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Driving Perpendicular Heat Flow: \( p \times n \) Transverse Thermoelectrics for Microscale and Cryogenic Peltier Cooling

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Whereas thermoelectric performance is normally limited by the figure of merit \( ZT \), transverse thermoelectrics can achieve arbitrarily large temperature differences in a single leg even with inferior \( ZT \) by being geometrically tapered. We introduce a band-engineered transverse thermoelectric with p-type Seebeck in one direction and n-type orthogonal, resulting in off-diagonal terms that drive heat flow transverse to electrical current. Such materials are advantageous for microscale devices and cryogenic temperatures – exactly the regimes where standard longitudinal thermoelectrics fail. InAs/GaSb type II superlattices are shown to have the appropriate band structure for use as a transverse thermoelectric.

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In spite of their widespread success, conventional longitudinal thermoelectrics¹ have limited use in microscale devices, at cryogenic temperatures, and over large thermal gradients, whereas transverse thermoelectrics have distinct advantages in all these regimes. Longitudinal thermoelectrics require multicomponent device structures with extrinsic p- and n-doped materials and multiple stages to achieve large thermal differences, while transverse thermoelectrics require only one single thermoelectric material, making microscaled devices straightforward. In addition, whereas longitudinal thermoelectrics suffer from dopant freeze-out at low temperatures, transverse thermoelectric phenomena can be optimal near intrinsic doping when both electrons and holes transport heat, making them operable at cryogenic temperatures. Exponentially tapered transverse thermoelectrics² have demonstrated an additional advantage as infinite-stage Peltier refrigerators, predicted to cool to arbitrarily large temperature differences even with small figure of merit \( ZT \), whereas longitudinal thermoelectrics require multiple stages³ and large \( ZT \) values.¹

Transverse thermoelectric phenomena require the directional symmetry of the Seebeck tensor to be broken. The Nernst-Ettingshausen (N-E) effect uses an external magnetic field to break time-reversal symmetry thereby introducing off-diagonal terms in the Seebeck tensor and generating transverse heat flow.⁴ However practical application of the N-E effect is limited since a high 1.5 T magnetic field is required.⁵ Stacked synthetic transverse thermoelectrics have also been demonstrated which have structural asymmetry by alternately stacking macroscopic millimeter-thick slabs of semiconductor with large Seebeck coefficient upon (semi)metal slabs with large electrical and thermal conductivity.⁶⁻¹⁰ Transverse heat flow is induced when the current is skewed with respect to the layers. However, these macroscopic extrinsic slabs do not permit microscale or cryogenic devices.

We develop a band engineering strategy for \( p \times n \) transverse thermoelectrics ("\( p \)-cross-\( n \)"), whereby the anisotropic electron and hole conductivity tensors give rise to a large transverse Seebeck coefficient in the absence of an external magnetic field. \( p \times n \) type materials can be geometrically shaped to enhance thermoelectric performance. Transport equations based on an electron-hole two-band model define the optimal angle of electric current for inducing the maximum transverse figure of merit \( Z⊥T \). Bulk compounds are identified which have the necessary \( p \times n \) type characteristics. To illustrate band engineering strategies, Type II broken gap InAs/GaSb superlattices (T2SL)¹¹, which have been successfully used as infrared detectors¹², are shown here to give promising \( Z⊥T \) values at room temperature for use as nanoscale transverse thermoelectric refrigerators. The equations for thermoelectric transport in an exponentially tapered cooler are also derived. The concept of a crossover electric field \( E^\ast \) is introduced to distinguish optimal performance in thin and thick samples.

We begin with a description of how anisotropic electron and hole conduction gives rise to transverse thermoelectricity. Consider a semiconductor near intrinsic
doping with anisotropic electron and hole band conductivity tensors $\sigma_n, \sigma_p$ and isotropic Seebeck tensors $s_n, s_p$, where $a$ and $b$ axes define the principal material axes of anisotropy:

$$\sigma_n = \begin{bmatrix} \sigma_{n,aa} & 0 \\ 0 & \sigma_{n,bb} \end{bmatrix}, \quad \sigma_p = \begin{bmatrix} \sigma_{p,aa} & 0 \\ 0 & \sigma_{p,bb} \end{bmatrix},$$

$$s_n = \begin{bmatrix} s_n & 0 \\ 0 & s_n \end{bmatrix}, \quad s_p = \begin{bmatrix} s_p & 0 \\ 0 & s_p \end{bmatrix},$$

where $s_n < 0, s_p > 0$. The total conductivity tensor $\Sigma$ and total resistivity tensor $\rho$ are $\Sigma = P^{-1} = \sigma_n + \sigma_p$.

