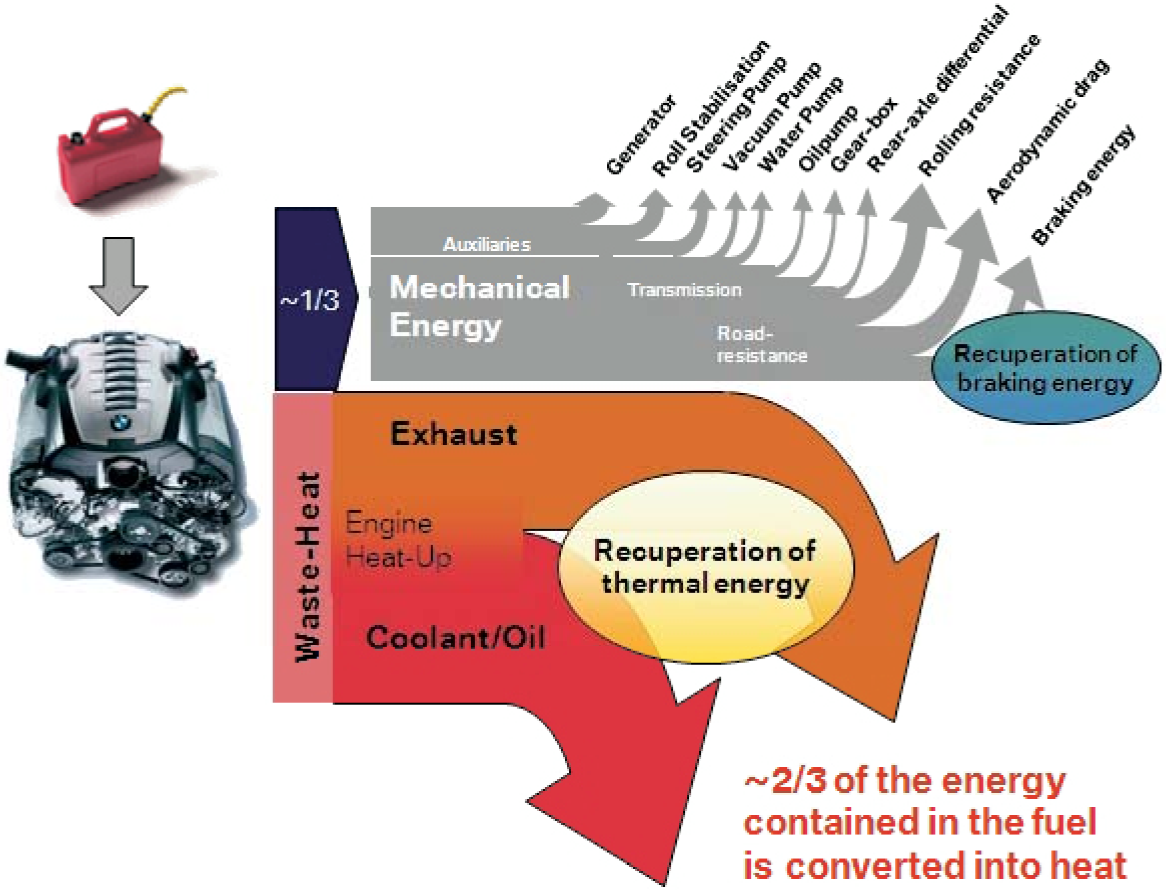
Thermal Energy Transport in Nanostructured and Complex Crystals

Li Shi

Department of Mechanical Engineering &
Texas Materials Institute
The University of Texas at Austin

BMW Wins ÿkoGlobe 2008 Award for Thermoelectric Generator

http://green.autoblog.com/2008/09/25/bmw-wins-koglobe-2008-award-for-thermoelectric-generator/



http://www.greencarcongress.com/2009/10/bmw-outlines-intelligent-heat-management-applications-for-reducing-fuel-consumption-and-co2-new-ther.html#more

