Optimal thermoelectric materials: beyond the Mahan-Sofo approach

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Outline

Statement of the problem

definition of transport coefficients & Onsager relations:

$$\begin{aligned} \mathbf{j} &= \sigma \mathbf{E} + K(-\nabla T) \\ \mathbf{j}_Q &= TK\mathbf{E} + \kappa_0(-\nabla T) \end{aligned}$$

Peltier and Seebeck coefficients, thermal conductivity at no current:

$$\mathbf{j}_Q = \Pi \mathbf{j} + \kappa(-\nabla T), \qquad \Pi = TS = TK/\sigma, \qquad \kappa = \kappa_0 - TK^2/\sigma$$

figure of merit:

$$ZT = \frac{T\sigma S^2}{\kappa}$$

question: within semi-classical Boltzmann's transport theory, what are the possibilities to achieve the highest possible ZT?

Thermodynamic inequalities

entropy production:

$$T\dot{\mathcal{S}} = \mathbf{j}\cdot\mathbf{E} + \frac{1}{T}\,\mathbf{j}_Q\cdot(-\nabla T) = (\mathbf{E}, -\nabla T)\begin{pmatrix} \sigma, & K \\ K, & \kappa_0/T \end{pmatrix}\begin{pmatrix} \mathbf{E} \\ -\nabla T \end{pmatrix} > 0$$

thermodynamic inequalities:

$$\sigma > 0, \qquad \kappa_0 > 0, \qquad \xi = \frac{TK^2}{\sigma\kappa_0} < 1$$

figure of merit:

$$ZT = \frac{T\sigma S^2}{\kappa} = \frac{\xi}{1-\xi} \to \infty \qquad \text{for} \qquad \xi \to 1$$

for $\xi \to 1$, $\mathbf{E}$ and $-\nabla T$ can be chosen so that $\dot{\mathcal{S}} \to 0$ (no dissipation)

Mahan-Sofo analysis: decoupling of electrons and phonons

Mahan and Sofo: standard transport theory with 2 additional assumptions:

- decoupled electrons and phonons (absence of phonon drag)
- relaxation time approximation

In absence of drag effects:

$$\kappa_0 = \kappa_{0e} + \kappa_p, \qquad \xi_e = \frac{TK^2}{\sigma\kappa_{0e}} < 1, \qquad ZT = \frac{\xi_e}{1 - \xi_e + \frac{\kappa_p}{\kappa_{0e}}}$$

Optimal thermoelectric material:

$$\kappa_p \ll \kappa_{0e} \qquad \text{(phonon glass/electron crystal)}$$
$$\xi_e \to 1 \qquad \text{(electronically optimal material)}$$

Mahan-Sofo analysis: relaxation time approximation

transport function: $\Sigma_{MS}(\varepsilon) = \frac{2}{\Omega}\sum_k (v_k \cdot n)^2 \tau_k \delta(\varepsilon - \varepsilon_k)$, transport coefficients:

$$\sigma = e^2 \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma_{MS}(\varepsilon), \qquad K = -e \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma_{MS}(\varepsilon) \frac{\varepsilon - \mu}{T}$$

$$\kappa_{0e} = T \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma_{MS}(\varepsilon) \left(\frac{\varepsilon - \mu}{T}\right)^2$$

Cauchy-Schwarz inequality: $\xi_e = \frac{TK^2}{\sigma \kappa_{0e}} < 1$

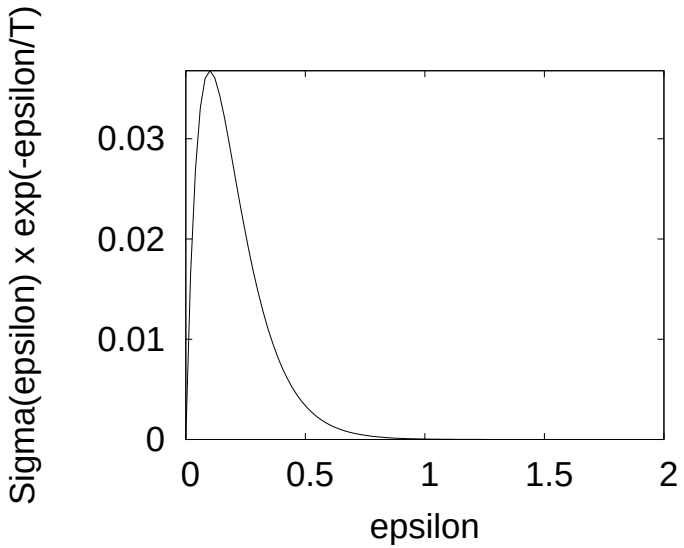
electronic optimum $\xi_e \to 1$ achieved for $\left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma_{MS}(\varepsilon) \propto \delta(\varepsilon - E_0)$, $E_0 \neq \mu$
but $\xi_e \to 1$ equivalent to $\kappa_e = \kappa_{0e}(1 - \xi_e) \to 0$, therefore $\mathbf{j}_{Qe} = \Pi \mathbf{j}$:

each electron carries the same charge $(-e)$ and the same heat $E_0 - \mu$

Electronically optimal thermoelectrics: trivial example

consider an n-type doped band insulator, $\Sigma_{MS}(\varepsilon) \propto \varepsilon^{3/2}$
the chemical potential μ lies outside the band, $\mu < 0$, and $|\mu| \gg T$; then

$$\xi_e = \frac{\left[\int_0^\infty \exp(-\varepsilon/T)\varepsilon^{3/2}(\varepsilon-\mu)\right]^2}{\int_0^\infty \exp(-\varepsilon/T)\varepsilon^{3/2} \int_0^\infty \exp(-\varepsilon/T)\varepsilon^{3/2}(\varepsilon-\mu)^2} \approx 1$$



