extreme limits of anisotropic band structure, the equations for calculating Seebeck tensors in such limits are also provided. Section 4 reviews how the transverse figure of merit is optimized for transverse materials in general, and Section 5 identifies the cooling power for devices made of such transverse materials.

2. $(p \times n)$ -type transverse thermoelectric devices

$(p \times n)$ -Type transverse thermoelectrics have potential device advantages over other thermoelectric solutions when considering microscale devices or cryogenic operation. Conventional

longitudinal thermoelectric devices (**Figure 2**) [6] or multilayer composite transverse thermoelectrics (**Figure 3**) [4, 5, 17] require at least one component with extrinsic p - or n -type doping, which limits their use at cryogenic temperatures since the dopants freeze out. A typical minimum operation temperature is $T = 150$ K. Similarly, the minimum device size is limited for the multileg structure of conventional longitudinal thermoelectric in **Figure 2**. And for multilayer composite transverse thermoelectrics of **Figure 3**, the macroscopic stacked sublayers set a minimum device size on the order of centimeters. For this reason, submillimeter scale devices are not feasible with either of the above thermoelectric paradigms.

On the other hand, $(p \times n)$ -type transverse thermoelectric bulk materials have distinct advantages in the cryogenic and size-scaling regimes since they operate as nominally undoped, single-leg devices. Transverse thermoelectric bulk materials have optimal performance near intrinsic doping with ambipolar electron and hole transport. As a consequence, narrow gap $(p \times n)$ -type materials should be able to work at arbitrarily low temperatures down to the cryogenic limit. The single-leg geometry also makes it straightforward to scale up to unconventional sheet-like geometries or to scale down to microscale devices since the full thermoelectric function is contained within a single material.

Figure 2. The conventional thermoelectric heat pump or Peltier refrigerator with one p -type leg and the other n -type leg will drive heat flow Q parallel or antiparallel, respectively, to the conventional electrical current J . Solid gray rectangles represent metal contacts.

Figure 3. Stacked multilayer synthetic transverse thermoelectric. Alternating layers of p -type semiconductor and n -type (semi)metal create a stacked composite whose behavior in a tilted electric field results in skewed electron and hole currents within each layer, giving a net transverse Seebeck effect. Solid gray rectangles represent metal contacts.

There are additional device advantages to single-leg thermoelectrics that result from the reduced fabrication complexity. For conventional two-leg thermoelectric devices, it is known that by stacking thermoelectric units one on top of the other with ever smaller areas, the resulting thermoelectric cascade can achieve a lower base temperature than a single stage, alone. When longitudinal thermoelectrics require multiple devices and multiple stages [18] to create such a cascade structure, transverse thermoelectrics can achieve the same “cascade” function by simply tapering a single thermoelectric leg [19]. The result acts as an “infinite-stage” Peltier refrigerator, which achieves superior cooling efficiency compared to the multiple discrete-element cascade stages by simply tapering a piece of transverse thermoelectric as a trapezoid or exponential taper. The tapering strategy allows one to achieve enhanced temperature differences even with a somewhat smaller transverse figure of merit $z_{xy}T$ [1, 19].

A typical longitudinal thermoelectric device structure is shown in **Figure 2**. As can be observed from the schematic diagram, each thermocouple unit has two legs, one p -type leg and one n -type leg. For Peltier refrigeration, the common side of both legs on the top is connected to the object to be cooled while the other side is connected to the heat sink. Following the flow of heat Q_p and Q_n in each leg, the top junction is cooled and the heat is transferred to the bottom heat sink.

The TTE unit in **Figure 4**, on the other hand, is made of one single material. Depending on the direction of current flow, only one kind of charge carrier, holes or electrons, will dominate conduction within each leg. For instance, we can observe electron current J_n in the right branch and hole current J_p in the left counterpart. Moreover, the heat current of both legs is flowing downward, just like the heat flow of the conventional device.

As demonstrated in **Figure 5**, a simpler single-leg geometry is possible with transverse thermoelectrics. With the electrons and holes, transportation directions of the $p \times n$ -type transverse thermoelectric are indicated with the crossed-arrow symbol on the upper right. The macroscopic transport of charge and heat is a vector sum of the net electron-hole electrical and heat currents, respectively. This picture depicts net charge current J_x to the right and net heat current Q_y up.

Figure 4. Sketch of $p \times n$ -type transverse thermoelectrics in a device structure mimicking that of the standard double-leg thermoelectric device in **Figure 2**. Here, the same material can be used for both legs, as long as the crystal axis is oriented parallel to the p -type direction for the p -leg current J_p and parallel to the n -type direction for the n -leg current J_n . Solid gray rectangles represent metal contacts.

Figure 5. Microscopic electron-hole picture of the $p \times n$ -type transverse thermoelectric depicts net charge current J_{total} to the right, and net particle or heat current Q_{total} up, based on the vector sum of charge current of holes Q_p and charge current of electrons Q_n , heat current of holes J_p and heat current of electrons J_n . Solid gray rectangles represent metal contacts.

