Ab initio thermoelectric properties

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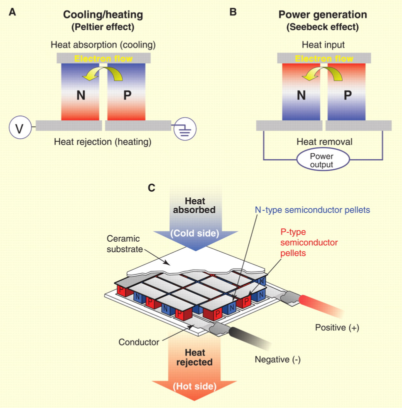
Nov 07, 2012

Outline

1. Introduction
2. Theory
3. Results
4. Conclusions & Discussion

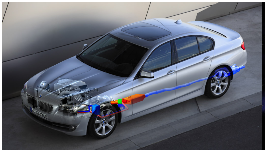
Thermoelectric effect

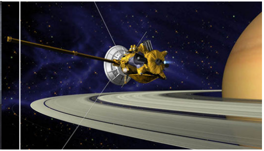


L.E. Bell, Science ***321****, 1457 (2008)*

- Seebeck effect: $\mathbf{E} = \mathbf{S}\nabla T$
- Peltier effect: $\dot{Q}_P = \Pi I = STI$

Advantages

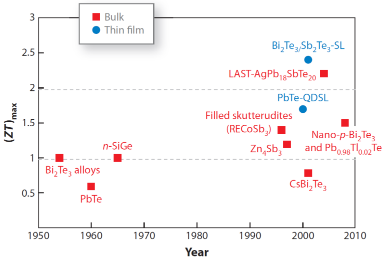




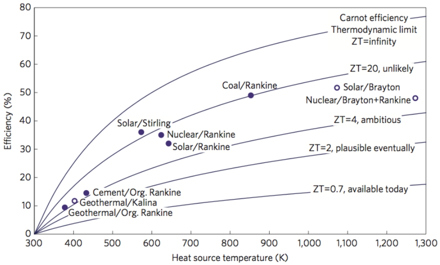
- Solid state
  - durable
  - small size
  - no moving parts
  - quiet
  - alternative to fossil fuels
  - no greenhouse gas emission
- Power generation
  - waste heat harvesting
  - conditions where no other energy sources are suitable (Radioisotope Thermoelectric Generator, RTG)
- Cooling/Heating
  - reversibility (to cool or heat with the same module)
  - spot cooling/heating

Disadvantages

- Cost
- Efficiency
  Figure of merit: $ZT = \frac{\sigma S^2 T}{\kappa_l + \kappa_e}$



T.M. Tritt, Annu. Rev. Mater. Res. **41**, *433 (2011)*



C.B. Vining, Nature Materials **8**, *83 (2009)*

To maximize ZT

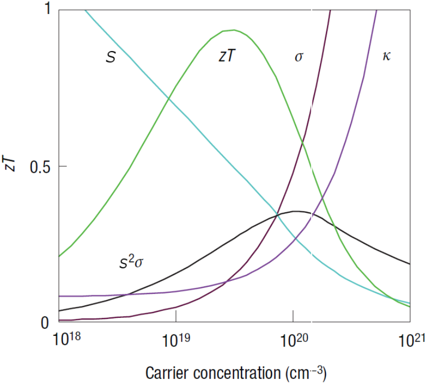
$$ZT = \frac{\sigma S^2 T}{\kappa_l + \kappa_e}$$

- Phonon Glass-Electron Crystal
  - Minimize lattice thermal conductivity κ_l
  - Maximize power factor σS^2

G.A. Slack, CRC Handbook of Thermoelectrics, ed. by D.M. Rowe, CRC Press, Boca Raton, FL, 1995, p. 407.