$\Sigma_{MS}(\varepsilon)\exp(-\varepsilon/T)$ for $T = 0.1$

figure of merit in an electronically optimal material:

$$ZT = \frac{\xi_e}{1 - \xi_e + \frac{\kappa_p}{\kappa_{0e}}} = \frac{\kappa_{0e}}{\kappa_p}$$

Outline

Boltzmann equation: variational solution

distribution function: $f_k = f_k^0 + \Phi_k \left(-\frac{\partial f^0}{\partial \varepsilon_k}\right)$
linearized Boltzmann eq. for scattering off impurities and collective modes:

$$\left[v_k^z(-eE) + \frac{\varepsilon_k - \mu}{T} v_k^z(-\nabla_z T)\right]\left(-\frac{\partial f^0}{\partial \varepsilon_k}\right) = \sum_{k'} W_{k,k'}(\Phi_k - \Phi_{k'})$$

variational ansatz (Ziman): $\Phi_k = \alpha X_k^1 + \beta X_k^2$, $X_k^1 = v_k^z$, $X_k^2 = \frac{\varepsilon_k - \mu}{T} v_k^z$
scattering matrix: $P_{ij} = \frac{1}{\Omega} \sum_{k,k'} W_{k,k'}(X_k^i - X_{k'}^i)(X_k^j - X_{k'}^j)$
electric and thermal currents in the variational states X^i:

$$J_i = \frac{2}{\Omega} \sum_k \left(-\frac{\partial f^0}{\partial \varepsilon_k}\right) v_k^z X_k^i, \qquad U_i = \frac{2}{\Omega} \sum_k \left(-\frac{\partial f^0}{\partial \varepsilon_k}\right) \frac{\varepsilon_k - \mu}{T} v_k^z X_k^i$$

Mahan-Sofo coefficient for the variational solution

transport coefficients

$$\sigma = e^2 J_i \left(P^{-1}\right)_{ij} J_j, \qquad K = -eJ_i \left(P^{-1}\right)_{ij} U_j, \qquad \kappa_{0e} = TU_i \left(P^{-1}\right)_{ij} U_j$$

Mahan-Sofo coefficient:

$$\xi_e = \frac{\left[J_i \left(P^{-1}\right)_{ij} U_j\right]^2}{\left[J_i \left(P^{-1}\right)_{ij} J_j\right] \left[U_i \left(P^{-1}\right)_{ij} U_j\right]}$$

inverse matrix: $P^{-1} = \frac{1}{P_{11}P_{22}-P_{12}^2} \begin{pmatrix} P_{22}, & -P_{12} \\ -P_{12}, & P_{11} \end{pmatrix}$

Cauchy-Schwarz: $P_{11}P_{22} - P_{12}^2 > 0$
P^{-1} is a positive-definite real symmetric matrix

Electronically optimal thermoelectrics

P^{-1} is a positive-definite real symmetric matrix, therefore

$$P^{-1} = O^T \Lambda O, \qquad O^T O = 1, \qquad \Lambda = \begin{pmatrix} \lambda_1, & 0 \\ 0, & \lambda_2 \end{pmatrix} \qquad \lambda_1, \lambda_2 > 0$$

define $\mathcal{J} = \Lambda^{1/2} O J$ and $\mathcal{U} = \Lambda^{1/2} O U$
Cauchy-Schwarz inequality for the Mahan-Sofo coefficient

$$\xi_e = \frac{\left[J_i \left(P^{-1}\right)_{ij} U_j\right]^2}{\left[J_i \left(P^{-1}\right)_{ij} J_j\right] \left[U_i \left(P^{-1}\right)_{ij} U_j\right]} = \frac{\left(\mathcal{J}^T \mathcal{U}\right)^2}{\left(\mathcal{J}^T \mathcal{J}\right)\left(\mathcal{U}^T \mathcal{U}\right)} < 1$$

optimal thermoelectric material:

- $\mathcal{J} \propto \mathcal{U}$ and therefore $J \propto U$
- singular scattering matrix, $P_{11} P_{22} - P_{12}^2 \to 0$ (not considered)

Mahan-Sofo like parameter η

define a new transport function $\Sigma(\varepsilon) = \frac{2}{\Omega} \sum_k (v_k \cdot n)^2 \delta(\varepsilon - \varepsilon_k)$
charge and thermal currents in the variational states X^1 and X^2:

$$J_1 = \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma(\varepsilon), \qquad J_2 = \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma(\varepsilon) \frac{\varepsilon - \mu}{T}$$

$$U_1 = \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma(\varepsilon) \frac{\varepsilon - \mu}{T}, \qquad U_2 = \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma(\varepsilon) \left(\frac{\varepsilon - \mu}{T}\right)^2$$

define an analog of the Mahan-Sofo parameter ξ

$$\eta = \frac{J_2 U_1}{J_1 U_2} = \frac{\left[\int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma(\varepsilon) \frac{\varepsilon - \mu}{T}\right]^2}{\left[\int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma(\varepsilon)\right] \left[\int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma(\varepsilon) \left(\frac{\varepsilon - \mu}{T}\right)^2\right]}$$

optimal material: $\eta \to 1$; this is realized for $\left(-\frac{\partial f^0}{\partial \varepsilon}\right) \Sigma(\varepsilon) \propto \delta(\varepsilon - E_0)$, $E_0 \neq \mu$