An important quantity in comparing different transverse thermoelectric materials is the transverse figure of merit $z_{xy}T$, which is used in the expressions of device efficiency and performance (see Section 5). For transverse materials, the dimensionless figure of merit $z_{xy}T$ is given as:

$$z_{xy}T = \frac{S_{xy}^2}{\rho_{xx}\kappa_{yy}} T \quad (8)$$

In the transverse figure of merit expression above, the off-diagonal Seebeck element S_{xy} in the numerator is clearly the relevant component for generating a transverse thermoelectric response. In the denominator, to minimize Joule heating along the x -direction of current flow, a small resistivity component ρ_{xx} is needed; and to minimize passive return of Fourier heat in the y -direction of the temperature differential, a small thermal conductivity κ_{yy} is needed. Note that for longitudinal thermoelectrics, the expression for zT typically includes the conductivity in the numerator since the scalar equation $\sigma = 1/\rho$ is valid. However, when solving for transverse thermoelectric tensors, which by necessity have anisotropic conductivities, one must take care to calculate the resistivity component and place it in the denominator of the expression above, since, in general $\sigma_{xx} \neq 1/\rho_{xx}$.

3. Seebeck tensor of $(p \times n)$ -type transverse thermoelectrics

3.1. Thermoelectric tensors definition

Below, we derive how parallel anisotropic electron and hole conductivity give rise to the observed transverse thermoelectric behavior in $(p \times n)$ -type thermoelectrics. For an intrinsic semiconductor with anisotropic conductivity, we describe the electrical conductivity of the separate electron and hole bands with tensors σ_n and σ_p and the Seebeck response with tensors as s_n and s_p . Considering the conduction along the two principal axes of interest

labeled a and b , which manifest the transport anisotropy, we obtain the following diagonal matrices:

$$\begin{aligned}\sigma_n &= \begin{bmatrix} \sigma_{n,aa} & 0 \\ 0 & \sigma_{n,bb} \end{bmatrix}, & \sigma_p &= \begin{bmatrix} \sigma_{p,aa} & 0 \\ 0 & \sigma_{p,bb} \end{bmatrix} \\ s_n &= \begin{bmatrix} s_n & 0 \\ 0 & s_n \end{bmatrix}, & s_p &= \begin{bmatrix} s_p & 0 \\ 0 & s_p \end{bmatrix},\end{aligned}\quad (9)$$

where the diagonal elements satisfy $s_n < 0$, $s_p > 0$. Note that single-band Seebeck tensors s_n and s_p are typically isotropic, but conductivity tensors σ_n and σ_p can be strongly anisotropic (see Sections 3.3–3.5). The total conductivity tensor Σ and total resistivity tensor $\mathbf{P}$ are related by $\Sigma = \mathbf{P}^{-1} = \sigma_n + \sigma_p$.

The total Seebeck tensor for the two-band system is defined as the weighted sum of the single-band Seebeck tensors by the conductivity tensors:

$$\mathbf{S} = (\sigma_p + \sigma_n)^{-1} (\sigma_p s_p + \sigma_n s_n) \quad (10)$$

We remark again that this *parallel conduction* of bands within the same material is fundamentally different from stacked synthetic multilayer transverse thermoelectrics of **Figure 3** in which the out-of-plane Seebeck arises from *series* electrical and thermal *resistances* of two different materials. From Eq. (10), if oppositely charged carriers dominate conduction along a and b , respectively, the total Seebeck coefficients in the two orthogonal directions will have opposite signs. If we assume that p -type conduction dominates along a – and n -type, conduction dominates along b , then the total Seebeck tensor is

$$\mathbf{S} = \begin{bmatrix} S_{p,aa} & 0 \\ 0 & S_{n,bb} \end{bmatrix}, \quad (11)$$

with elements

$$\begin{aligned}S_{p,aa} &= \frac{S_p \sigma_{p,aa} + S_n \sigma_{n,aa}}{\sigma_{p,aa} + \sigma_{n,aa}} > 0, \\ S_{n,bb} &= \frac{S_p \sigma_{p,bb} + S_n \sigma_{n,bb}}{\sigma_{p,bb} + \sigma_{n,bb}} < 0,\end{aligned}\quad (12)$$

where the first inequality is valid provided that p -type conduction in the a -direction is sufficiently dominant $\sigma_{p,aa}/\sigma_{n,aa} > \left| \frac{s_n}{s_p} \right|$, and the second valid provided n -type conduction in the b -direction is sufficiently dominant $\sigma_{n,bb}/\sigma_{p,bb} > |s_p/s_n|$. The result is the desired ambipolar Seebeck tensor where one of the diagonal elements has opposite sign.