Trade-off among the transport coefficients

- σ v.s. S
  Mott relation
  $S_d = \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{1}{\sigma}\frac{d\sigma(E)}{dE}\right\}_{E=\epsilon_F}$
- σ v.s. κ_e
  Wiedemann-Franz law
  $\kappa_e = L_0 \sigma T$

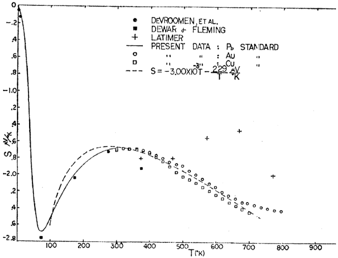


G.J. Snyder and E.S. Toberer, Nature Materials **7**, *105-114 (2008)*

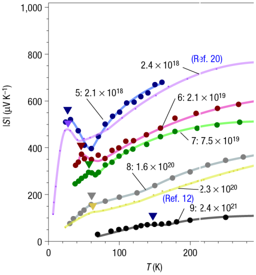
Phonon-drag effect

- $S_g \sim \frac{C_v}{Ne}\alpha = \frac{C_v}{Ne}\frac{P_{el-ph}}{P_{el-ph}+P_{ph-ph}+P_{ph-else}}$
- When el-ph interaction is strong
- Important at low temperatures

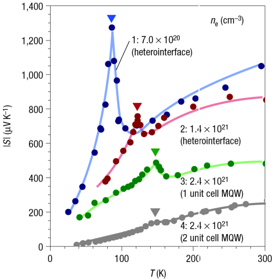
Al



doped $SrTiO_3$



$SrTiO_3$ MQW



R. Gripshover et al., Phys. Rev. (1967)

Ohta et al., Nat. Mater. (2007)

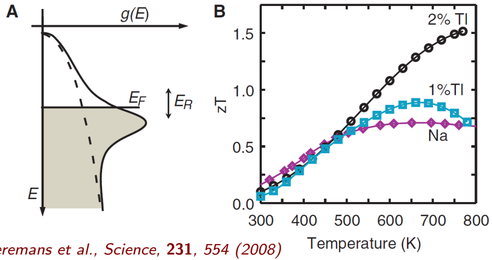
Minimizing the lattice thermal conductivity

$$\kappa_l = \frac{1}{3} v c_v l$$

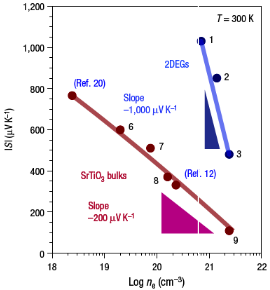
- Mass fluctuation (ternary/quaternary compounds)
- Rattling (clathrates, skutterudites)
- Grain boundary (nano composites)
- Interface (thin films, multilayer systems)
- The minimum κ_l is limited, when the phonon mean free path becomes close to the interatomic distance.

Enhancing the power factor σS^2

- Doping in semiconductors: $\sigma \nearrow$
- Mott relation: $S = \frac{\pi^2}{3}\frac{k_B}{q}k_B T \left\{ \frac{1}{n}\frac{dn(E)}{dE} + \frac{1}{\mu}\frac{d\mu(E)}{dE} \right\}_{E=\epsilon_F}$
- DOS engineering
  - resonant scattering (Tl impurity levels in PbTe)
- Low dimensionality (quantum confinement)
  - 0D: quantum dots
  - 1D: nanowires
  - 2D: quantum wells and superlattices



J.P. Heremans et al., Science, **231**, *554 (2008)*



Ohta et al., Nat. Mater. (2007)

Outline

Theoretical predictions

- Phonon-phonon interactions
  - lattice thermal conductivity
- Electron-phonon interactions
  - Electrical conductivity
  - Seebeck coefficient
  - Electronic thermal conductivity
- Coupled term
  - Phonon drag Seebeck
- Other interactions
  - Impurity scattering with electrons and phonons
  - Defects, grain boundaries

BTE approach

- Boltzmann's transport equation (BTE without magnetic field)

$$-\mathbf{v_k} \cdot \frac{\partial f_\mathbf{k}}{\partial T} \nabla T - \mathbf{v_k} \cdot e \frac{\partial f_\mathbf{k}}{\partial \epsilon_\mathbf{k}} \mathbf{E} = - \frac{\partial f_\mathbf{k}}{\partial t}\Big|_{scatt}$$