The Seebeck tensor for these two parallel bands,

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

is fundamentally different from stacked synthetic transverse thermoelectrics\textsuperscript{6–10} whose out-of-plane Seebeck is set by series electrical and thermal resistances of two different materials. Whereas single-band Seebeck tensors $s_n$ and $s_p$ are typically isotropic, conductivity tensors $\sigma_n$ and $\sigma_p$ can be strongly anisotropic, and Eq. (2) allows one to exploit this to weight the total Seebeck tensor to opposite signs for orthogonal directions. Defining a small parameter $\xi$ as the ambipolar conductivity ratio for a given direction, we define the $x$-direction as dominated by $p$-type conduction $\xi_a = \sigma_{p,aa}/\sigma_{n,aa} < 1$, and the $y$-direction by $n$-type $\xi_b = \sigma_{n,bb}/\sigma_{p,bb} < 1$. The variable $\xi$ determines how much the electron and hole contributions compensate the Seebeck effect in a given direction. The total Seebeck tensor

$$S = \begin{bmatrix} S_{p,aa} & 0 \\ 0 & S_{n,bb} \end{bmatrix},$$

has matrix elements which are positive and negative, respectively, provided $\xi_a < |s_p/s_n|$ and $\xi_b < |s_n/s_p|$,

$$S_{p,aa} = \frac{s_n + \xi_b s_p}{1 + \xi_b} > 0, \quad S_{n,bb} = \frac{s_p + \xi_a s_n}{1 + \xi_a} < 0,$$

(4)

As shown for stacked synthetic transverse thermoelectrics,\textsuperscript{6–10} such a diagonal tensor can yield off-diagonal Seebeck terms in a rotated $(x, y)$ transport basis, with current flow $\mathbf{J} = J_\mathbf{x} \mathbf{x}$ defining the $x$-axis [Fig. 2 (a)]. Equations (5)-(13) apply in general to all transverse thermoelectrics,\textsuperscript{6–10} but are rederived here to aid our subsequent discussion of tapered geometries. With Peltier tensor $\Pi$, the total Peltier heat flux density becomes $Q_{\Pi} = \Pi \mathbf{J} = (TS)\mathbf{J}$ with longitudinal and transverse components,

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

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

(5)

The total heat flux density $Q = Q_{\Pi} - \kappa^c \nabla T$ includes both Peltier and thermal conduction effects, where $\kappa^c$ as noted in Ref.\textsuperscript{5} defines the open-circuit thermal conductivity tensor at $\mathbf{J} = 0$. Provided the thermal gradient is orthogonal to the current density $\nabla T = \frac{dT}{dy} \mathbf{y}$, the longitudinal electric field component $E_x$ is constant everywhere,$^5$ and the heat flux component $Q_x$ will depend only on $y$. The longitudinal current and transverse flow are

$$J_x = \frac{1}{\rho_{xx}} E_x - \frac{S_{xx}}{\rho_{xx}} \frac{dT}{dy},$$

$$Q_y = T \frac{S_{xy}}{\rho_{xx}} E_x - (1 + Z_{xy}) T \kappa_{yy} \frac{dT}{dy},$$

(7)

with transverse figure of merit $Z_{xy} T = S_{xy} S_{yy}/\kappa_{yy}$. Steady state requires $\nabla \cdot \mathbf{J} = 0$ and $\nabla \cdot (q + \Pi \mathbf{J}) = 0$, where the scalar $q$ is the electrochemical potential, and $-\nabla T = E$ the electric field. Longitudinal Joule heating $E_x J_x$ sourced a divergence in the transverse heat flux density $Q_y$:

$$\frac{dQ_y}{dy} = E_x J_x.$$

(9)

Equations (7)-(9) define the differential equation,

$$0 = -\frac{1}{S_{xx} S_{yy}} E_x^2 - \frac{S_{xx} + S_{yy}}{S_{xx} S_{yy}} + \left[ \frac{d\ln(S_{xx}/\rho_{xx})}{dT} + \frac{1 + Z_{xx} T}{Z_{xx} T} \right] \left( \frac{dT}{dy} \right)^2 + \frac{1 + Z_{xx} T}{Z_{xx} T} \frac{d^2 T}{dy^2}$$

(10)

which with constant thermoelectric coefficients becomes

$$0 = \left( \frac{E_x}{S_{xx}} - \frac{dT}{dy} \right)^2 + \frac{1 + Z_{xx} T}{Z_{xx} T} \frac{d^2 T}{dy^2}.$$

(11)

Note this equation differs from the N-E effect, whose magnetic field requires $S_{xy} = -S_{yx}$ cancelling all $\frac{dT}{dy}$ terms in (10) and permitting analytical integration, whereas for transverse thermoelectrics $S_{xy} = S_{yx}$, preserving the $\frac{dT}{dy}$ term and requiring numerical integration.