Systems with a structure in the transport function

assume that $\Sigma(\varepsilon)$ varies in the vicinity of μ at an energy scale Δ

Sommerfeld expansion: $\eta \approx \frac{\pi^2}{3}\left[\frac{T\Sigma'(\mu)}{\Sigma(\mu)}\right]^2 \sim \left(\frac{T}{\Delta}\right)^2$

need a small energy scale Δ

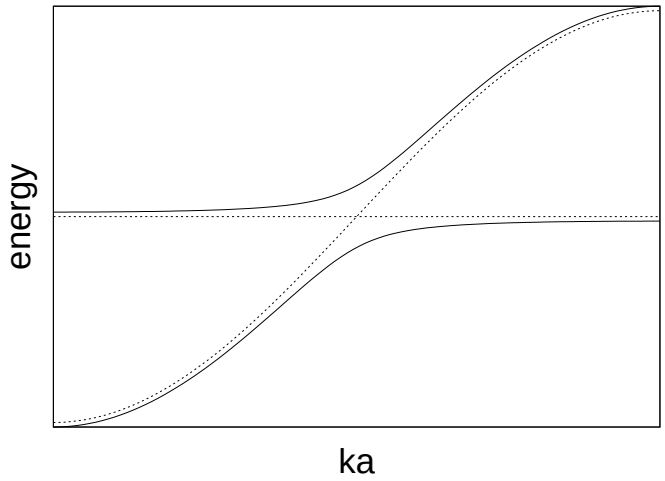
possible realizations:

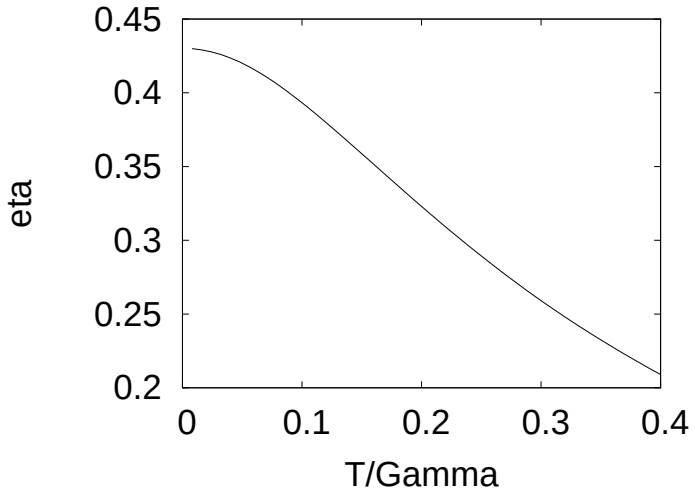
- doped semiconductors
- hybridization with localized levels (Mahan & Sofo)
- van Hove singularities
- resonant tunneling (Murphy, Mukerjee, & Moore for molecular junctions)
- Kondo effect (not considered here)
- ...

Example: hybridization with localized levels

band states ε_k hybridized with (periodically positioned) localized levels E_0

transport function $\Sigma(\varepsilon) = \frac{2}{3\Omega} \sum_{k\pm} (v_{k\pm})^2 \, \delta(\varepsilon - E_{k\pm}) \propto \frac{(\varepsilon - E_0)^2}{(\varepsilon - E_0)^2 + \Gamma^2}$





dispersion

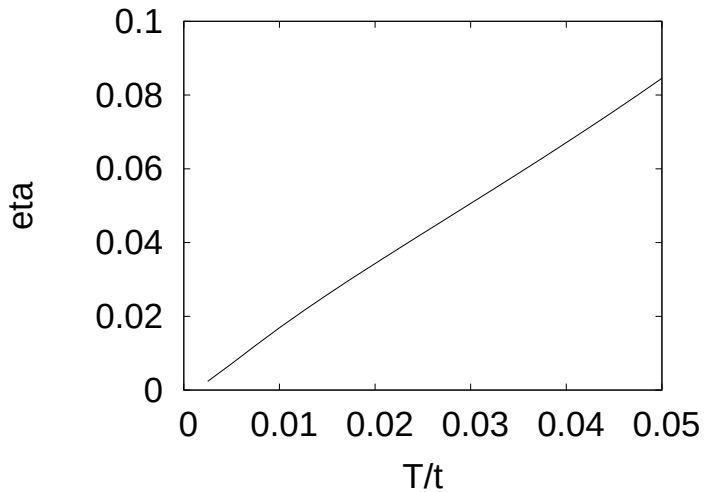
$$E_{k\pm} = \frac{\varepsilon_k + E_0}{2} \pm \sqrt{\left(\frac{\varepsilon_k - E_0}{2}\right)^2 + \Gamma^2}$$

Mahan-Sofo like parameter η as a function of temperature for optimal $\mu \approx E_0 \pm 2T$