1. Standard solution with relaxation time approximation

$$-\frac{\partial f_\mathbf{k}}{\partial t}\Big|_{scatt} = \frac{f_\mathbf{k} - f^0_\mathbf{k}}{\tau_\mathbf{k}}$$

2. Variational method

$$f_\mathbf{k} \equiv f^0_\mathbf{k} - \phi_\mathbf{k} \frac{\partial f^0_\mathbf{k}}{\partial \epsilon_\mathbf{k}}$$

$$-\frac{\partial f_\mathbf{k}}{\partial t}\Big|_{scatt} = \sum_{\mathbf{k'}} Q_{\mathbf{kk'}} \phi_{\mathbf{k'}}$$

Constant relaxation time approximation

- Advantage: simple calculation (band structure)
- Disadvantage:
  - unknown constant relaxation time
  - system with anisotropic scattering

$$\sigma_{\alpha\beta}(\epsilon) = e^2 \sum_{\mathbf{k}} \tau_{\mathbf{k}} v_\alpha(\mathbf{k}) v_\beta(\mathbf{k}) \delta(\epsilon - \epsilon_{\mathbf{k}})$$

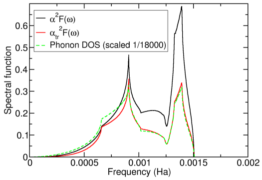
$$\rightarrow e^2 \tau \sum_{\mathbf{k}} v_\alpha(\mathbf{k}) v_\beta(\mathbf{k}) \delta(\epsilon - \epsilon_{\mathbf{k}})$$

$$\sigma_{\alpha\beta} = \frac{1}{V_{cell}} \int \sigma_{\alpha\beta}(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right) d\epsilon$$

$$S_{\alpha\beta} = \frac{1}{eT} \frac{\int \sigma_{\alpha\beta}(\epsilon)(\epsilon - \mu) \left(-\frac{\partial f}{\partial \epsilon} \right) d\epsilon}{\int \sigma_{\alpha\beta}(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right) d\epsilon}$$

G. Madsen et al. Comput. Phys. Commun. **175**, *67 (2006)*

Variational solution to the BTE†



- Scattering operator

$$Q_{\alpha n,\beta n'} = \frac{2\pi V_{cell} N(\epsilon_F)}{\hbar k_B T} \int d\epsilon \int d\epsilon' \int d\omega$$
$$\alpha_{tr}^2 F(\omega) J(n, n', \epsilon, \epsilon') f(\epsilon) \left[1 - f(\epsilon')\right]$$
$$\times \left\{ \left[N(\omega) + 1\right] \delta(\epsilon - \epsilon' - \hbar\omega) + N(\omega) \delta(\epsilon - \epsilon' + \hbar\omega) \right\}$$

- Transport spectral function

$$\alpha_{\mathrm{tr}}^2(s, s', \alpha, \beta, \epsilon, \epsilon') F(\omega) = \frac{1}{2N(\epsilon_F)} \sum_{\mathbf{kk'}} |g_{\mathbf{kk'}}|^2 \left[F_\alpha(\mathbf{k}) - s F_\alpha(\mathbf{k'})\right]$$
$$\times \left[F_\beta(\mathbf{k}) - s' F_\beta(\mathbf{k'})\right] \delta(\epsilon_{\mathbf{k}} - \epsilon) \delta(\epsilon_{\mathbf{k'}} - \epsilon') \delta(\omega_{\mathbf{q}} - \omega)$$

† *P. B. Allen, Phys. Rev. B* **17**, *3725 (1978)*

LOVA (lowest-order variational approximation) and beyond

- Transport coefficients

$$\rho_{\alpha\beta} = \left(\frac{m}{n}\right)_{\text{eff}} \frac{1}{e^2}\frac{1}{\tau_{\alpha\beta}} = \frac{1}{2e^2(Q^{-1})_{\alpha 0,\beta 0}} \approx \frac{1}{2e^2} Q_{\alpha 0,\beta 0}$$

$$S_{\alpha\beta} = -\frac{\pi k_B}{\sqrt{3}e}\frac{(Q^{-1})_{\alpha 0,\beta 1}}{(Q^{-1})_{\alpha 0,\beta 0}} \approx \frac{\pi k_B}{\sqrt{3}e} Q_{\alpha 0,\beta 1}/Q_{\alpha 1,\beta 1}$$