Thermoelectric Energy Conversion

Waste Heat Recovery

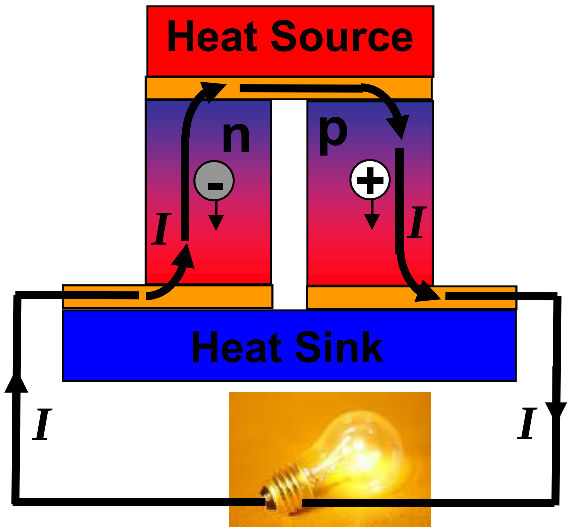


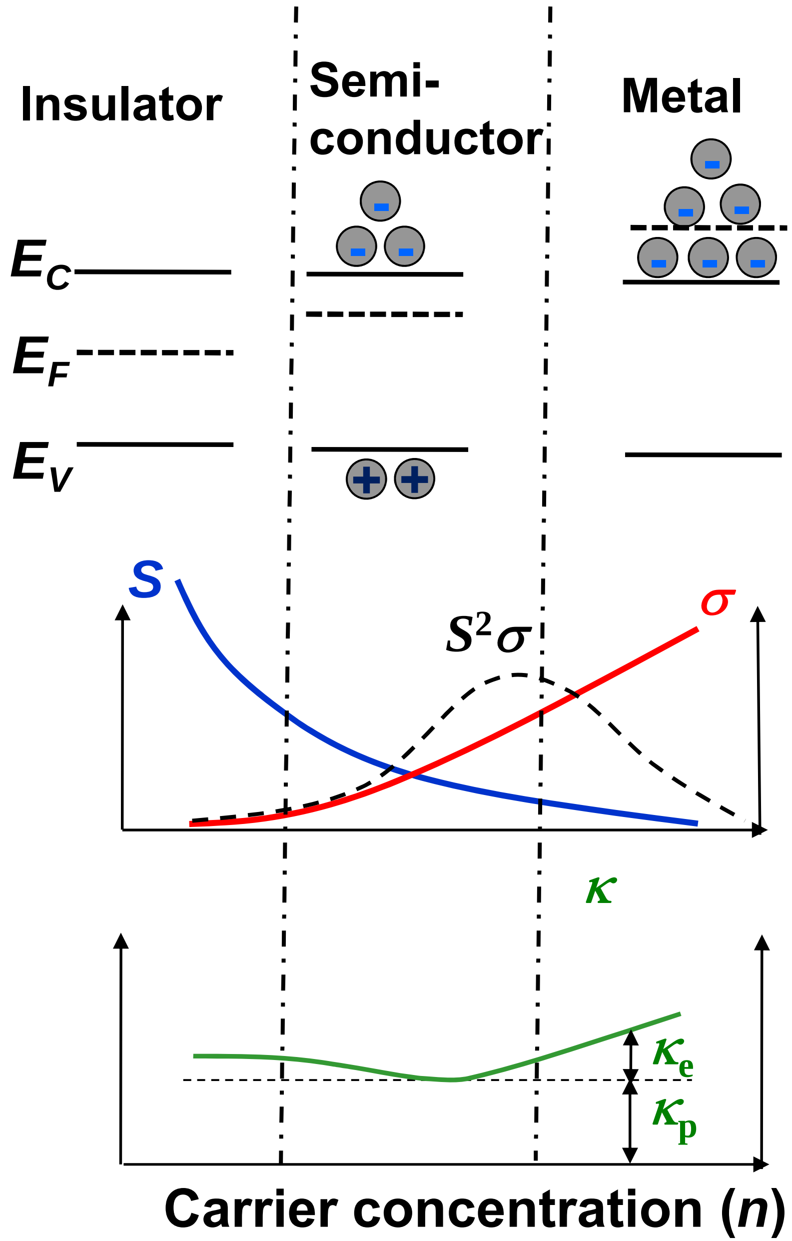
Figure of Merit (*ZT*)

Seebeck coefficient

Electrical conductivity

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

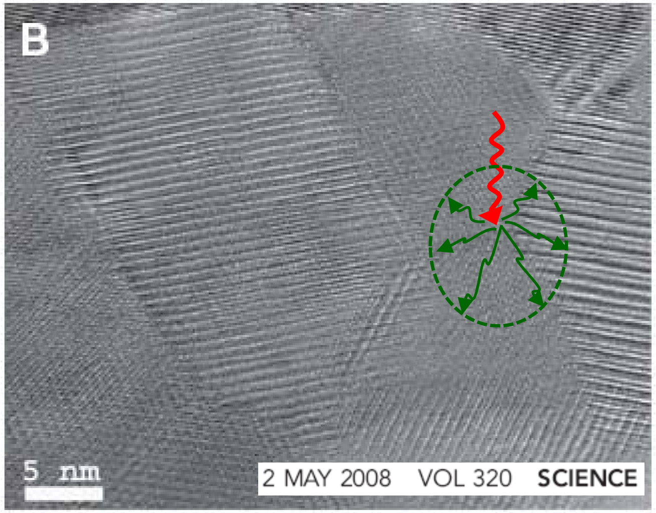
Thermal conductivity



ZT Progress and Materials Issues

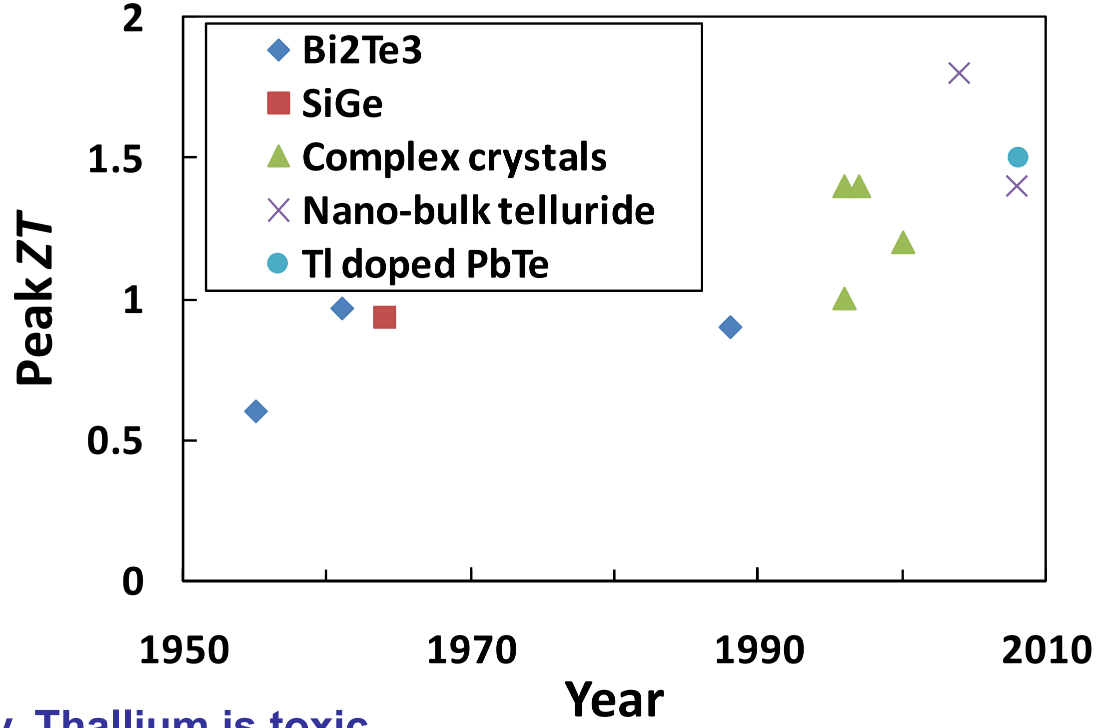
High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys

Bed Poudel,[1,2*] Qing Hao,[3*] Yi Ma,[1,2] Yucheng Lan,[1] Austin Minnich,[3] Bo Yu,[1] Xiao Yan,[1] Dezhi Wang,[1] Andrew Muto,[3] Daryoosh Vashaee,[3] Xiaoyuan Chen,[3] Junming Liu,[4] Mildred S. Dresselhaus,[5] Gang Chen,[3]† Zhifeng Ren[1]†



- *ZT* enhancement in complex or nanostructured bulk materials is caused by lattice thermal conductivity suppression.