When transverse thermoelectric materials are cut into a shape such that the transport directions x, y are at an angle θ to the principal axes a and b , as shown in **Figure 1**, the Seebeck tensor in the x - y transport basis can yield the necessary off-diagonal terms:

$$\begin{aligned}
 \mathbf{S}' &= \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} S_{p,aa} & 0 \\ 0 & S_{n,bb} \end{bmatrix} \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \\
 &= \begin{bmatrix} \cos^2\theta S_{p,aa} + \sin^2\theta S_{n,bb} & \sin\theta\cos\theta(S_{p,aa} - S_{n,bb}) \\ \sin\theta\cos\theta(S_{p,aa} - S_{n,bb}) & \cos^2\theta S_{n,bb} + \sin^2\theta S_{p,aa} \end{bmatrix} \\
 &= \begin{bmatrix} S_{xx} & S_{xy} \\ S_{yx} & S_{yy} \end{bmatrix}
 \end{aligned} \tag{13}$$

This nonzero off-diagonal component of the Seebeck tensor S_{xy} in the transport basis is the essential prerequisite for any transverse thermoelectric effect.

3.2. Thermoelectric tensor calculation

In the following, we will demonstrate how the anisotropic electrical transport tensors of each separate band can be calculated. Standard longitudinal thermoelectric devices have both heat and electrical current flowing along the same axis, so their electrical resistivity, thermal conductivity, and Seebeck coefficient can be treated as scalars. In contrast, the thermoelectric properties in an anisotropic thermoelectric material must be described by tensors for the electrical conductivity σ , the Seebeck coefficient S and the thermal conductivity κ . The anisotropic transport tensors of each electron or hole band can be calculated according to the material's band structure, and then the equations of the previous section can be used to determine the total Seebeck and resistivity tensors of the two-band system. Because the compounds of interest tend to be highly anisotropic, in addition to the 3D effective mass model, we will also consider the case of quasi-2D and quasi-1D materials, which host effective mass band-conduction along two axes or one axis, respectively, and hopping transport along the remaining orthogonal axes.

We, therefore, perform a complete derivation of the thermoelectric tensor components from first principles corresponding to 3D, 2D, and 1D anisotropic transport scenarios. The thermal conductivity tensor κ is ideally obtained from experimental measurements of the material of interest, whereas transport tensors of the Seebeck S and electrical resistivity ρ can be calculated with simple assumptions outlined below if the band structure is known. The derivation of thermoelectric equations uses the intuitive notations borrowed from Chambers [20] except that instead of scalar coefficients, here, we show the complete tensor derivations.

When both an electric field $\mathbf{E}$ and a temperature gradient $\mathbf{G} = -\nabla T$ are present, the electrical current $\mathbf{J}$ and heat flow $\mathbf{Q}$ are given by

$$\begin{aligned}
 \mathbf{J} &= \sigma \mathbf{E} + \mathbf{C} \mathbf{G} \\
 \mathbf{Q} &= \mathbf{D} \mathbf{E} + \kappa \mathbf{G}
 \end{aligned} \tag{14}$$

where σ is the electrical conductivity tensor, κ is the thermal conductivity tensor, $\mathbf{D}$ is related to the Peltier tensor Π and σ by $\Pi = \mathbf{D}\sigma^{-1}$, $\mathbf{C}$ is related to the Seebeck tensor S and σ by $\mathbf{S} = \mathbf{C}\sigma^{-1}$, and $\mathbf{S}$ follows the Kelvin relation $\mathbf{S} = \Pi/T = \mathbf{D}\sigma^{-1}/T$. These equations are typically transformed so that $\mathbf{J}$ and $\mathbf{G}$ are the independent variables

$$\begin{aligned}\mathbf{E} &= \boldsymbol{\rho}\mathbf{J} - \mathbf{S}\mathbf{G} \\ \mathbf{Q} &= \boldsymbol{\Pi}\mathbf{J} + \boldsymbol{\kappa}^c\mathbf{G}.\end{aligned}\quad (15)$$

where $\boldsymbol{\rho}=\boldsymbol{\sigma}^{-1}$ is the electrical resistivity tensor, and the normally measured open circuit thermal conductivity $\boldsymbol{\kappa}^c$ is defined as $\boldsymbol{\kappa}^c=\boldsymbol{\kappa}-\boldsymbol{\sigma}\mathbf{S}\boldsymbol{\Pi}$.

$\boldsymbol{\sigma}$ and $\mathbf{D}$ tensor components σ_{ij} and D_{ij} can be calculated from the band structure

$$\sigma_{ij} = \int_0^\infty d\epsilon \frac{\partial f_0}{\partial \epsilon} \sigma_{ij}(\epsilon) \quad (16)$$

$$\sigma_{ij}(\epsilon) = \frac{e^2}{4\pi^3\hbar} \int \frac{v_{ki}}{|v_k|} v_{kj} \tau_k dS_k \quad (17)$$

$$D_{ij} = \int d\epsilon \frac{\partial f_0}{\partial \epsilon} D_{ij}(\epsilon) \quad (18)$$

$$D_{ij}(\epsilon) = \frac{1}{e} (\epsilon - \mu) \sigma_{ij}(\epsilon) \quad (19)$$

where ϵ is the carrier energy relative to the edge of the energy band, $f_0(\epsilon) = 1/(1 + e^{-\epsilon/k_B T})$ is the Fermi-Dirac distribution function, e is the electron charge, and E_F is the chemical potential. We assume that the scattering time $\tau = \gamma\epsilon^s$ obeys a power law in the energy of the carrier relative to the band minimum with exponent s . $\mathbf{v}_k$ is the carrier velocity vector for wave vector $\mathbf{k}$, which is defined as $\mathbf{v}_k = v_{ka}\hat{\mathbf{a}} + v_{kb}\hat{\mathbf{b}} + v_{kc}\hat{\mathbf{c}}$ with each velocity component $v_{ki} = \frac{d\epsilon}{\hbar dk_i}$. S_k is the equienergy k -space surface area at energy ϵ and wave vector k . The indices i, j, l in the subscripts represent three orthogonal crystal axes a, b , and c .