- Elastic LOVA
  - $\epsilon = \epsilon' = \epsilon_F$
  - valid when $\alpha^2_{tr}F$ depends weakly on ϵ and ϵ'
  - Seebeck coefficient vanishes! (el-hole symmetric)

$\frac{1}{\tau_{\alpha\beta}} = \frac{4\pi k_B T}{\hbar}\int_0^\infty \frac{d\omega}{\omega}\frac{x^2}{\sinh^2 x}\alpha^2_{tr}F(\omega)$ where $x = \omega/2k_B T$

- Beyond LOVA
  - with higher-order terms of $Q_{\alpha n,\beta n'}$
  - including Fermi smearing

$\frac{1}{\tau_{\alpha\beta}} = N(\epsilon_F)v_\alpha(\epsilon_F)v_\beta(\epsilon_F)Q_{\alpha 0,\beta 0}$

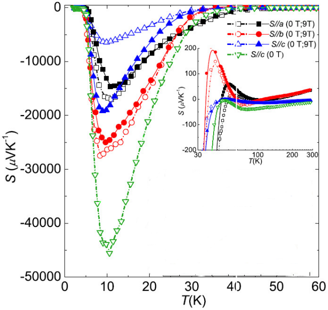
Outline

Constant τ

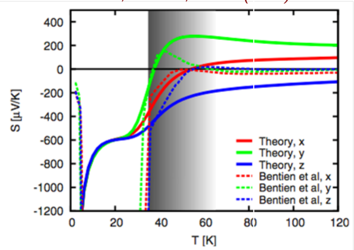
$FeSb_2$: Colossal Seebeck coefficient at low T

- Experiment
  - Record low-T thermopower
  - $S_{max} \approx -45000\mu$VK^{-1} at $T \approx 10$ K
- Theory (J.M. Tomczak *et al.*)
  - Kubo approach
  - Agreement only at intermediate temperatures
- Theory (M. Diakhate *et al.*)
  - Boltzmann approach
  - Constant relaxation time

M. Diakhate et al., Phys. Rev. B ***84****, 125210 (2011)*

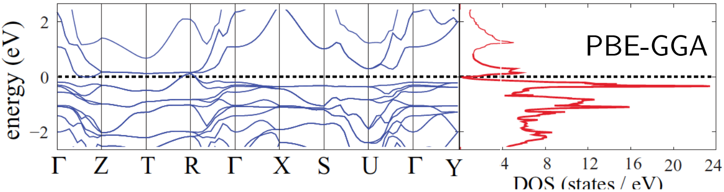


A. Bentien et al., EPL ***80****, 17008 (2007)*

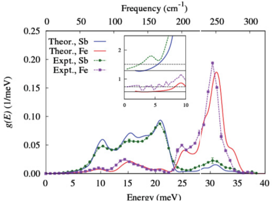


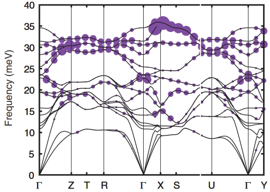
J.M. Tomczak et al., Phys. Rev. B ***82****, 085104 (2010)*

FeSb$_2$: electron, phonon and el-ph coupling



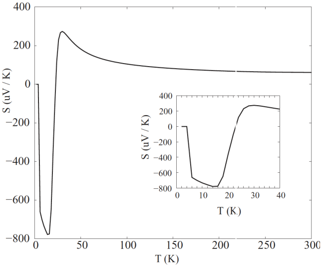
- Electronic band structure
  - $E_g = 37$ meV experimentally
  - semimetal from DFT
- Phonon DOS
  - Agree with expt.
  - Low-freq. Sb modes
  - High-freq. Fe modes
- Phonon linewidths due to EPC
  - Significant around Z, X, S
  - Future expt. needed