•Thallium (Tl) doping in PbTe increases $S^2\sigma$ and *ZT*.

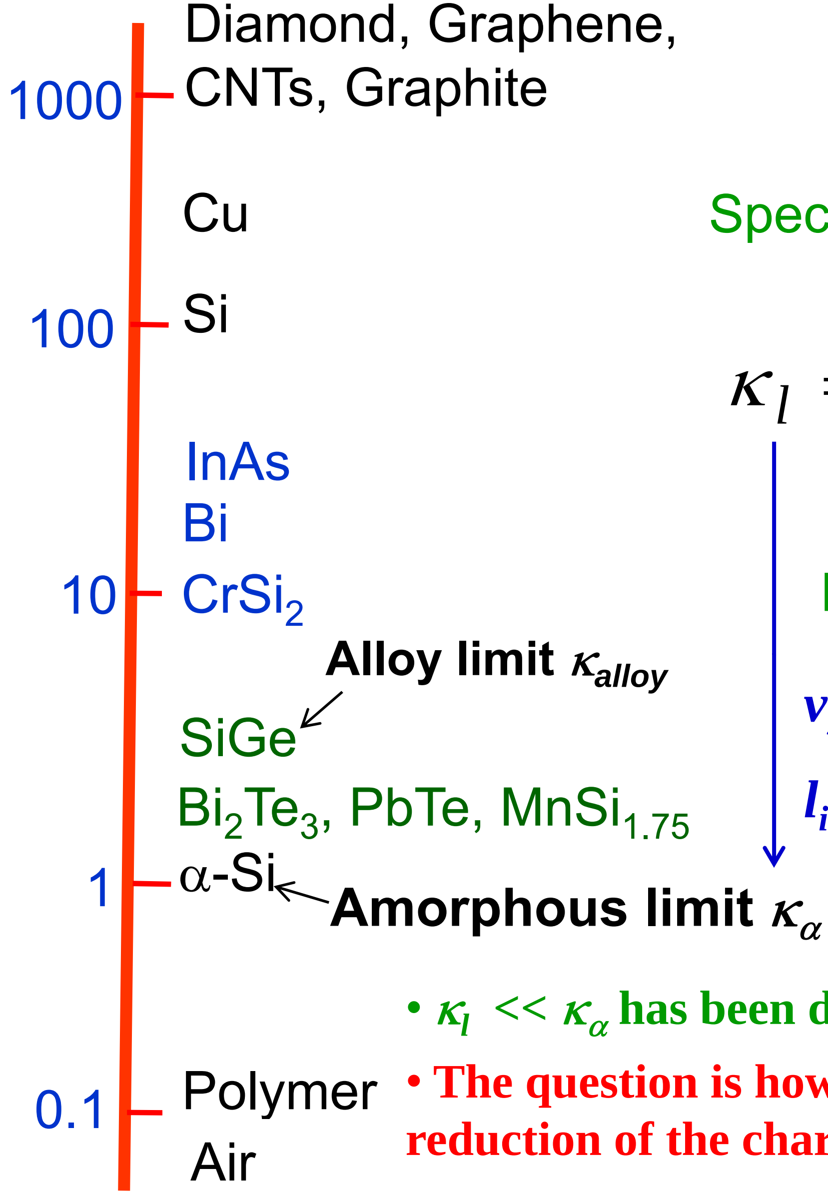


•Tellurium and germanium are costly. Thallium is toxic.

• Low-cost, abundant, and environmentally-friendly materials with *ZT* > 1.5 are needed for large-scale deployment of thermoelectric generators.

Thermal Conductivity (κ)

κ (W/m-K) @ 300 K



$$\kappa \approx \kappa_E + \kappa_l$$

Electronic — Lattice vibration or phonon

$$\kappa_l = \sum_i \int_{\lambda_{\min,i}}^{\lambda_{\max,i}} C_i(\lambda)\, v_{x,i}(\lambda)\, l_i(\lambda)\, d\lambda$$

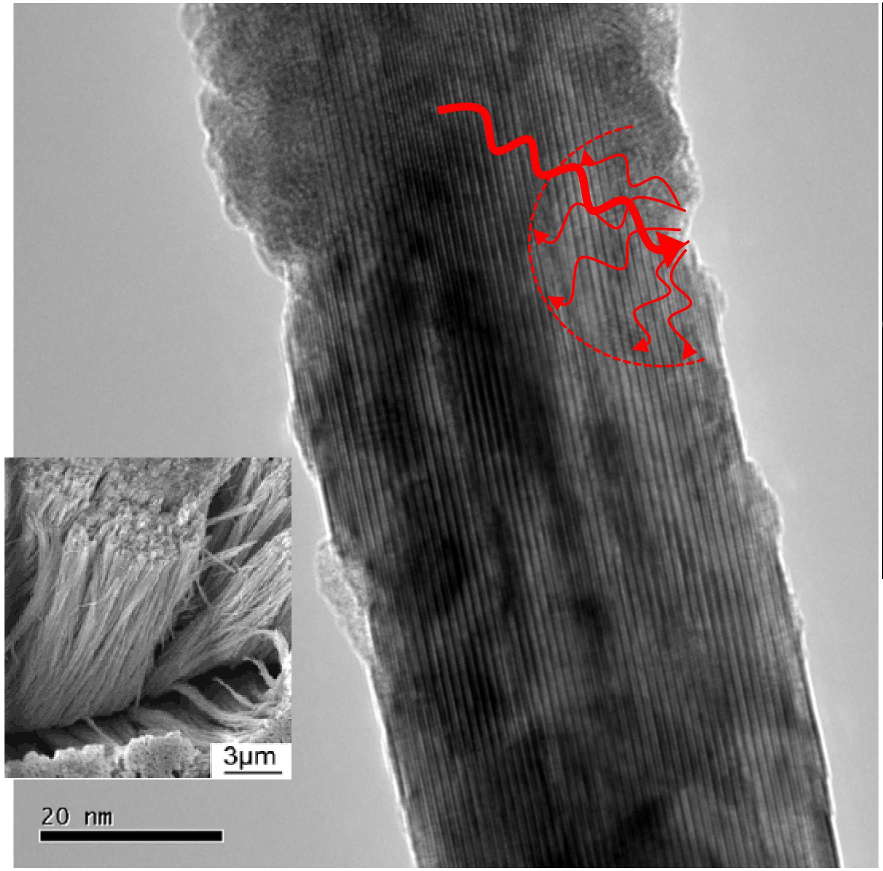
Spectral specific heat — Wavelength — Polarizations — Group velocity — m.f.p.