In the next subsections, we will analyze 3D, 2D, and 1D transport and deduce their thermoelectric tensors. The 3D anisotropic case is for anisotropic effective mass in bulk materials, e.g., an ellipsoidal effective mass such as in noncubic lattices. The 2D anisotropic case is relevant for quasi-2D materials and can be found in parallel quantum wells or weakly coupled superlattice layers with approximately infinite cross-plane effective mass. The 1D anisotropic case can be applied to quasi-1D materials or arrays of nanowires or nanotubes, which have weak tunnel coupling in two directions.

3.3. Three-dimensional transport

For a general orthorhombic lattice, the carrier energy relative to the band edge in a given energy band can be expressed with a three-dimensional (3D) effective mass approximation:

$$\epsilon = \frac{\hbar^2 k_a^2}{2m_a} + \frac{\hbar^2 k_b^2}{2m_b} + \frac{\hbar^2 k_c^2}{2m_c} \quad (20)$$

where m_i is the effective mass in the i direction. In spherical coordinates, the wave vectors and the velocity are as follows:

$$k_a = \frac{\sqrt{2m_a\epsilon}}{\hbar} \sin\alpha \cos\phi \quad (21)$$

$$k_b = \frac{\sqrt{2m_b\epsilon}}{\hbar} \sin\alpha \sin\phi \quad (22)$$

$$k_c = \frac{\sqrt{2m_c\epsilon}}{\hbar} \cos\alpha \quad (23)$$

$$v_k = \sqrt{\frac{2\epsilon}{m_a}} \sin\alpha \cos\phi \hat{a} + \sqrt{\frac{2\epsilon}{m_b}} \sin\alpha \sin\phi \hat{b} + \sqrt{\frac{2\epsilon}{m_c}} \cos\alpha \hat{c} \quad (24)$$

where α is the polar angle and ϕ is the azimuthal angle.

If the principle axes of mass anisotropy are chosen as the coordinate, then the transport tensors are all diagonal, and the diagonal components of the energy-dependent 3D conductivity become as

$$\begin{aligned} \sigma_{ii}^{3D}(\epsilon) &= \frac{e^2}{4\pi^3\hbar} \int_0^{2\pi} d\phi \int_0^\pi d\alpha \frac{v_{ki}}{|v_k|} v_{ki} \tau_k dS_k \\ &= \frac{e^2\gamma\epsilon^s}{4\pi^3\hbar} \int_0^{2\pi} d\phi \int_0^\pi d\alpha \frac{v_{ki}^2 \frac{2\epsilon\sqrt{m_i m_j m_l}}{\hbar} \sqrt{\frac{\sin^2\alpha \cos^2\phi}{m_i} + \frac{\sin^2\alpha \sin^2\phi}{m_j} + \frac{\cos^2\alpha}{m_l}}}{\sqrt{2\epsilon} \sqrt{\frac{\sin^2\alpha \cos^2\phi}{m_i} + \frac{\sin^2\alpha \sin^2\phi}{m_j} + \frac{\cos^2\alpha}{m_l}}} \\ &= \frac{2\sqrt{2}e^2\gamma}{3\pi^2\hbar^3} \sqrt{\frac{m_j m_l}{m_i}} \epsilon^{s+3/2} \end{aligned} \quad (25)$$

Integrating this expression in Eq. (16) yields the final conductivity tensor:

$$\sigma_{ii}^{3D} = \frac{2\sqrt{2}e^2\gamma}{3\pi^2\hbar^3} \sqrt{\frac{m_j m_l}{m_i}} (k_B T)^{s+\frac{3}{2}} \Gamma\left(s + \frac{5}{2}\right) F_{\frac{3}{2}+s}\left(\frac{\mu_o}{k_B T}\right), \quad (26)$$

where $E_F = 0$ is defined at the valence band edge, E_g is the bandgap, the chemical potential μ_o is defined relative to the band edge $\mu_o = E_F - E_g$ for the conduction band and $\mu_o = -E_F$ for the valence band, and $F_n(\xi)$ is the Fermi integral $F_n(\xi) = \int_0^\infty \frac{t^n}{1+e^{t-\xi}} dt$.