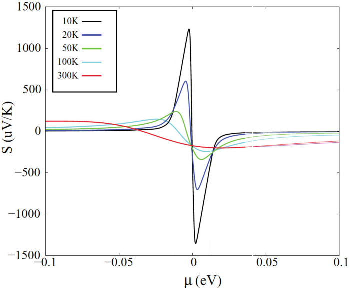




$FeSb_2$: Seebeck coefficient

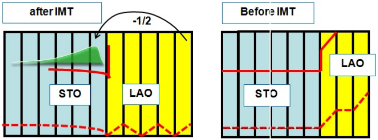
- $S_{max} \approx -800\mu$VK^{-1} at $T \approx$ 15 K
- Phonon drag?
  $\lambda = 0.24$ is weak
- S becomes positive above $T \approx$ 25 K
- To maximize thermopower
    - Donor doping
    - $n = 3.2 \times 10^{15}$ cm^{-3}



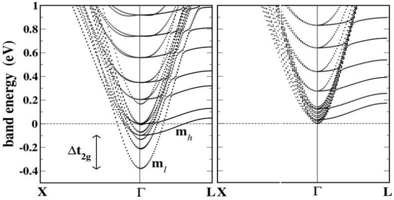


Model $\tau(\epsilon, T)$

STO/LAO interface



- 2DEL at the interface
  - Tightly confined
- Polar catastrophe with > 4 LAO layers
- t_{2g} bands between bulk STO and STO/LAO
  - band effective mass
  - on-site band offset
  - inter-site band offset



pSIC-LDA

Relaxation time model

- For elastic scattering
- For parabolic band

$$\tau(\epsilon, T) = F(T) \left(\frac{\epsilon - \epsilon_0}{k_B T} \right)^{\lambda}$$

$$F(T) = \tau_0 \left[\left(\frac{T_0}{T} \right)^{-\gamma} + \left(\frac{\tau_0}{\tau_{\text{res}}} \right) \left(\frac{T_0}{T} \right)^{\lambda} \right]^{-1}$$

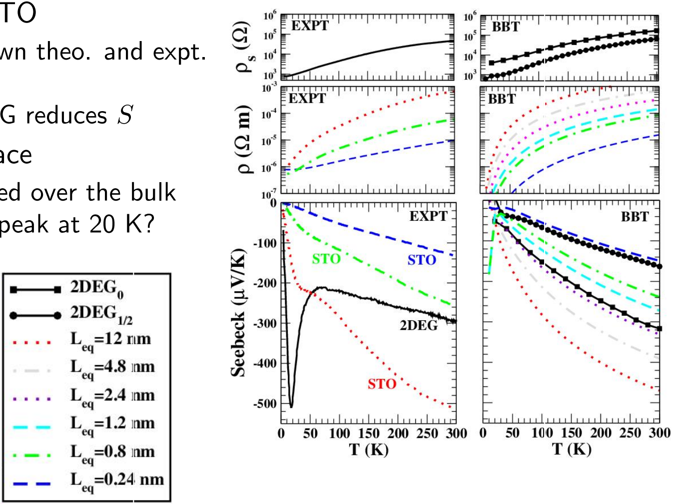
$\lambda = \gamma = 3/2$, $\tau_0 = 3$ fs, $T_0 = 20$ K

$\tau_0/\tau_{\text{res}} = 0$ for bulk STO
$\tau_0/\tau_{\text{res}} = 40$ for STO/LAO

K. Durczewski and M. Ausloos, Phys. Rev. B **61**, *5303 (2000)*

Is Seebeck enhanced?

- Nb-doped bulk STO
  - agreement btwn theo. and expt.
  - $L_{\text{eq}} \searrow S \searrow$
  - confined 2DEG reduces S
- STO/LAO interface
  - S not improved over the bulk
  - phonon drag peak at 20 K?