Example: van Hove singularities

3D: no singularities of $\Sigma_i(\varepsilon) = \frac{2}{\Omega}\sum_k \left(v_k^i\right)^2 \delta(\varepsilon - \varepsilon_k)$;
2D & current along the plane: singularity of $N(\varepsilon)$ cancelled by $v_k^{x,y} \to 0$;
2D & current across the planes, if $\varepsilon_k = \varepsilon_{\|} - 2t_\perp \cos k_\perp a_\perp$:

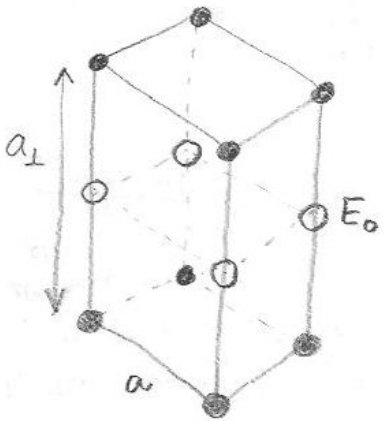
$$\Sigma_\perp(\varepsilon) = \frac{8t_\perp^2 a_\perp}{\pi\hbar^2}\int_{-1}^{1} dx\sqrt{1-x^2}N_{\|}(\varepsilon - 2t_\perp x) \sim \frac{t_\perp^2 a_\perp}{\hbar^2 t a^2}\ln\left(\frac{t^2}{\varepsilon^2 + t_\perp^2}\right)$$

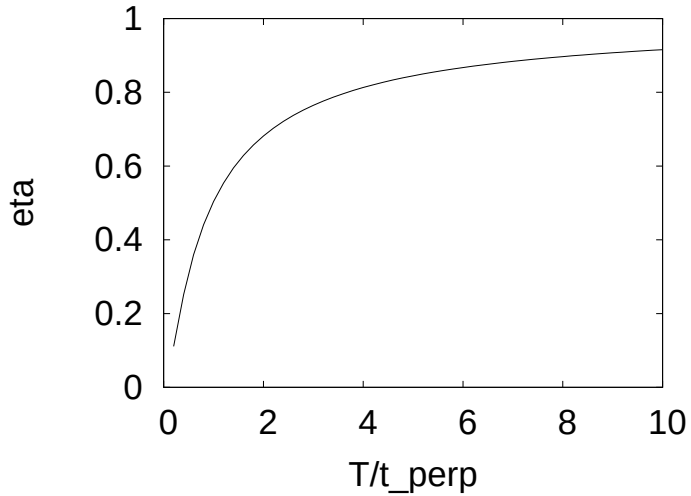


Mahan-Sofo like parameter η as a function of temperature for $t_\perp/t = 0.01$ and optimal μ

Example: resonant interlayer tunneling

spectrum $\varepsilon_{k\pm} = \frac{\varepsilon_\parallel(k)+E_0}{2} \pm \sqrt{\left(\frac{\varepsilon_\parallel(k)-E_0}{2}\right)^2 + 4t_\perp^2 \cos^2\left(\frac{k_\perp a_\perp}{2}\right)}$





transport function

$$\Sigma_\perp(\varepsilon) \sim \frac{t_\perp^2 a_\perp N_\parallel(0)/\hbar^2}{1+\left|\frac{\varepsilon-E_0}{t_\perp}\right|+(\frac{\varepsilon-E_0}{t_\perp})^2}$$

Mahan-Sofo like parameter η as a function of temperature for optimal $\mu \approx E_0 \pm 2.5T$

$\eta \to 1$ realized for $t_\perp \ll T$; need small $t_\perp$
small $t_\perp$ implies small κ_{0e}; need a phonon glass to increase κ_{0e}/κ_p

Outline

Coupled Boltzmann eqs. for electrons and phonons

distribution functions for electrons and phonons

$$f_k = f_k^0 + \Phi_k \left(-\frac{\partial f^0}{\partial \varepsilon_k} \right), \qquad n_q = n_q^0 + \Psi_q \left(-\frac{\partial n^0}{\partial \hbar\omega_q} \right)$$

linearized Boltzmann eqs. for electron-phonon and impurity scattering:

$$\left[v_k^z(-eE) + \frac{\varepsilon_k - \mu}{T} v_k^z(-\nabla_z T) \right] \left(-\frac{\partial f^0}{\partial \varepsilon_k} \right) = \sum_q W_{k,k+q}^{ep(1)} (\Phi_k - \Phi_{k+q} + \Psi_q) + \sum_{k'} W_{k,k'}^{e} (\Phi_k - \Phi_{k'})$$

$$\frac{\hbar\omega_q}{T} v_q^z(-\nabla_z T) \left(-\frac{\partial n^0}{\partial \hbar\omega_q} \right) = \sum_k W_{k,k+q}^{ep(2)} (\Phi_k - \Phi_{k+q} + \Psi_q) + \sum_{q'} W_{q,q'}^{p} (\Psi_q - \Psi_{q'})$$