The Seebeck tensor is isotropic for a single band, and the diagonal Seebeck component is

$$S_{ii}^{3D} = \frac{1}{eT} \frac{\int d\epsilon \frac{\partial f_o}{\partial \epsilon} (\epsilon - \mu_o) \sigma_{ii}^{3D}(\epsilon)}{\sigma_{ii}^{3D}} = \frac{k_B}{e} \left[\frac{(5/2 + s) F_{s+3/2}\left(\frac{\mu_o}{k_B T}\right)}{(3/2 + s) F_{s+1/2}\left(\frac{\mu_o}{k_B T}\right)} - \frac{\mu_o}{k_B T} \right] \quad (27)$$

3.4. Quasi-two-dimensional transport

If carriers propagate in one direction via weak tunnel coupling, then the lattice behaves as a quasi-2D lattice or as a superlattice with weak tunneling between layers. If, for example, carriers follow the effective mass approximation in the $a - c$ plane and obey a weak-coupling model in the b direction, the following energy dispersion can be assumed as follows:

$$\epsilon = \frac{\hbar^2 k_a^2}{2m_a} + \frac{\hbar^2 k_c^2}{2m_c} + 2t_b(1 - \cos k_b d) \quad (28)$$

where d is the superlattice period or quantum well width and t_b is the nearest neighbor hopping matrix element between the weakly coupled layers. In-plane momenta are

$$\begin{aligned} k_a &= \frac{\sqrt{2m_a(\epsilon - 2t_b(1 - \cos(k_b d)))}}{\hbar} \cos\phi \\ k_c &= \frac{\sqrt{2m_c(\epsilon - 2t_b(1 - \cos(k_b d)))}}{\hbar} \sin\phi. \end{aligned} \quad (29)$$

Assuming that the in-plane mass $m_a = m_c$ and that k_r is the wave vector in $a - c$ plane, we obtain the conductivity tensor components:

$$\begin{aligned} \sigma_{aa}^{2D} &= \sigma_{cc}^{2D} = \frac{e^2 \gamma}{\pi \hbar^2 d} (k_B T)^{s+1} \Gamma(s+2) F_{1+s} \left(\frac{\mu_o}{k_B T} \right) \\ \sigma_{bb}^{2D} &= \frac{2e^2 \gamma m_a t_b^2 d}{\pi \hbar^4} (k_B T)^s \Gamma(s+1) F_s \left(\frac{\mu_o}{k_B T} \right) \end{aligned} \quad (30)$$

The Seebeck tensor remains diagonal with components:

$$\begin{aligned} S_{ii}^{2D} &= \frac{1}{eT} \frac{\int d\epsilon \frac{\partial f_0}{\partial \epsilon} (\epsilon - \mu_o) \sigma_{ii}^{2D}(\epsilon)}{\sigma_{ii}^{2D}} \\ &= \frac{k_B}{e} \left[\frac{(2+s) F_{s+1} \left(\frac{\mu_o}{k_B T} \right)}{(1+s) F_s \left(\frac{\mu_o}{k_B T} \right)} - \frac{\mu_o}{k_B T} \right] \end{aligned} \quad (31)$$

3.5. Quasi-one-dimensional transport

If carriers propagate in two orthogonal directions via weak tunnel coupling, the lattice is a quasi-1D lattice with weak coupling between chains. Hence, if carriers obey the effective mass approximation in the a -direction only and tunnel perpendicularly in the b - and c -directions, the following energy dispersion can be assumed:

$$\epsilon = \frac{\hbar^2 k_a^2}{2m_a} + 2t_b(1 - \cos k_b d_b) + 2t_c(1 - \cos k_c d_c) \quad (32)$$

where t_b and t_c are the nearest neighbor hopping matrix elements between the weakly coupled nanowires, and d_b and d_c are the distances between nanowires in the b - and c -directions. We can arrive at an analytical solution in the second line of $\sigma_{ii}^{1D}(\epsilon)$ derivations only under the assumption that the carrier velocity in the tunnel directions is much smaller than that in the wire direction, $|v_{ka}| \gg |v_{kb}|, |v_{kc}|$. So, the conductivity components are as follows:

$$\begin{aligned}\sigma_{aa}^{1D} &= \frac{\sqrt{2}e^2\gamma}{\pi\hbar d_b d_c \sqrt{m_a}} (k_B T)^{s+1/2} \Gamma\left(s + \frac{3}{2}\right) F_{1/2+s}\left(\frac{\mu_o}{k_B T}\right) \\ \sigma_{bb}^{1D} &= \frac{\sqrt{2}e^2\gamma t_b^2 d_b \sqrt{m_a}}{\pi\hbar^3 d_c} (k_B T)^{s-1/2} \Gamma\left(s + \frac{1}{2}\right) F_{s-1/2}\left(\frac{\mu_o}{k_B T}\right)\end{aligned}\quad (33)$$

The diagonal Seebeck tensor components are

$$\begin{aligned}S_i^{1D} &= \frac{1}{eT} \frac{\int d\epsilon \frac{\partial f_0}{\partial \epsilon} (\epsilon - \mu_o) \sigma_i^{1D}(\epsilon)}{\sigma_i^{1D}} \\ &= \frac{k_B}{e} \left[\frac{(3/2 + s) F_{s+1/2}\left(\frac{\mu_o}{k_B T}\right)}{(1/2 + s) F_{s-1/2}\left(\frac{\mu_o}{k_B T}\right)} - \frac{\mu_o}{k_B T} \right]\end{aligned}\quad (34)$$