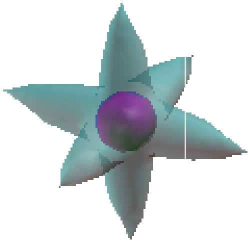


Multiband model

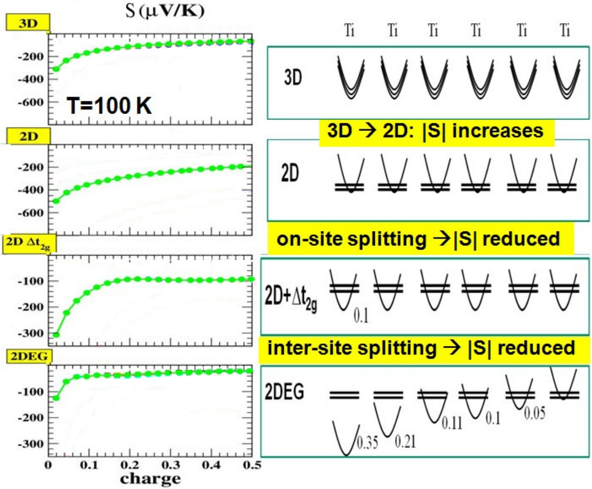
- Bulk STO:
  t_{2g} effective masses are anisotropic

  $m^*_{xy,j}$ =(0.7,0.7,8.8)
  $m^*_{xz,j}$ =(0.7,8.8,0.7)
  $m^*_{yz,j}$ =(8.8,0.7,0.7)

  $$\epsilon_{v\alpha\mathbf{k}} = \epsilon^0_{v\alpha} + \frac{\hbar^2}{2}\left(\frac{k_x^2}{m_{\alpha x}} + \frac{k_y^2}{m_{\alpha y}} + \frac{k_z^2}{m_{\alpha z}}\right)$$



Multiband model



Ab initio el-ph τ

LOVA (lowest-order variational approximation) and beyond

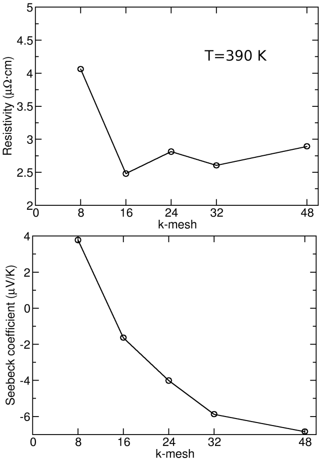
- Elastic LOVA
  - $\epsilon = \epsilon' = \epsilon_F$
  - valid when $\alpha_{tr}^2 F$ depends weakly on ϵ and ϵ'
  - Seebeck coefficient vanishes! (el-hole symmetric)

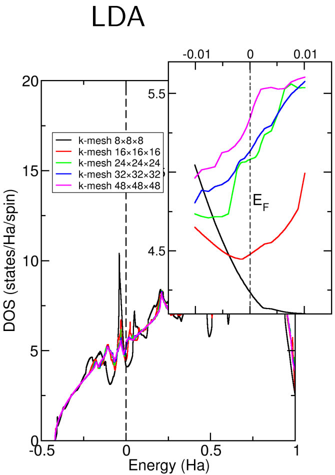
$$\frac{1}{\tau_{\alpha\beta}} = \frac{4\pi k_B T}{\hbar} \int_0^\infty \frac{d\omega}{\omega} \frac{x^2}{\sinh^2 x} \alpha_{tr}^2 F(\omega) \text{ where } x = \omega/2k_B T$$

- Beyond LOVA
  - with higher-order terms of $Q_{\alpha n, \beta n'}$
  - including Fermi smearing

$$\frac{1}{\tau_{\alpha\beta}} = N(\epsilon_F) v_\alpha(\epsilon_F) v_\beta(\epsilon_F) Q_{\alpha 0, \beta 0}$$