Variational solution for electrons and phonons

variational ansatz with parameters $c^T = (c_1, c_2, c_3)$:

$$\Phi_k = c_1 X_k^1 + c_2 X_k^2, \qquad \Psi_q = c_3 X_q^3$$

after projecting on X^i, the Boltzmann equations read

$$P_{ij} c_j = (-eE) J_i + (-\nabla_z T) U_i$$

J_i and U_i are electric and thermal currents in the variational states X^i:

$$J_1 = \frac{2}{\Omega} \sum_k \left(-\frac{\partial f^0}{\partial \varepsilon_k} \right) v_k^z X_k^1, \qquad U_2 = \frac{2}{\Omega} \sum_k \left(-\frac{\partial f^0}{\partial \varepsilon_k} \right) \frac{\varepsilon_k - \mu}{T} v_k^z X_k^2$$

$$J_2 = \frac{2}{\Omega} \sum_k \left(-\frac{\partial f^0}{\partial \varepsilon_k} \right) v_k^z X_k^2, \qquad U_2 = \frac{2}{\Omega} \sum_k \left(-\frac{\partial f^0}{\partial \varepsilon_k} \right) \frac{\varepsilon_k - \mu}{T} v_k^z X_k^2$$

$$J_3 = 0, \qquad U_3 = \frac{1}{\Omega} \sum_q \left(-\frac{\partial n^0}{\partial \hbar\omega_q} \right) \frac{\hbar\omega_q}{T} v_q^z X_q^3$$

Definition and properties of the scattering matrix P_{ij}

$$
\begin{aligned}
P_{ij} &= \frac{1}{\Omega}\sum_{k,k'}(W^{ep}_{k,k'}+W^{e}_{k,k'})(X^i_k - X^i_{k'})(X^j_k - X^j_{k'}), \qquad i,j=1,2\\
P_{i3} &= P_{3i} = \frac{1}{\Omega}\sum_{k,q} W^{ep}_{k,k+q}(X^i_k - X^i_{k+q})X^3_q\\
P_{33} &= \frac{1}{\Omega}\sum_{k,q} W^{ep}_{k,k+q}(X^3_q)^2 + \frac{1}{2\Omega}\sum_{q,q'} W^{p}_{q,q'}(X^3_q - X^3_{q'})^2
\end{aligned}
$$

entropy production in a variational state described by c: $T\dot{\mathcal{S}} = c^T P c > 0$
P_{ij} is a positive definite matrix:

$$P_{11}, P_{22}, P_{33} > 0, \qquad P_{11}P_{33} > P_{13}^2, \qquad \ldots$$

Mahan-Sofo parameter of the electron-phonon system

formal solution for the transport coefficients:

$$\sigma = e^2 J^T P^{-1} J, \qquad K = -eJ^T P^{-1} U, \qquad \kappa_0 = TU^T P^{-1} U$$

Mahan-Sofo parameter:

$$\xi = \frac{\left(J^T P^{-1} U\right)^2}{\left(J^T P^{-1} J\right)\left(U^T P^{-1} U\right)}, \qquad ZT = \frac{\xi}{1-\xi}$$

optimal thermoelectrics $\xi \to 1$ realized for $J \propto U$ (Cauchy-Schwarz)
this is however impossible, since $J_3 = 0$ and $U_3 \neq 0$

solutions:
1. look for systems with $U_1, U_2 \gg U_3$; optimize the purely electronic problem
2. nearly singular scattering matrix, $P_{11}P_{33} - P_{13}^2 \to 0$

Thermopower in a particle-hole symmetric system

assume $P_{12} = P_{23} = J_2 = U_1 = 0$; in that case

$$\sigma = \frac{e^2 J_1^2}{P_{11} - P_{13}^2/P_{33}}, \qquad S = \frac{1}{e}\frac{U_3}{J_1}\frac{(-P_{13})}{P_{33}}, \qquad \kappa = \frac{TU_2^2}{P_{22}} + \frac{TU_3^2}{P_{33}} = \kappa_e + \kappa_p$$

figure of merit:

$$ZT = \frac{r}{1-r} \times \frac{\kappa_p}{\kappa_p + \kappa_e}, \qquad r = \frac{P_{13}^2}{P_{11} P_{33}}$$

contributions of various scattering processes:

$$\begin{aligned} P_{11} &= P_{11}^{ep} + P_{11}^{imp} + P_{11}^{ee} + \dots \\ P_{33} &= P_{33}^{ep} + P_{33}^{imp} + P_{33}^{pp} + P_{33}^{bound} + \dots \\ P_{13} &= P_{13}^{ep} \end{aligned}$$

novel strategy: look for $\kappa_p \gg \kappa_e$ and $r \to 1$

Electron-phonon coupling

choose $X^1_k = \frac{\hbar k_z}{m^*}$ and $X^3_q = \frac{\hbar v_s^2 q_z}{T}$; then (with no umklapps)

$$P^{ep}_{11} = \frac{1}{\Omega}\sum_{k,q} W^{ep}_{k,k+q}(X^1_k - X^1_{k+q})^2 = \left(\frac{\hbar}{m^*}\right)^2 \times \frac{1}{\Omega}\sum_{k,q} W^{ep}_{k,k+q} q_z^2$$

$$P^{ep}_{33} = \frac{1}{\Omega}\sum_{k,q} W^{ep}_{k,k+q}(X^3_q)^2 = \left(\frac{\hbar v_s^2}{T}\right)^2 \times \frac{1}{\Omega}\sum_{k,q} W^{ep}_{k,k+q} q_z^2$$

$$P^{ep}_{13} = \frac{1}{\Omega}\sum_{k,q} W^{ep}_{k,k+q}(X^1_k - X^1_{k+q})X^3_q = -\frac{\hbar}{m^*}\frac{\hbar v_s^2}{T} \times \frac{1}{\Omega}\sum_{k,q} W^{ep}_{k,k+q} q_z^2$$