4. Transverse thermoelectric figure of merit $z_{xy}T$

Inserting the conductivity and Seebeck tensors for the individual bands from Sections 3.3–3.5 into Eq. (10), and then rotating according to Eq. (13), the tensor components of all transport quantities in the x - y transport basis can be determined. The transverse thermoelectric figure of merit $z_{xy}(\theta)T$ is defined as:

$$z_{xy}(\theta)T = \frac{S_{xy}^2}{\kappa_{yy}\rho_{xx}} = \frac{\sin^2\theta \cos^2\theta (S_{p,aa} - S_{n,bb})^2}{(\sin^2\theta \kappa_{aa} + \cos^2\theta \kappa_{bb})(\cos^2\theta \rho_{aa} + \sin^2\theta \rho_{bb})}.\quad (35)$$

We define the angle $\theta_\perp$ as that which maximizes $z_{xy}(\theta)T$:

$$\cos^2\theta_\perp = \frac{1}{1 + \sqrt{\kappa_{bb}/\kappa_{aa}} \sqrt{\rho_{bb}/\rho_{aa}}}\quad (36)$$

and the maximum value $z_\perp T$ becomes

$$z_\perp T = z_{xy}(\theta_\perp)T = \frac{(S_{p,aa} - S_{n,bb})^2 T}{(\sqrt{\rho_{aa}\kappa_{aa}} + \sqrt{\rho_{bb}\kappa_{bb}})^2}\quad (37)$$

Eq. (36) shows that $\theta_\perp$ is independent of the Seebeck anisotropy, and it approaches $\frac{\pi}{4}$ when the thermal conductivity anisotropy matches the resistivity anisotropy $\frac{\kappa_{bb}}{\kappa_{aa}} = \frac{\rho_{bb}}{\rho_{aa}}$.

In semiconductors, the thermal conductivity is usually dominated by the lattice thermal conductivity [2]. Therefore, under the assumption of isotropic κ , we define a transverse power factor $PF_{\perp}$ as

$$PF_{\perp} = \frac{(S_{p,aa} - S_{n,bb})^2}{(\sqrt{\rho_{aa}} + \sqrt{\rho_{bb}})^2}, \quad (38)$$

where $\mathbf{S}$ and $\mathbf{\rho}$ tensors can be calculated by the use of semiclassical Boltzmann transport theory for the corresponding scattering mechanisms [2]. Thus, for a given band structure, $PF_{\perp}$ can be theoretically estimated to evaluate the performance of transverse thermoelectrics.

4.1. Transport equations

The current flow $\mathbf{J} = J_x \hat{\mathbf{x}}$ defines the x -axis. Eqs. (35)–(37) in general apply to all transverse thermoelectrics [4, 5, 17], but they are rederived above for completeness. The dependence of temperature on position within the transverse thermoelectric must now be carefully derived. The derivation below most closely follows that of Ref. [23] for the Nernst-Ettingshausen effect, but the errors in that reference are corrected below.

With Peltier tensor $\mathbf{\Pi}$, the total Peltier heat flux density becomes $\mathbf{Q}_{\Pi} = \mathbf{\Pi}\mathbf{J} = (T\mathbf{S})\mathbf{J}$ with longitudinal and transverse components:

$$Q_{\Pi,x} = \mathbf{Q}_{\Pi} \cdot \hat{\mathbf{x}} = (S_{p,aa} \cos^2 \theta + S_{n,bb} \sin^2 \theta) T J_x \quad (39)$$

$$Q_{\Pi,y} = \mathbf{Q}_{\Pi} \cdot \hat{\mathbf{y}} = (S_{p,aa} - S_{n,bb}) \cos \theta \sin \theta T J_x \quad (40)$$

The total heat flux density $\mathbf{Q} = \mathbf{Q}_{\Pi} - \kappa^c \nabla T$ includes both Peltier and thermal conduction effects, κ^c as notated in Ref. [23] defines the open-circuit thermal conductivity tensor at $\mathbf{J} = 0$. The thermal gradient is orthogonal to the current density $\nabla T = \frac{dT}{dy} \hat{\mathbf{y}}$; the longitudinal electric field component E_x is constant everywhere [23]; and the heat flux component Q_y depends only on y . Therefore, the longitudinal current and transverse heat flow are

$$J_x = \frac{1}{\rho_{xx}} E_x - \frac{S_{xy}}{\rho_{xx}} \frac{dT}{dy} \quad (41)$$

$$Q_y = T \frac{S_{yx}}{\rho_{xx}} E_x - (1 + z_{xy} T) \kappa_{yy}^c \frac{dT}{dy} \quad (42)$$