Preliminary results of FCC aluminium

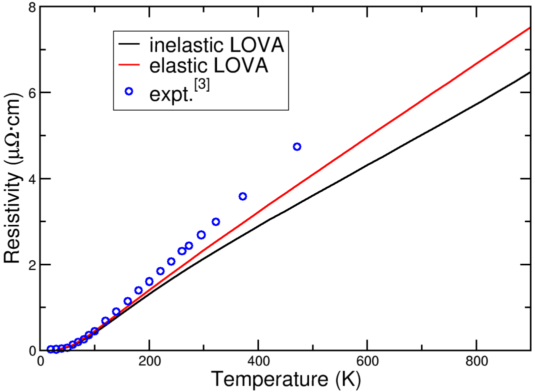




- Seebeck coefficient converges much slower than resistivity
- Seebeck coefficient is sensitive to the DOS around E_F

Electrical resistivity of Al

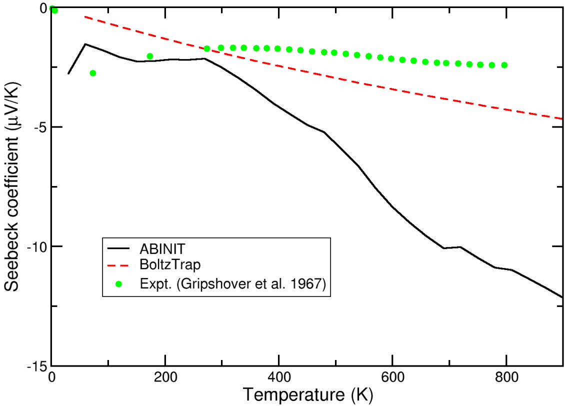
Both agree well with expt.



[Expt.] *Metals: Electronic Transport Phenomena, edited by K.H. Hellwege et al., Group III, Vol. 15, Pt. a (1982)*

Seebeck coefficient of Al

- RTA result agrees better, with slightly larger T dependence
- Variational result overestimates at high T
- The curve is unsmooth



[Expt.] *R. J. Gripshover et al., Phys. Rev. B* **163**, *598 (1967)*

Outline

Conclusions & Discussion

- Constant/model relaxation time approach
  - less computationally demanding
  - reasonable result for S
  - not parameter free
  - τ is difficult to estimate
  - anisotropy in $\tau_{\mathbf{k}}$ is lost
  - to improve, fully *ab initio* $\tau_{\mathbf{k}}$
- Variational approach
  - fully *ab initio*, where the EPC is considered explicitly
  - calculated ρ is robust for metals
  - computationally demanding
  - for large systems, difficult to converge
  - Q may not be truncated at lowest order for insulators
  - to improve, efficient interpolation scheme is expected
  - to improve, new formulae for non-metals?

Collaborations

Momar Diakhate ($FeSb_2$)
Alessio Filippetti (STO/LAO)
Bin Xu (Al)
Matthieu Verstraete (All above)

Discussion: RTA (relaxation time approximation)

- First-principles $\tau_{\mathbf{k}}$ from EPC

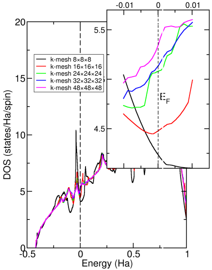
$$\frac{1}{\tau_{\mathbf{k}}} = \frac{2\pi}{\hbar} \sum_{\mathbf{q}} |g_{\mathbf{k},\mathbf{k}+\mathbf{q}}|^2 \Big\{ \big[f(\epsilon_{\mathbf{k}+\mathbf{q}}) + n_{\mathbf{q}} \big] \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}}) + \big[1 + n_{\mathbf{q}} - f(\epsilon_{\mathbf{k}+\mathbf{q}}) \big] \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}}) \Big\}$$

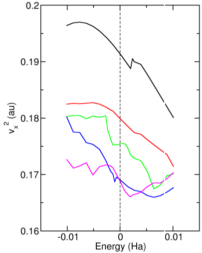
- Convergence

G. Grimvall, The Electron-Phonon interaction in Metals, (North-Holland, Amsterdam, 1981)

O.D. Restrepo et al., Appl. Phys. Lett. **94**, *212103 (2009)*

Discussion: variational approach

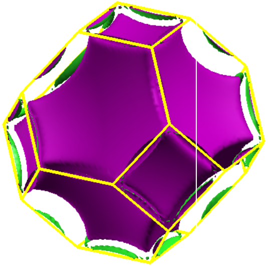




- Metals
  - convergence of S
  - better DOS and $v_{\mathbf{k}}$ around ϵ_F
  - numerical-integration-caused uncertainty
- Intrinsic or lightly doped semiconductors/insulators
  - elastic LOVA does not work
  - new variational formulae?