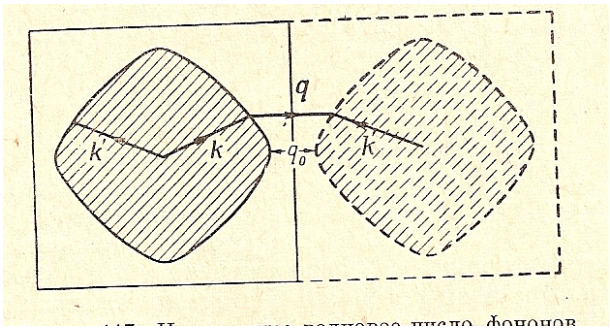
therefore (with no umklapps) $(P_{13})^2 = (P^{ep}_{13})^2 = P^{ep}_{11} P^{ep}_{33}$
thus $(ZT)^{ep} \to \infty$; why?

from X^1_k and X^3_q one can construct Φ_k and Ψ_q so that $\Phi_k - \Phi_{k+q} + \Psi_q = 0$ for all $\mathbf{k}, \mathbf{q}$; therefore $T\dot{\mathcal{S}} = \frac{1}{\Omega}\sum_{k,q} W^{ep}_{k,k+q}(\Phi_k - \Phi_{k+q} + \Psi_q)^2 = 0$

Phonon drag route to high ZT

3 requirements:

1) metallic system with a sufficiently small Fermi surface $2k_F$ so that $\kappa_e \ll \kappa_p$



Ziman: Electrons and phonons

2) minimal umklapp wavevector: q_0
$q_0 \approx \frac{2\pi}{a} - 2k_F$
sound velocity v_s sufficiently large so that $\hbar\omega(q_0) \gg T$
(no umklapp processes)

3) if 1) and 2) hold, then $ZT = \frac{r}{1-r}$, where $r = \frac{(P_{13})^2}{P_{11}P_{33}} = \frac{P_{11}^{ep}}{P_{11}} \times \frac{P_{33}^{ep}}{P_{33}}$

high figure of merit achieved for $P_{11}^{ep} \approx P_{11}$ and $P_{33}^{ep} \approx P_{33}$

B-doped diamond: a possible phonon drag material

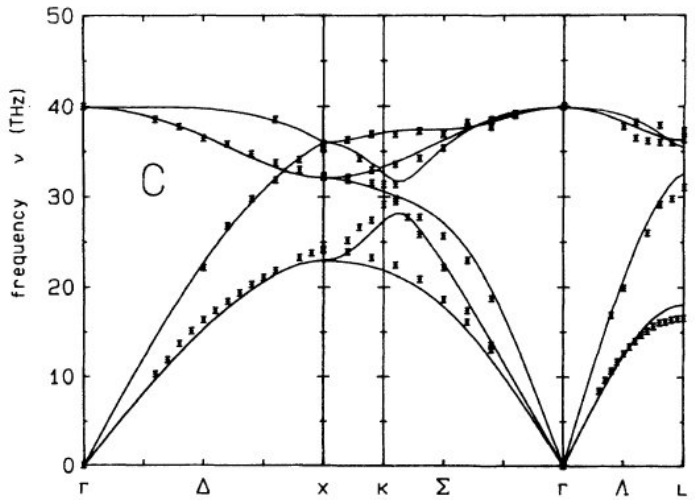
achievable boron doping: 1% (1.8×10^{21} cm^{-3}) Bustarret 08

resistivity $\rho \sim 10^3$ $\mu\Omega$cm at 300 K

electronic thermal conductivity (WF estimate) $\kappa_{0e} \sim 1$ WK^{-1}m^{-1}

experimental thermal conductivity at 300 K: $\kappa > 10^3$ WK^{-1}m^{-1} (different samples!)

1) therefore probably $\kappa_e \ll \kappa_p$



phonon dispersion of diamond (Goldammer et al 87)
umklapps possible for phonon energies ≈ 500 K
2) sound velocity sufficiently large

Phonon scattering processes

$T \gg \Theta_D$: phonon-phonon scattering (anharmonicity) always dominates P_{33}
$T \ll \Theta_D$: phonon-phonon scattering is exponentially suppressed