The angle $\theta_\perp$, which maximizes $Z_{xy}(\theta) T$ defines\textsuperscript{6–10} the parameter $Z_{\perp} T$

$$\cos^2 \theta_\perp = \frac{1}{1 + \left( \frac{S_{xx} - S_{yy}}{\rho_{xx} \kappa_{aa}} \right)^2}$$

(12)

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

(13)

The angle $\theta_\perp$ is independent of the Seebeck anisotropy, and approaches $\pi/4$ when the thermal conductance anisotropy matches the resistance anisotropy $\frac{\kappa_{bb}}{\kappa_{aa}} = \frac{\rho_{bb}}{\rho_{aa}}$. To optimize the electronic band structure it is useful to define a power factor $PF_\perp$ from Eq. (13) under the assumption of isotropic $\kappa$ because $S$ and $\rho$ tensors can be readily calculated with simple scattering assumptions:

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

(14)

The signature of $p \times n$ type materials is thus the $p$-type Seebeck in one direction, and $n$-type perpendicular, arising from anisotropic band conductivity as shown above. Compounds have been shown to exhibit this property, with two noteworthy candidates RhGe$_2$Si$_{1.75-x}$.
with $S_p = +160 \, \mu V/K$ and $S_n = -300 \, \mu V/K$ in the $a$-
and $c$-directions, and CsBi$_4$Te$_6$ with $S_p = +100 \, \mu V/K$
and $S_n = -80 \, \mu V/K$ in the $b$- and $c$-directions
respectively. In addition, weaker ambipolar Seebeck
anisotropies have been reported for PtCoO$_2$, PdCoO$_2$
and related materials.\textsuperscript{15} Although unipolar oxides like
YBCO,\textsuperscript{16} LCMO,\textsuperscript{17} and stoichiometries of CaCoO$_3$\textsuperscript{18}
have been shown to exhibit a weak transverse Seebeck
component $S_{ab} \approx 1 - 35 \, \mu V/K$ when heat flows off-axis,
the ambipolar effect introduced here can exceed this by
an order of magnitude.

To illustrate how $p \times n$ type behavior arises microscopically,
we consider a band engineering example below. We
introduce the InAs/GaSb T2SL\textsuperscript{11} as a promising $p \times n$
type material with its tunable band gap and anisotropic
electrical conductivity tensor. The bandgap is tunable
down to zero gap since the GaSb valence band lies ener-
getically above the InAs conduction band, thus the addi-
tional quantum confinement energy can tune the gap
as the superlattice period is varied. The tunable gap has
made the T2SL useful material for low-dark current in-
frared detectors and emitters.\textsuperscript{12} The relatively large tun-
neling mass of holes and small tunneling mass of electrons
makes the electrons to dominate the out-of-plane transport
and with the appropriate chemical potential, the
holes will dominate the in-plane transport. In the effec-
tive mass approximation, the conductivity and Seebeck
tensor components become\textsuperscript{19}

$$
\sigma_{n,aa} = \frac{2\sqrt{\pi} \gamma}{3\pi^2 h^2} \sqrt{m_{n,b}} (k_B T)^{s+1/2} \Gamma(s + \frac{5}{2}) F_{s+1/2} \left( \frac{\mu - E_g}{k_B T} \right)
$$

$$
\sigma_{n,bb} = \frac{2\sqrt{\pi} \gamma}{3\pi^2 h^2} \sqrt{m_{n,b}} (k_B T)^{s+1/2} \Gamma(s + \frac{5}{2}) F_{s+1/2} \left( \frac{\mu - E_g}{k_B T} \right)
$$

$$
\sigma_{p,aa} = \frac{2\sqrt{\pi} \gamma}{3\pi^2 h^2} (k_B T)^{s+1/2} \Gamma(s + 2) F_{s+1} \left( \frac{\mu}{k_B T} \right)
$$

$$
\sigma_{p,bb} = 0
$$

$$
s_n = \frac{k_B}{e} \left[ \frac{(s + 2) F_{s+1} \left( \frac{\mu - E_g}{k_B T} \right)}{(s + \frac{5}{2}) F_{s+1/2} \left( \frac{\mu - E_g}{k_B T} \right)} - \frac{\mu - E_g}{k_B T} \right]
$$