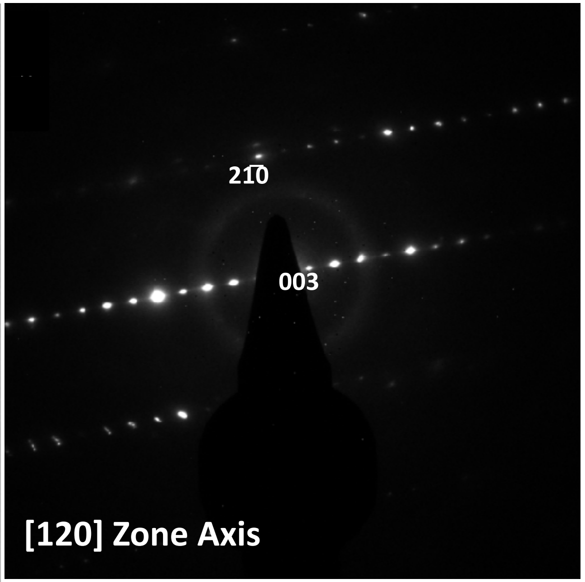
$v_{x,i}(\lambda)$ = speed of sound

$l_i(\lambda) = \lambda/2$

- **$\kappa_l \ll \kappa_\alpha$ has been demonstrated in disordered, layered thin films.**
- **The question is how much κ_l can be lowered without considerable reduction of the charge mobility.**

Nanowire Model Systems





- Bi_2Te_3 NW Sample 3
  - Electrodeposited
  - Single crystalline
  - Growth direction
    <110>

- Boundary scattering m.f.p.:

$$l_b = \frac{1+p}{1-p} d \rightarrow d \text{ for } p \rightarrow 0$$

- Effective m.f.p.:

$$l(\omega) = \left(l_U{}^{-1} + l_i{}^{-1} + l_b{}^{-1} \right)^{-1}$$

- Callaway-type model:

$$\kappa_l = \sum_i \int_0^{\omega_{ZBi}} C_i(\omega) v_{x,i}(\omega) l_i(\omega) d\omega$$

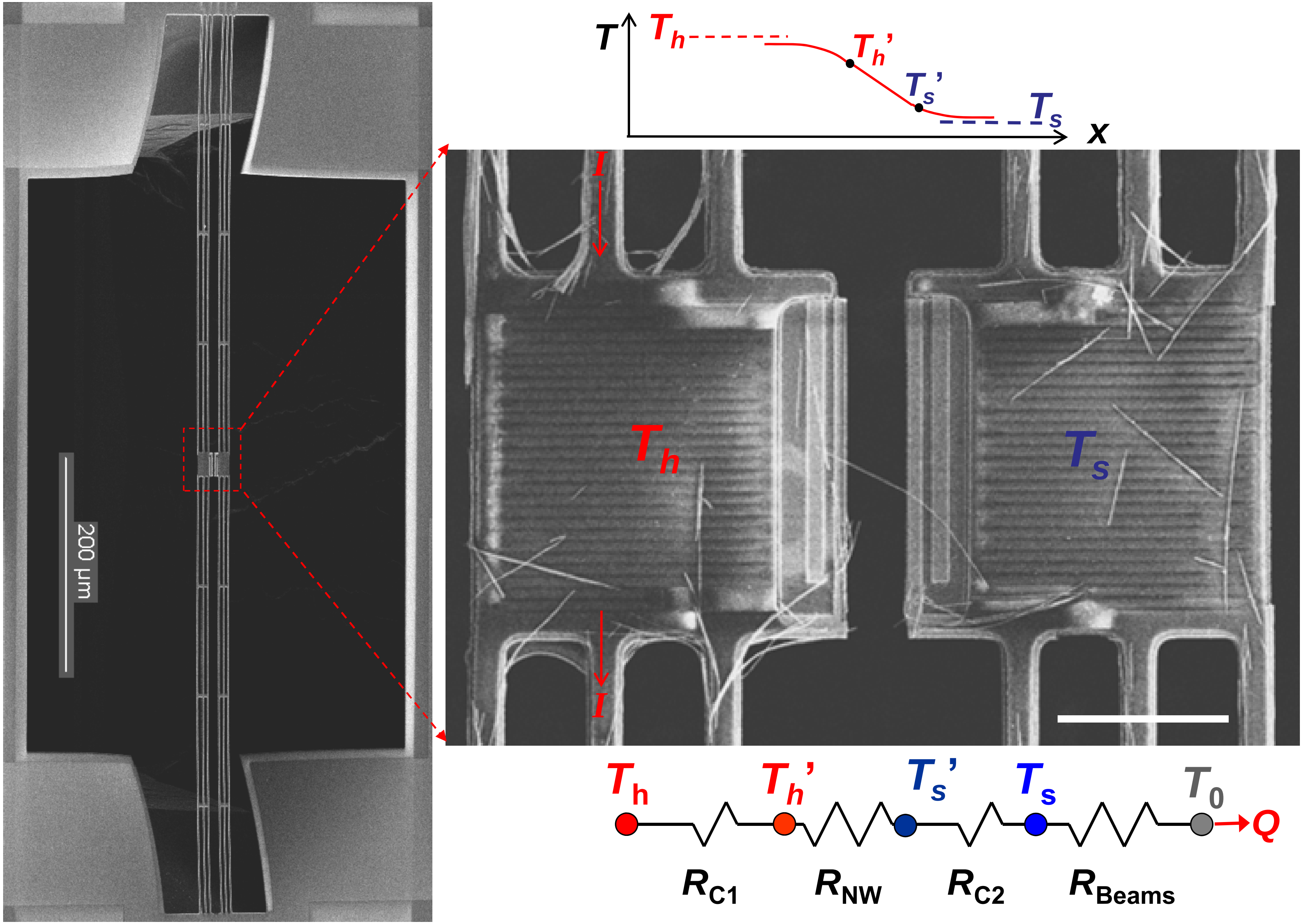
$$\rightarrow \kappa_{diffuse} \quad \text{when} \quad l_b \rightarrow d$$