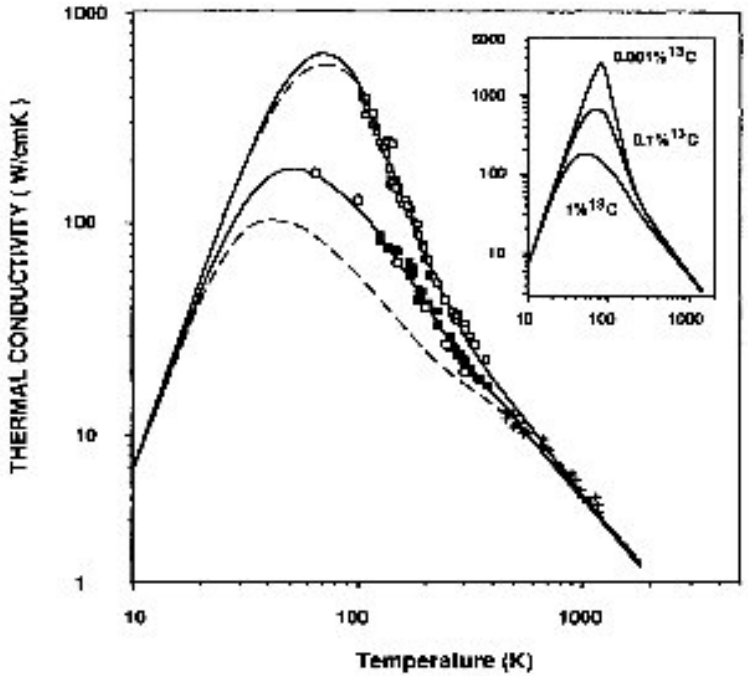
contributions to P_{33} at $T \ll \Theta_D$:

- boundary scattering:
  dominant at the lowest temperatures, where $P_{33}^{bound} \propto T^2$
- electron-phonon scattering:

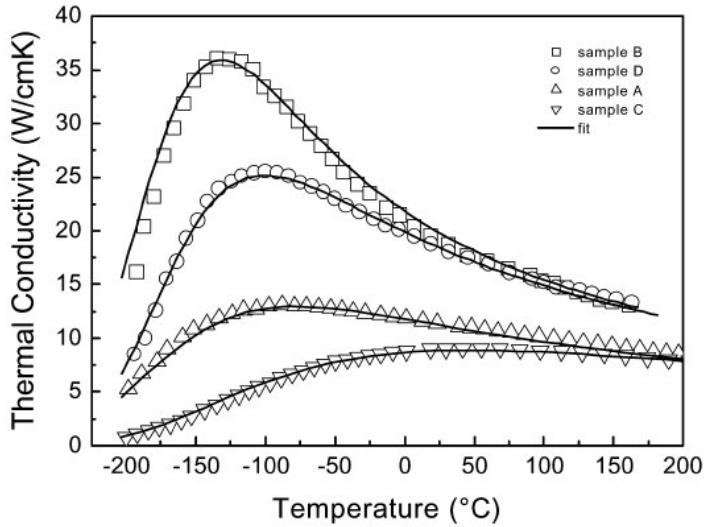
  relevant at intermediate temperatures, since $P_{33}^{ep} \sim \left(\frac{m^* v_s^2}{T}\right)^2 P_{11}^{ep} \propto T^3$
- impurity scattering:
  relevant at high temperatures, since $P_{33}^{imp} \propto T^6$

allowed temperature range: $P_{33}^{bound} \ll P_{33}^{ep} \ll P_{33}^{imp}$

Diamond: thermal conductivity



κ of pure diamond (Wei et al, 93)
compositions: 1% and 0.1% of ^{13}C



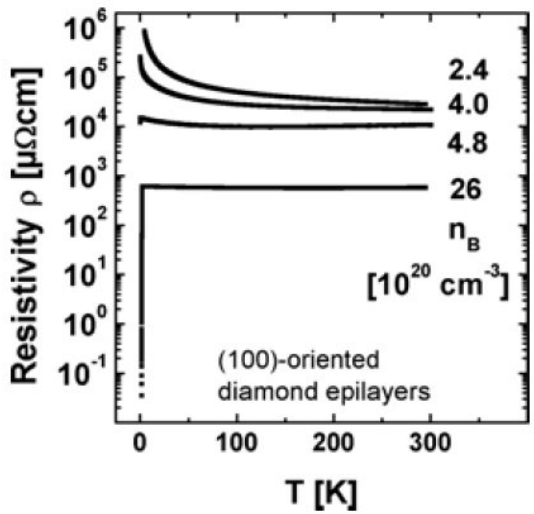
κ of N-doped diamond (A,B,C)
κ of B-doped diamond (sample D);
2.8×10^{18} cm^{-3}; (Worner et al 03)

needed: thermal conductivity data of conducting and non-conducting samples with comparable purity

Electron scattering processes

assume $P_{11} = P_{11}^{imp} + P_{11}^{ep}$; then $\rho = \rho_{imp} + \rho_{ep}$ where $\rho_{imp} = \frac{P_{11}^{imp}}{e^2 J_1^2}$

and $\rho_{ep} = \frac{P_{11}^{ep}}{e^2 J_1^2}\left(1 - \frac{P_{33}^{ep}}{P_{33}}\right) \ll \frac{P_{11}^{ep}}{e^2 J_1^2}$ = Bloch-Gruneisen, if $P_{33}^{ep} \approx P_{33}$



B-doped diamond (Bustarret 08)

$\rho_{ep}(T)$ up to 300 K consistent with $P_{33}^{ep} \approx P_{33}$ (need higher-T data to confirm)