Discussion: Convergence

- Interpolation scheme
  - Wannier functions (F. Giustino *et al.* Phys. Rev. B **76**, 165108 (2007))
- Symmetry in DFPT GKK calculation
  - less direct calculations
  - need implementation
- **k** sampling for Fermi-surface integral
  - Fermi surface is usually complicated
  - Only include **k** points near the Fermi surface?



Thank you!

If needed

Supplementary slides.

Variational solution to the BTE†

- Scattering operator

$$Q_{\alpha n,\beta n'} = \frac{2\pi V_{cell} N(\epsilon_F)}{\hbar k_B T} \int d\epsilon \int d\epsilon' \int d\omega$$
$$\alpha^2_{\mathsf{tr}} F(\omega) J(n, n', \epsilon, \epsilon') f(\epsilon) \left[1 - f(\epsilon')\right]$$
$$\times \left\{\left[N(\omega) + 1\right] \delta(\epsilon - \epsilon' - \hbar\omega) + N(\omega)\delta(\epsilon - \epsilon' + \hbar\omega)\right\}$$

- Transport coefficients

$$\rho_{\alpha\beta} = \frac{1}{2e^2 (Q^{-1})_{\alpha 0,\beta 0}} \approx \frac{1}{2e^2} Q_{\alpha 0,\beta 0}$$

$$S_{\alpha\beta} = -\frac{\pi k_B}{\sqrt{3}e} \frac{(Q^{-1})_{\alpha 0,\beta 1}}{(Q^{-1})_{\alpha 0,\beta 0}} \approx \frac{\pi k_B}{\sqrt{3}e} Q_{\alpha 0,\beta 1}/Q_{\alpha 1,\beta 1}$$

Ingredients

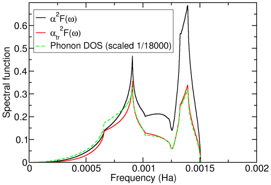
- Generalized spectral functions

$$\alpha^2_{\text{tr}}(s,s',\alpha,\beta,\epsilon,\epsilon')F(\omega) = \frac{1}{2N(\epsilon_F)}\sum_{\mathbf{kk'}}|g_{\mathbf{kk'}}|^2\left[F_\alpha(\mathbf{k}) - sF_\alpha(\mathbf{k'})\right]$$

$$\times\left[F_\beta(\mathbf{k}) - s'F_\beta(\mathbf{k'})\right]\delta(\epsilon_{\mathbf{k}}-\epsilon)\delta(\epsilon_{\mathbf{k'}}-\epsilon')\delta(\omega_{\mathbf{q}}-\omega)$$

- Joint energy polynomials

$$J(s,s',n,n',\epsilon,\epsilon') = \frac{1}{4}\left[(n\epsilon)+s(n\epsilon')\right]\left[(n'\epsilon)+s'(n'\epsilon')\right]$$



$$F_\alpha(\mathbf{k}) = v_\alpha(\mathbf{k})/v_\alpha(\epsilon)$$

$$(n\epsilon) = \sigma_n(\epsilon)/N(\epsilon)v(\epsilon)$$

$$v_\alpha(\epsilon) = \left[\frac{1}{N(\epsilon)}\sum_{\mathbf{k}} v^2_\alpha(\mathbf{k})\delta(\epsilon_{\mathbf{k}}-\epsilon)\right]^{1/2}$$

$$\sigma_0 = 1, \sigma_1 = \sqrt{3}\epsilon/\pi k_B T$$