- At 300 K, phonon wavelength (λ) ~1 nm ~ surface roughness (δ)

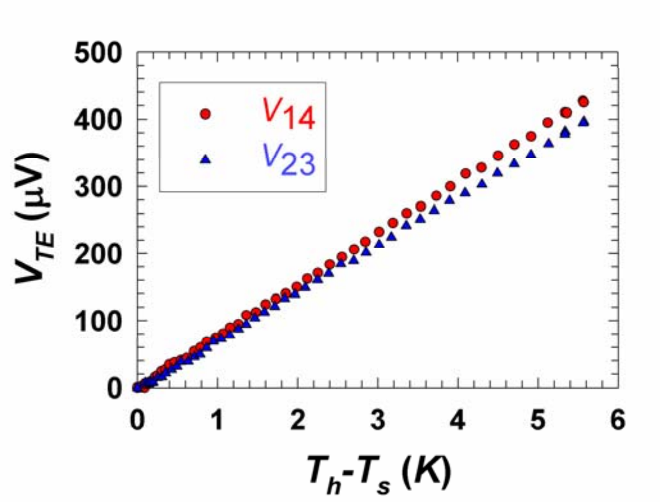
- Ziman's surface specularity:

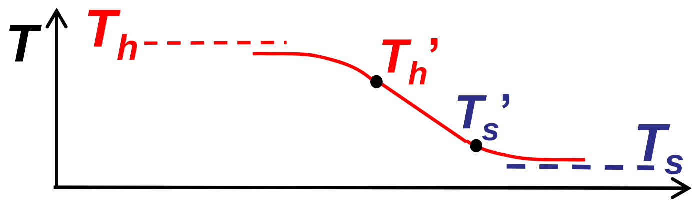
$$p = \exp(-16\pi^3 \delta^2 / \lambda^2) \geq 0$$

Thermal Measurement of Individual NWs

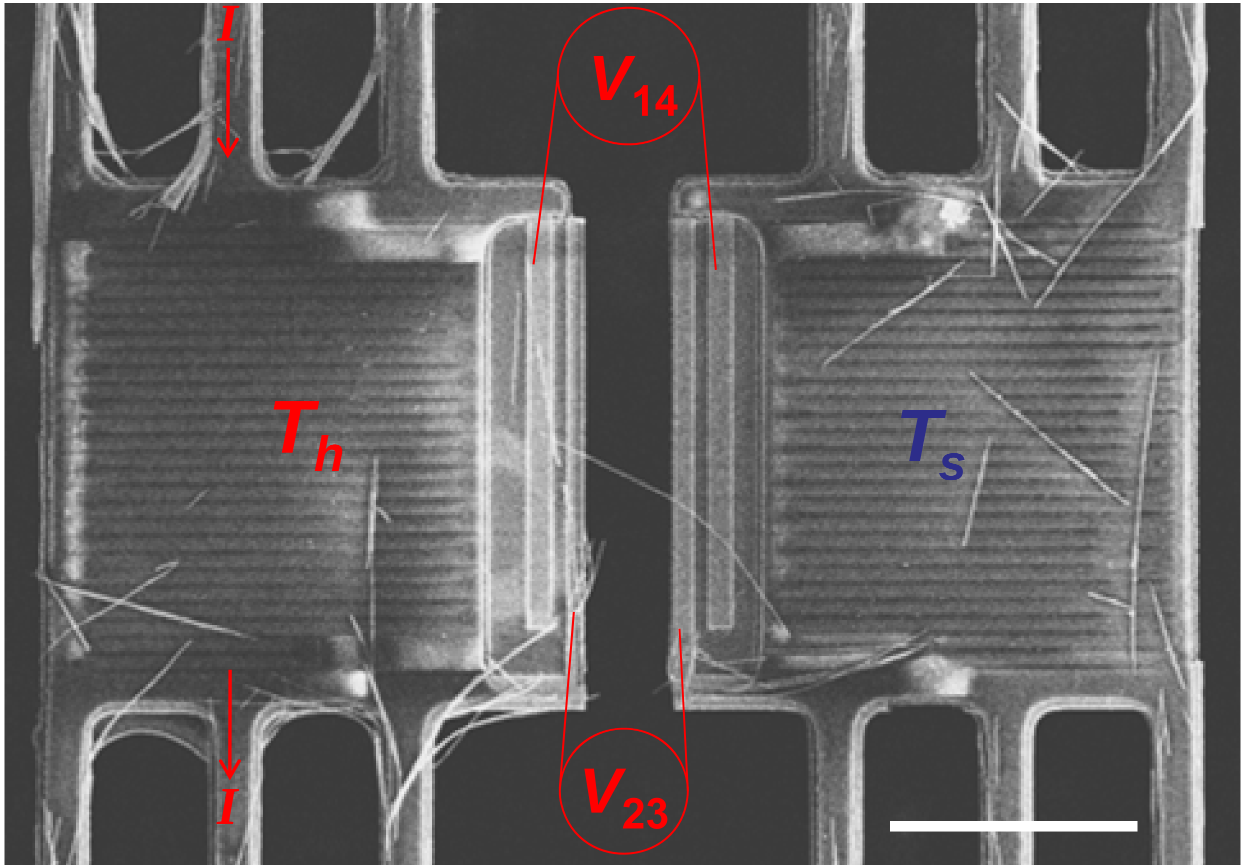


Contact Thermal Resistance and Seebeck Measurements





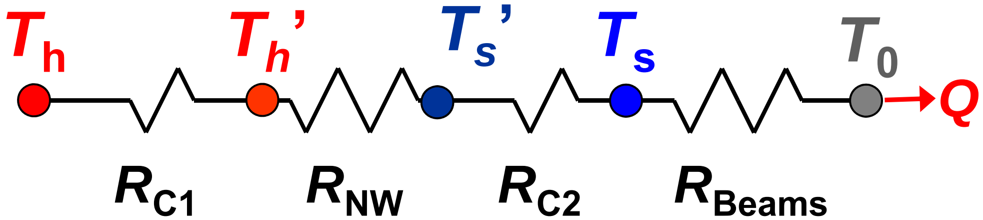
Mavrokefalos et al., Rev. Sci. Instr. 78, 034901 (2007):