with transverse figure of merit $z_{xy} T = \frac{S_{xy} S_{yx} T}{\rho_{xx} \kappa_{yy}^c}$. Steady state requires $\nabla \cdot \mathbf{J} = 0$ and $\nabla \cdot (\mathbf{Q} + \bar{\mu} \mathbf{J}) = 0$, where the scalar $\bar{\mu}$ is the electrochemical potential and $-\nabla \bar{\mu} = \mathbf{E}$ is the electric field. Longitudinal Joule heating $E_x J_x$ sources a divergence in the transverse heat flux density Q_y :

$$\frac{dQ_y}{dy} = E_x J_x. \quad (43)$$

Eqs. (41)–(43) define the differential equation for temperature-dependent thermoelectric coefficients:

$$0 = \frac{1}{S_{xy} S_{yx}} E_x^2 - \left[\frac{S_{xy} + S_{yx}}{S_{xy} S_{yx}} + \frac{d \ln(S_{yx}/\rho_{xx})}{d \ln T} \frac{1}{S_{xy}} \right] E_x \frac{dT}{dy} + \left[1 + \frac{d \ln(S_{yx} S_{xy}/\rho_{xx})}{d \ln T} + \frac{1}{z_{xy}} \frac{d \ln \kappa_y^c}{dT} \right] \left(\frac{dT}{dy} \right)^2 + \frac{1 + z_{xy} T}{z_{xy}} \frac{d^2 T}{dy^2} \quad (44)$$

Note for constant thermoelectric coefficients, the derivatives with respect to temperature are zero, and for transverse thermoelectrics, $S_{xy} = S_{yx}$. Eq. (44) thus becomes:

$$\left(\frac{E_x}{S_{xy}} - \frac{dT}{dy} \right)^2 + \frac{1 + z_{xy} T}{z_{xy}} \frac{d^2 T}{dy^2} = 0. \quad (45)$$

This equation can be integrated to determine the temperature profile inside a rectangular solid of transverse thermoelectric material under constant current density. Note again, that unlike for the Nernst-Ettingshausen effect, the above Eq. (45) must be integrated numerically and does have an analytical solution.

5. Cooling power for transverse thermoelectrics

The cooling power for transverse Peltier refrigeration has recently been studied in detail [3]. The transport equations have no analytical solution, so the graphical results are presented here to allow simple estimations of cooling power for generic transverse thermoelectric scenarios. Here, we identify the characteristic heat flux scale and electric field scale for a transverse thermoelectric to define a normalized expression for thermoelectric transport [3]. The resulting study demonstrates the superiority of transverse thermoelectric coolers over longitudinal coolers with identical figure of merit.

One starts with the expression in Eq. (45) to identify the temperature distribution in a transverse cooler. To generalize this expression, the following heat flux and electric field scales $Q_0 = (\kappa_{yy}^c T_h/L)$ and $E_0 = (S_{xy} T_h/L)$, respectively, are introduced, generating normalized versions of the Eqs. (42) and (45):

$$Q_y^* = -(z_{xy} T_h) E^* T^* - (1 + (z_{xy} T_h) T^*) \frac{dT^*}{dy^*}, \quad (46)$$

$$0 = \left(E^* - \frac{dT^*}{dy^*} \right)^2 + \frac{1 + (z_{xy} T_h) T^*}{z_{xy} T_h} \frac{d^2 T^*}{d(y^*)^2}, \quad (47)$$

where $T^* = (T/T_h)$, $E^* = (E/E_0)$, $y^* = (y/L_y)$, and $Q^* = (Q_y/Q_0)$ are normalized temperature, electric field, y coordinate, and heat flux density, respectively. Eqs. (46) and (47) indicate that the normalized heat flux density Q_y^* and the normalized temperature profile $T^*(y^*)$ only depend on the normalized electrical field E^* and transverse figure of merit $z_{xy}T_h$. To determine the maximum normalized temperature difference, one sets the cooling power at the cold side Q_c^* to zero, to achieve $\Delta T^* = 1 - T_c^* = 1 - T^*(y^* = 1)$ whereby the optimal E^* is determined by

$$\left. \frac{\partial \Delta Q_c^*}{\partial E^*} \right|_{E^* = E_{opt}^*} = 0 \quad (48)$$

Thus, $\Delta T_{max}^*(z_{xy}T_h)$ is only a function of $z_{xy}T_h$. Similarly, the maximum of the cooling power at the cold side $Q_c^* = Q_y^*(y^* = 1)$ for a given T_c^* can be obtained when E^* satisfies:

$$\left. \frac{\partial \Delta T^*}{\partial E^*} \right|_{E^* = E_{opt}^*} = 0 \quad (49)$$

and $Q_{c,max}^*$ depends only on T_c^* and zT_h .

But because Eqs. (46)–(49) cannot be exactly solved with analytical methods, it is illustrative to plot the numerically calculated temperature profile and heat flux, and thereby investigate the cooling power of the transverse coolers.