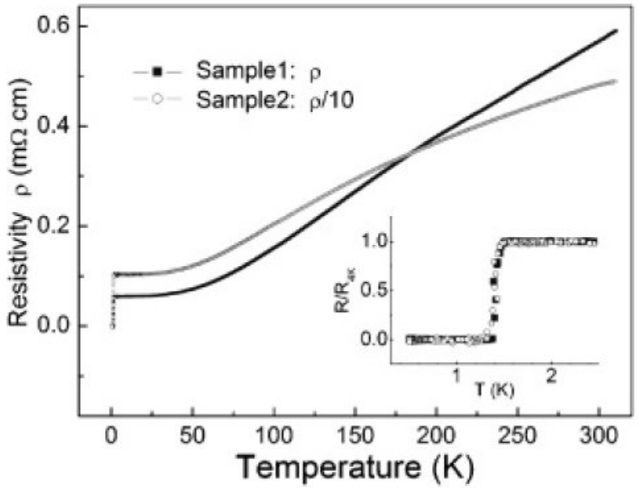
for $n \approx 2 \times 10^{21}$ cm^{-3}, $\rho \approx 10^3$ $\mu\Omega$cm, $\kappa \approx 10^3$ Wm^{-1}K^{-1}:

$$\frac{P_{11}^{imp}}{P_{11}^{ep}} \approx 6\frac{e^2\rho\kappa}{T}n^2\left(\frac{\hbar v_s}{T}\right)^6 \sim 10^3$$

need less impurity scattering for the electrons!

Reduction of electron-impurity scattering

B-doped SiC:



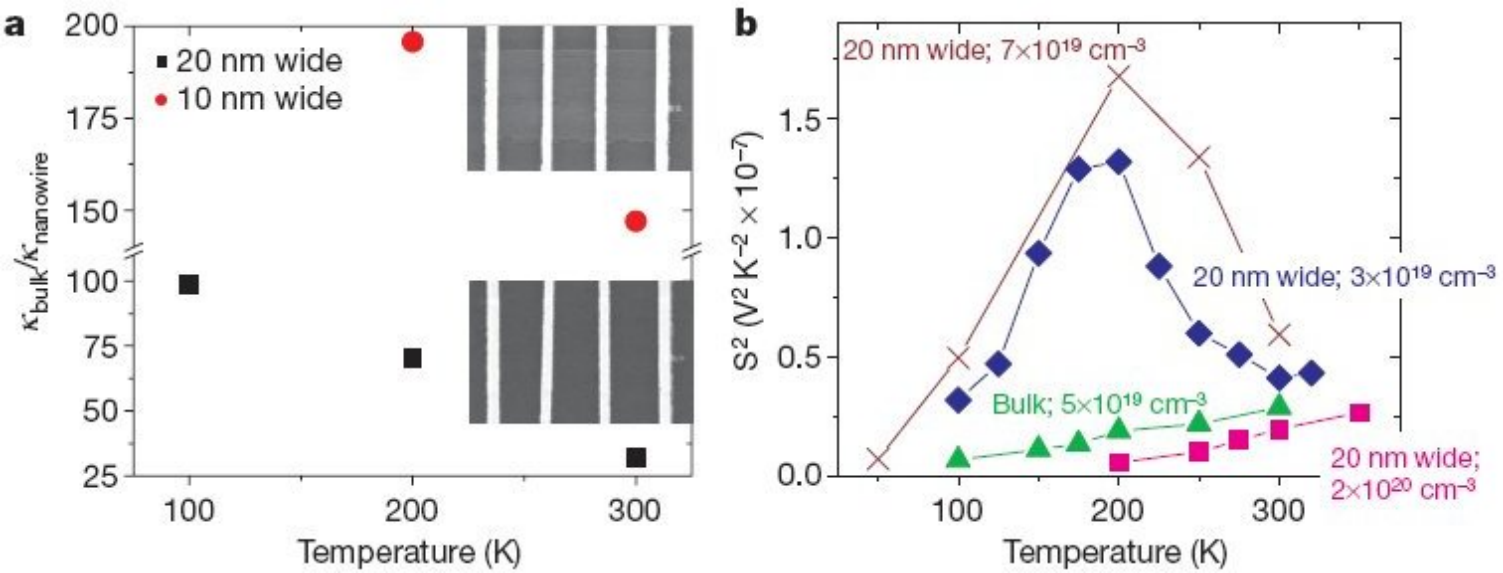
(Ren et al 07)
$\rho_{imp} \approx 60\ \mu\Omega$cm and
$\rho(300\ K)/\rho(5\ \mathrm{K}) \approx 10$,
but $\Theta_D \approx 590$ K compared to
$\Theta_D \approx 1440$ K for diamond;
also $\rho_{ep} \propto T^3$ at low T; no drag?

doped diamond:

- boron superlattice
- surface doping, field effect doping, ...

Silicon nanowires (Boukai et al, Nature 2008)

Si wires with cross-section 10 nm$\times$ 20 nm and 20 nm$\times$ 20 nm
B doping levels 3×10^{19} to 2×10^{20} cm^{-3}
reported $ZT \approx 1$ at 200 K



left: $\kappa_{bulk}/\kappa_{wire}$; note the large increase of scattering in wires
right: thermopower squared, S^2; the peak at 200 K has been interpreted as a phonon drag effect

Outline

Conclusions

- we have studied the simplest variational solutions to the Boltzmann equation for coupled electrons and phonons
- criteria for an optimal thermoelectric material similar to those of Mahan and Sofo have been formulated both, for systems without and with phonon drag
- systems with a structure (of single particle origin) in the transport function close to the chemical potential have been discussed in detail
- it was predicted that systems with a well-developed phonon drag should exhibit a large figure of merit ZT
- doped diamond (with reduced disorder scattering) might be a promising thermoelectric material

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