$V_{23} / V_{14} \rightarrow (T_h' - T_s') / (T_h - T_s)$

$S \approx V_{14} / (T_h - T_s)$

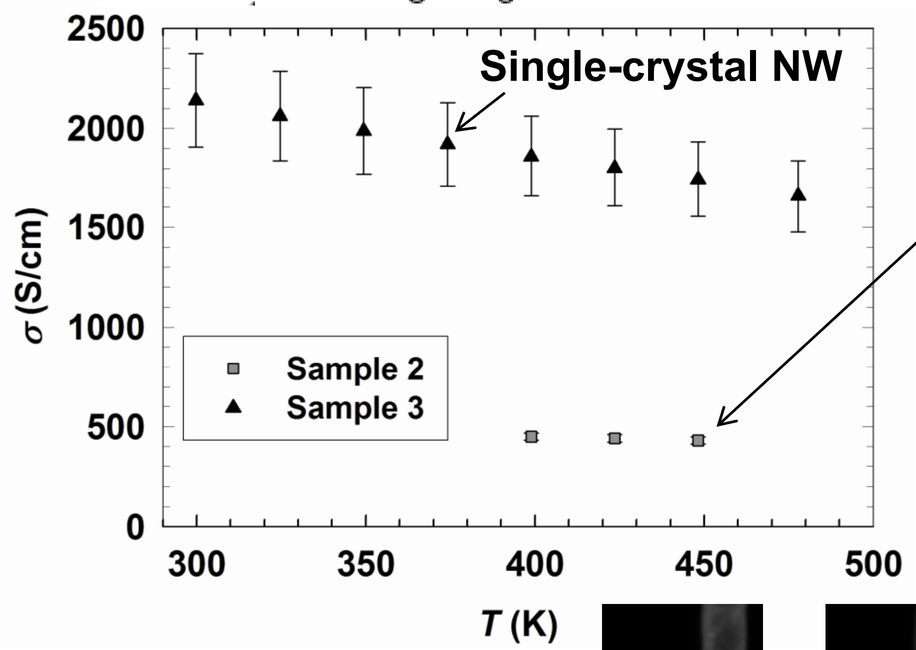
- **Electrical contact was made between the NW and the pre-patterned Pt electrodes via annealing in hydrogen.**



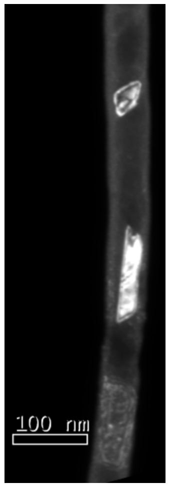
JOURNAL OF APPLIED PHYSICS **105**, 104318 (2009)

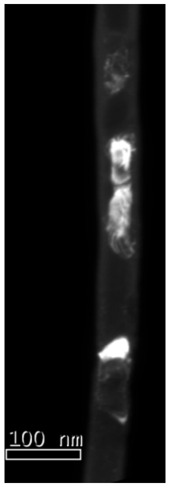
Thermoelectric and structural characterizations of individual electrodeposited bismuth telluride nanowires

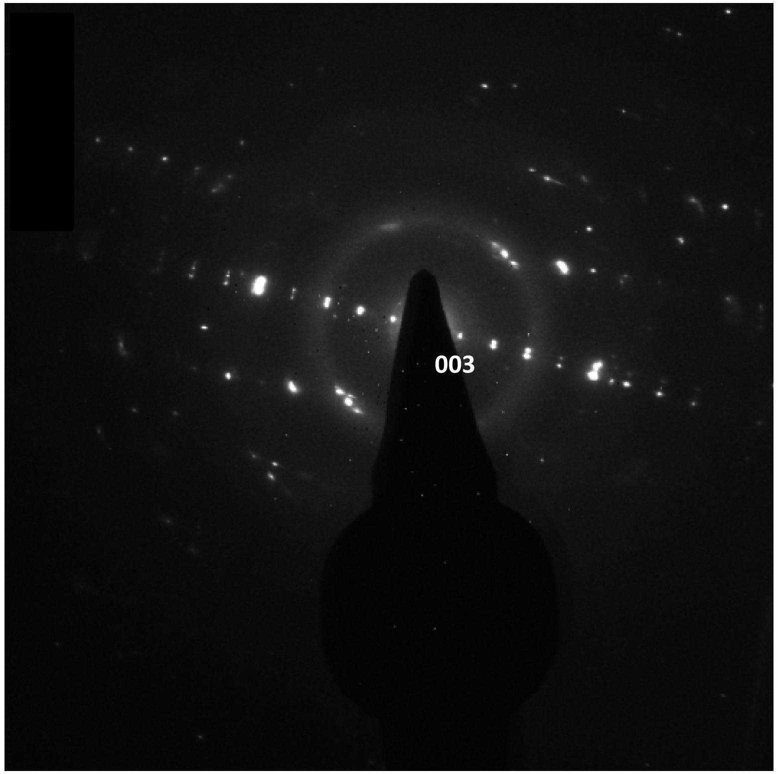
Anastassios Mavrokefalos,[1] Arden L. Moore,[1] Michael T. Pettes,[1] Li Shi,[1,a)] Wei Wang,[2] and Xiaoguang Li[2]