Figure 6 shows the normalized temperature profile under the condition of maximum temperature difference ($Q_c^* = 0$) for various transverse figures of merit $z_{xy}T_h$. The temperature gradient at the hot side ($y^* = 0$) is zero, indicating that there is no net heat diffusion from the heat sink into, or out of, the device. Thus, 100% of the Peltier cooling power compensates the Joule heating in the device. The temperature gradient from the hot to the cold side becomes steeper

Figure 6. Normalized temperature profile of transverse thermoelectric coolers operating at maximum temperature difference for various $z_{xy}T_h$ values. At $y^* = y/L_y = 0$, the heat sink temperature $T^* = T/T_h = 1$ and at the $y^* = 1$, the cold side heat flow $Q_c = Q_y(y^* = 1) = 0$.

as $z_{xy}T_h$ increases, indicating that the higher figure of merit can compensate a larger thermal diffusive flux under larger ohmic heating. **Figure 7**, left axis, shows the dependence of the maximum temperature difference $\Delta T^* = 1 - T_c^*$ on $z_{xy}T_h$, left axis. Transverse coolers (solid line) show a larger ΔT^* than the analytically solved $\Delta T^* = 1 + \frac{1 - \sqrt{1 + 2z_{xy}T_h}}{z_{xy}T_h}$ for longitudinal coolers (dashed line) [24]. For $z_{xy}T_h = 1$, a 30 % temperature reduction is observed for the transverse cooler, which is slightly larger than the 27 % reduction of the conventional longitudinal cooler with the same $z_{xy}T_h$. The trend becomes more obvious when an unphysically large $z_{xy}T_h$ of 4 results in a 60 % temperature reduction with the transverse cooler, whereas the longitudinal cooler achieves only 50%. Note that ΔT_{max}^* can be further increased with geometric tapering of the transverse cooler [1, 19], allowing for additional advantage over longitudinal cooling for achieving large temperature differences.

Figure 7, right axis, plots the normalized maximum cooling power $Q_{c,max}^*$ of the transverse cooler when $T_c = T_h$ as a function of $z_{xy}T_h$. Unlike the linear dependence in $Q_{c,max}^* = 1/2z_{xy}T_h$ for longitudinal coolers (dashed line) when $T_c^* = 1$, $Q_{c,max}^*$ shows a superlinear dependence on $z_{xy}T_h$ for transverse coolers (solid line), which exceeds the longitudinal limit for all $z_{xy}T_h$, approaching the longitudinal behavior only in the limit of small $z_{xy}T_h$. The cooling power enhancement in $Q_{c,max}^*$ for transverse coolers over longitudinal coolers with the same $z_{xy}T_h$ is 28 % when $z_{xy}T_h = 1$ and rapidly increases to 220 % when $z_{xy}T_h = 4$.

Figure 8 shows the cooling power $Q_{c,max}^*$ of transverse coolers as a function of T_c^* for various $z_{xy}T_h$ values. For a given $z_{xy}T_h$, the Fourier diffusion heat flow increases when T_c^* decreases; thus, a larger portion of the Peltier cooling power is used to compensate the diffusive heat flow, and the remaining cooling power at the cold side $Q_{c,max}^*$ will decrease.

Figure 7. The dependence on $z_{xy}T$ of maximum normalized temperature difference (left axis) whereby $\Delta T^* = (T_h - T_c)/T_h$ and maximum cooling power when $T_c = T_h$ (right axis) for transverse thermoelectric coolers in comparison with longitudinal coolers. ΔT_{max}^* and $Q_{c,max}^*(T_c^* = 1)$ are numerically calculated for the transverse coolers in this study and analytically solved for the longitudinal coolers according to standard equations in the literature [1, 22, 23].

Figure 8. The maximum normalized cooling power $Q_{c,max}^*$ for transverse thermoelectric cooling as a function of the normalized cold side temperature T_c^* for various $z_{xy}T_h$ values.

The intersection of the curves with the horizontal axis and vertical axis corresponds to the maximum normalized temperature difference case and maximum cooling power case in **Figure 7**, respectively. The performance of a transverse cooler can be readily predicted from **Figure 8** for any given heat load or cold side temperature, once the scales Q_0 and E_0 are known.

6. Conclusion

This review of $(p \times n)$ -transverse thermoelectrics explains the origin of materials with p -type Seebeck along one axis and n -type Seebeck orthogonal. The rigorous derivation of all thermoelectric transport tensors for anisotropic thermoelectric phenomena is given, as well as the transport equations from which one can derive all essential material performance parameters. The necessarily anisotropic band structure is expected to arise via anisotropic band or hopping conduction, whose transport tensors are derived for 3D, 2D and 1D effective mass approximations. The cooling power is expressed in a normalized notation relative to heat flux and electric field scales Q_0 and E_0 that are a function of the thermoelectric transport parameters. Numerical calculation of the maximum temperature difference and cooling power shows enhanced performance compared with longitudinal coolers with the same figure of merit. This work motivates the search for novel transverse thermoelectric materials with high figure of merit.

Acknowledgements

This work is supported by the Air Force Office of Scientific Research (AFOSR) Grant FA9550-15-1-0377 and the Institute for Sustainability and Energy at Northwestern (ISEN) Booster Award, and the work of M. Ma is supported by the China Scholarship Council program (No. 201406280070).

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