$$
s_p = \frac{k_B}{e} \left[ \frac{(s + 2) F_{s+1} \left( \frac{\mu}{k_B T} \right)}{(s + 1) F_s \left( \frac{\mu}{k_B T} \right)} + \frac{\mu}{k_B T} \right]
$$

where $m_i$ represents the effective mass of the band $n$ or $p$ in the direction $a$ or $b$. The electrochemical potential $\mu$
is measured relative to the valence band-edge, and $F$ is the Fermi-Dirac integral $F_r(x) = \int_0^\infty \frac{1}{1 + e^{-(x+\xi) r}}$. The scattering time $\tau = \gamma E^s$ obeys a power law in the kinetic
energy of the carrier $E$. Since T2SL scattering at room
temperature is dominated by interface scattering,\textsuperscript{20} we
assume the power $s = 0$. Then $\gamma$ can be calculated from
equation $\gamma = \tau = \frac{m^*}{m}$, $m^*$ where is the carrier effective
mass and $e$ is the electron charge.

The band structure of the T2SL is calculated with the
nextnano 8 $k$-$p$ envelope function method.\textsuperscript{21,22} Applying
Eq. (14) and Eq. (15), the power factor $PF_\tau$ can be
optimized over all possible $(N, M)$-SLs where integers $N$
and $M$ count monolayers per period for InAs and GaSb,
respectively. To minimize space-charge effects, we pin $\mu$
mid the mid-gap, but note that $p$-doping can improve the
performance. At 300 K, the results yield (27,10)-SL as
the optimal layer thicknesses. The electron and hole effec-
tive masses are $m_{n,a} = 0.028 m_0$, $m_{n,b} = 0.025 m_0$
and $m_{p,a} = 0.047 m_0$ where $m_0$ is the free electron mass.
The energy gap is $E_g = 34.2$ meV, with scattering coeffi-
cient $\gamma = 0.163$ ps from experimental T2SL data.\textsuperscript{20} The
longitudinal electrical resistivity is $\rho_{xx} = 255$ m$\Omega$ and
the transverse Seebeck coefficient is $S_{xx} = 320 \frac{V}{K}$. The
resulting optimal angle is $\theta_{\parallel} = 37^\circ$, which means that
most of the heat flow will be perpendicular to the su-
perlattice, so the thermal conductivity is dominated by
the out-of-plane component, experimentally measured\textsuperscript{23}
as $\kappa = 4 \frac{W}{m \cdot K}$. The room temperature optimal figure of
merit is $Z_{\parallel} T = 0.030$. Typically out-of-plane thermal
conductivity is less than in-plane $\frac{\kappa_{in}}{\kappa_{in}} < 1$, reducing
the optimal angle $\theta_{\parallel}$ even more according to Eq. (12).

Another recently developed type II superlattice mate-
rial, the InAs/InAs$_{1-x}$Sb$_x$ superlattice, may also prove
useful for $p \times n$ type materials, having wider gaps and
therefore operating at higher temperatures.\textsuperscript{24} The
ambipolar superlattices described here are to be contrasted
with unipolar superlattice strategies which rely on quan-
turn confinement\textsuperscript{25} or topological interface states\textsuperscript{26} to
enhance the unipolar Seebeck coefficient, but which do not
consider transverse heat flow or simultaneous ambipolar
contributions to the thermoelectric performance.

The maximum $\Delta T = T_H - T_C$ is reached when the
heat load at the cold side is zero, $Q_{in}(T_C) = 0$. The
temperature profile in Fig. 2 (a) for this $Z_{\parallel} T$ yields a
total temperature difference $\Delta T = 4.5$ K. To distinguish
from other Peltier strategies, we compare to both lon-
gitudinal and N-E cooling for the same $Z T$ values and
same Seebeck coefficient $320 \frac{V}{K}$, and solve the tempera-
ture profile with $ZT_H = 0.15$ or $ZT_H = 0.5$ in Fig. 2 (a).
The maximum temperature differences of 20 K and 56 K,
respectively, are shown. Transverse cooling (solid line) is slightly better than the longitudinal thermoelectric cooling (dotted line), and the thermal profile is distinctly different from the N-E effect for a hypothetical material with the same ZT value (dashed line).

Because of their ambipolar nature, n × p type material can cool to arbitrarily low temperatures. Unlike standard longitudinal thermoelectric semiconductors which rely on extrinsic doping that freezes out at low temperatures, the thermoelectric cooling mechanism here is fundamentally intrinsic. Low operation temperatures for n × p can be achieved with sufficiently small E_g such that electron and hole pairs can be thermally excited across the bandgap. Figure 2 (b) shows the temperature profile with the heat sink temperature T_H = 77 K for ZT = 0.030, 0.15 and 0.5, yielding the maximum temperature differences of 1.2 K, 5.3 K and 14.5 K, respectively.