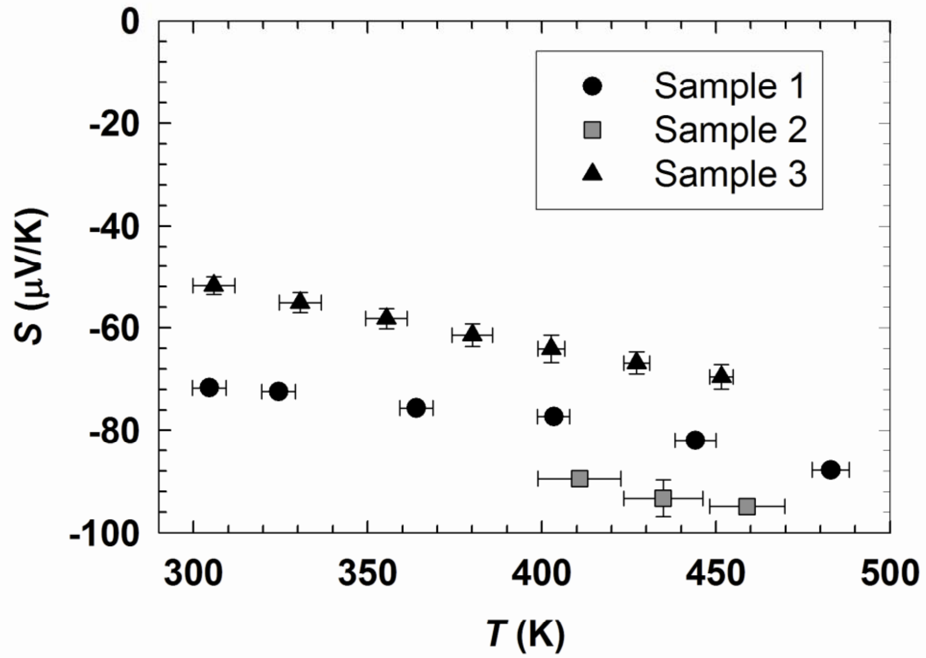
- **Polycrystalline NW**
- **Majority of the NW oriented within 3° along the binary direction**



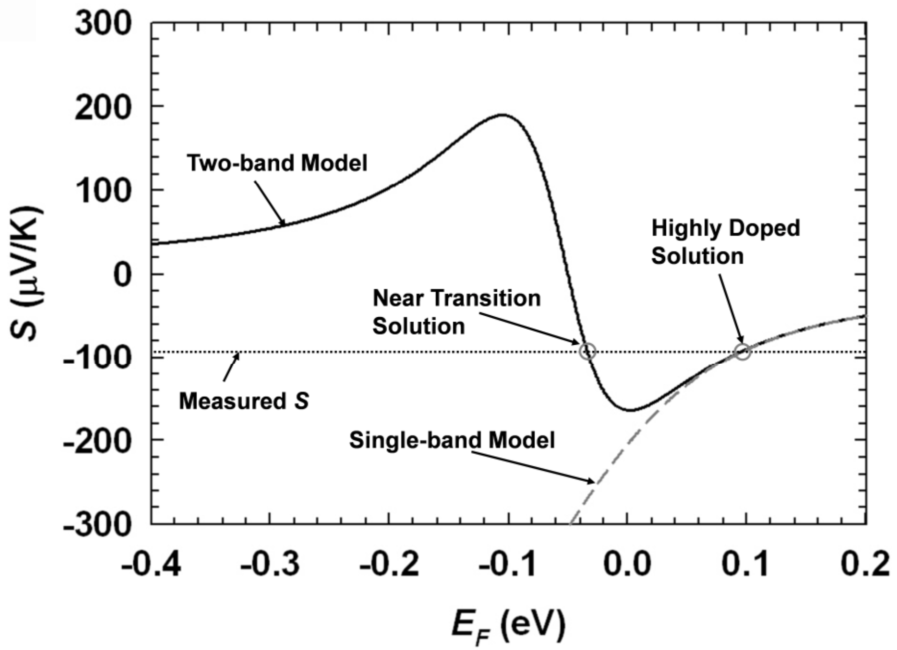




Seebeck Coefficient and Fermi Level (E_F)



• Hall measurements cannot be used to obtain carrier concentration & mobility in NWs.



Electron Concentration (n) and Mobility (μ)

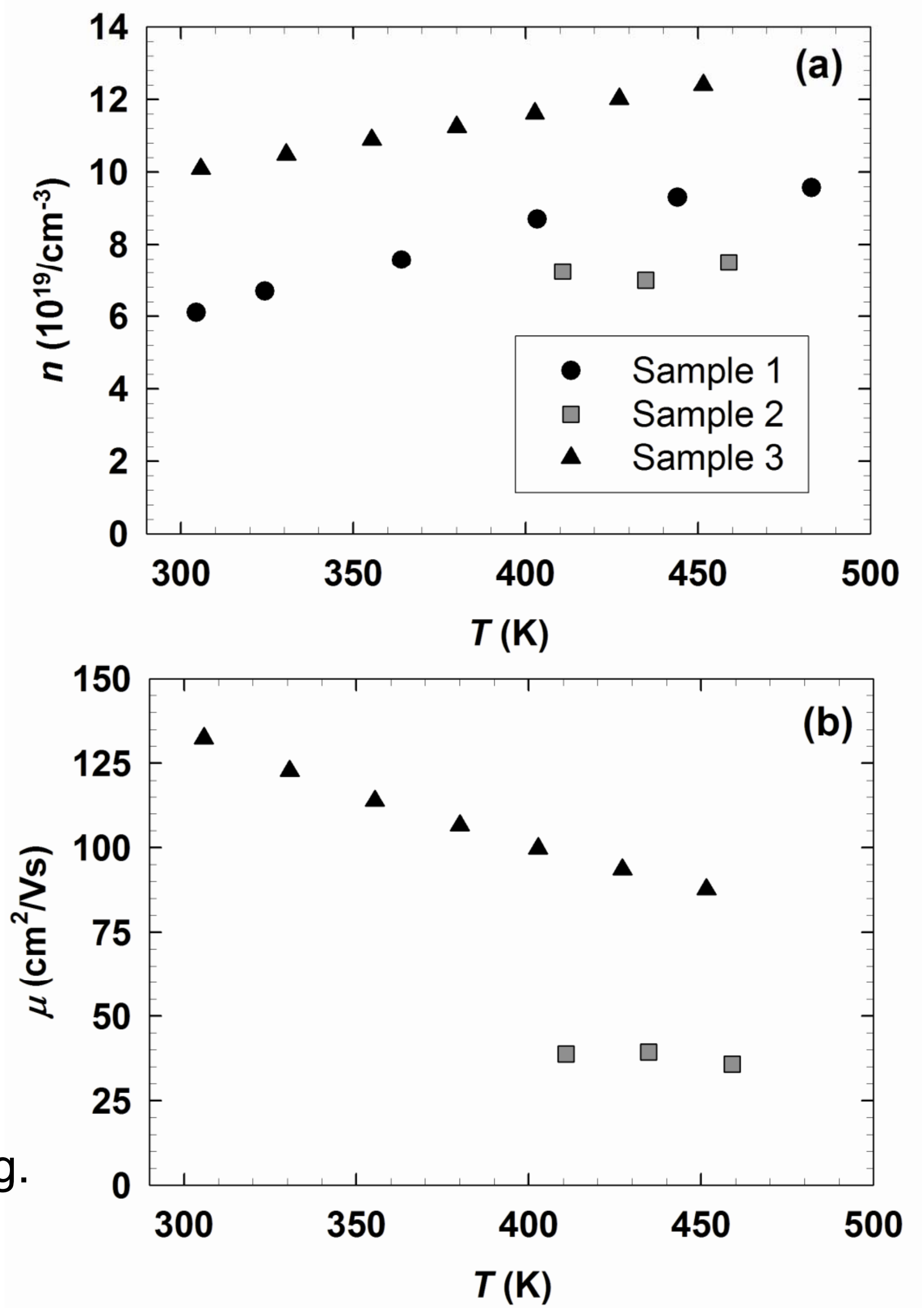
$$n = \frac{4\pi}{h^3}(2m_e^* k_B T)^{3/2} F_{1/2}(\zeta_e)$$