More dramatic improvements in cooling power can be expected for transverse thermoelectrics by exploiting tapered geometries. As shown in Fig. 3 (b), an exponentially tapered device has a wide base on the heat-sink side, and a narrow strip at the refrigerated load. The exponential taper is in the z-direction, orthogonal to both the current direction and the heat flow, z = z_0 e^{-y/L}, and L sets the characteristic length scale of the taper. Tapered N-E transverse coolers were shown to induce large temperature differences when a tapered Bi_2Se_3 semiconductor in a 1.5 T magnetic field cooled from 156 K down to 102 K. Whereas cascaded longitudinal Peltier coolers are limited by electrical and thermal contact resistance, tapered transverse thermoelectrics result in infinite-stage cascading since the current and heat flow are perpendicular to each other, allowing for much simpler device geometries and micron-scale fabrication. Following the analysis of Kooi et al., for the N-E effect, this exponential tapering adds the term of Q_y / dy to the right of Eq. (9), and the following term to the right of Eq. (11), \( -\left(1 + Z \frac{\Delta T}{(S \times T)} \frac{\partial T}{\partial y} - E / S \right) T / L. \)

Figure 3 shows the T2SL temperature profile solved for Z \( \Delta T = 0.030 \) with different device thicknesses at optimal electric fields for both (a) a rectangular cooler without tapering, and (b) an exponentially tapered device. For the rectangular cooler, \( \Delta T \) is independent of layer thickness, whereas the exponential tapering increases \( \Delta T \) with increasing sample thickness. Assuming an experimentally proven tapering factor of y/L = 2.77, the n × p temperature difference should double to \( \Delta T = 9.1 \) K. This is competitive with recent experimental results in on-chip cooling in significantly more complex device structures made of superlattice-based longitudinal thin-film thermoelectrics, which cooled only 7.1 K on average. For Z \( \Delta T = 0.15 \) and 0.5, the exponential tapering can also increase \( \Delta T \) to 40 K and 97 K, respectively, almost doubling the temperature drop for all cases. For micron scale applications, the tapered structure could be a 10 \( \mu \)m thick n × p type cooler with a 32 \( \mu \)m wide heat sink and a 2 \( \mu \)m wide cooled surface – dimensions far smaller than that achievable with standard longitudinal coolers which require both p- and n-doped legs.

By setting \( \frac{dT}{dy} = 0 \) in the modified Eq. (11), the solution for \( E \) defines an important electric field scale for tapered devices, \( E^\ast = \left(\frac{2 \pi}{3 \gamma} \right) \). When \( E > E^\ast \), n × p type cooling perfectly compensates Joule heating and \( T \) is everywhere constant. For \( E > E^\ast \), \( T(y) \) has a local maximum \( \frac{dT}{dy} = 0 \) at \( y = 0 \), and optimal thermal profiles for various sample thicknesses y/L are shown with solid lines in Fig. 3(b), top. For \( E < E^\ast \), \( \frac{dT}{dy} \neq 0 \) everywhere, and \( \frac{dT}{dy} \) has a finite slope at \( y = 0 \), plotted with dashed lines in Fig. 3(b), top. In the bottom of panels Fig. 3(a) and (b), the corresponding optimal electric fields are plotted, with a horizontal line indicating \( E^\ast \). Large electric fields \( E > E^\ast \) are seen to provide effective cooling for thin samples y/L \( \lesssim 1 \), whereas small electric fields \( E < E^\ast \) cool better for thick samples y/L \( \gtrsim 1 \).

In conclusion, p × n type materials will enable new regimes of thermoelectric operation in microscale and cryogenic devices. The intrinsic nature of the effect simplifies future thermoelectric devices, allowing a single layer of material to define a complete device, instead of traditional structures which require both n- and p-legs that become difficult to manufacture on the micron scale. One could envision, for example, a planar lithographic thin film of p × n type material to extract heat vertically from the surface upon applying an in-plane electrical current. The defining equations for the Seebeck tensor are shown to be distinctly different from previously studied stacked synthetic transverse thermoelectrics. Exponential tapering can enhance the thermoelectric performance.
formance, and even thin-film devices can be tapered to double the temperature difference. Thicker tapered materials will be able to cool to arbitrarily low temperatures even with small $Z_{\perp}T$. The intrinsic cooling mechanism can function at cryogenic temperatures, thus promising to fill a gap in thermoelectric cooling capabilities that currently exists below 150 K.

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