~0 for the highly doped E_F

$$\sigma = ne\mu_e + \cancel{p}e\mu_h$$

$$\longrightarrow \mu_e = \sigma / ne$$

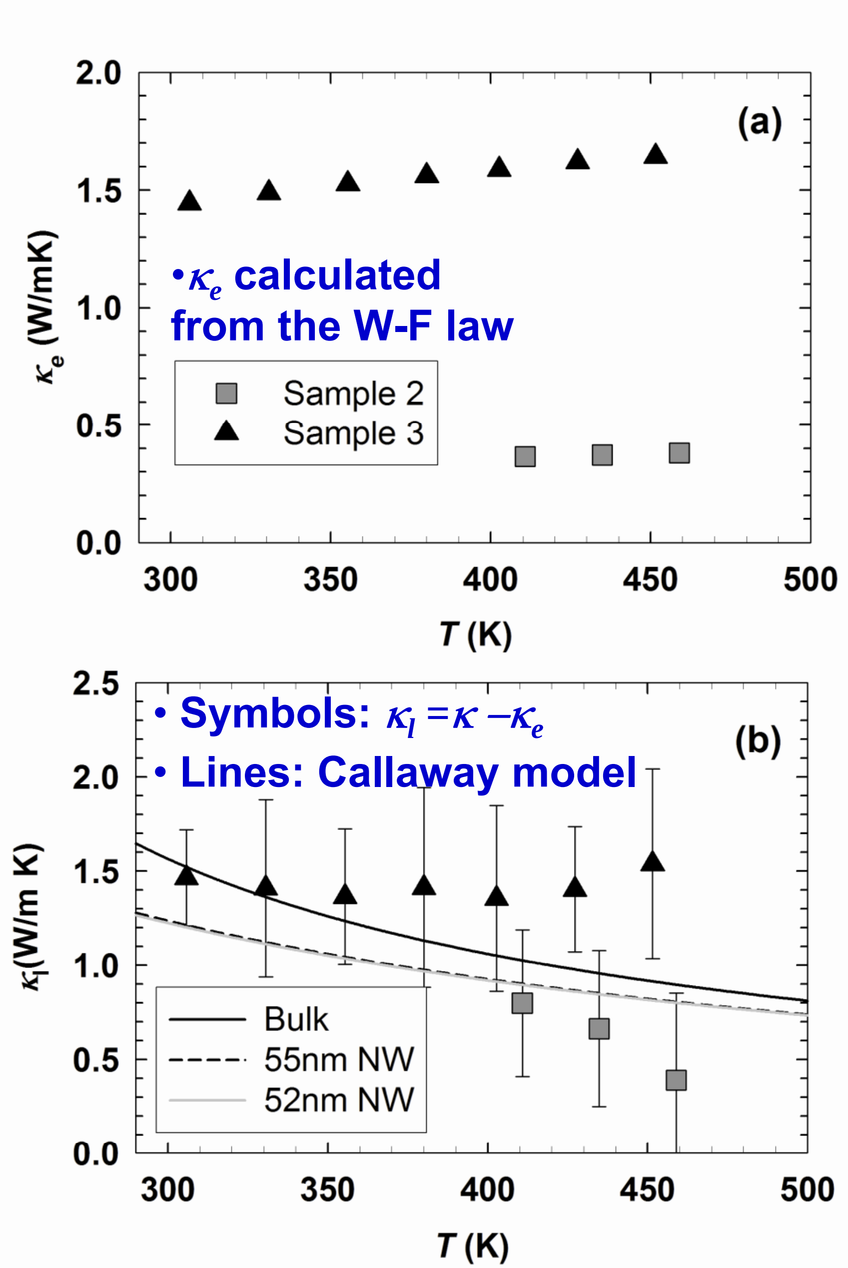
- The measured σ can only be fitted with the higher E_F



- The mobility of the single-crystal NW 3 is ~19% lower than the bulk value.

- The electron m.f.p. is reduced from 60 nm in bulk to 40 nm in NW 3 because of partially specular electron-surface scattering.

Electronic and Lattice Thermal Conductivity (κ_e & κ_l)



•For the polycrystalline NW 2, $\kappa < \kappa_{bulk}$ mainly because of κ_e suppression.

• For the single-crystal NW, the obtained κ_l is suppressed by <20% because of the short Umklapp m.f.p. (l_u~3 nm), so that *the size effects on κ_l and μ are similar in the 50-nm diameter Bi_2Te_3 NW.*

Determination of Transport Properties in Chromium Disilicide Nanowires via Combined Thermoelectric and Structural Characterizations

Feng Zhou,† Jeannine Szczech,‡ Michael T. Pettes,§ Arden L. Moore,§
Song Jin,‡ and Li Shi*,†,§,||

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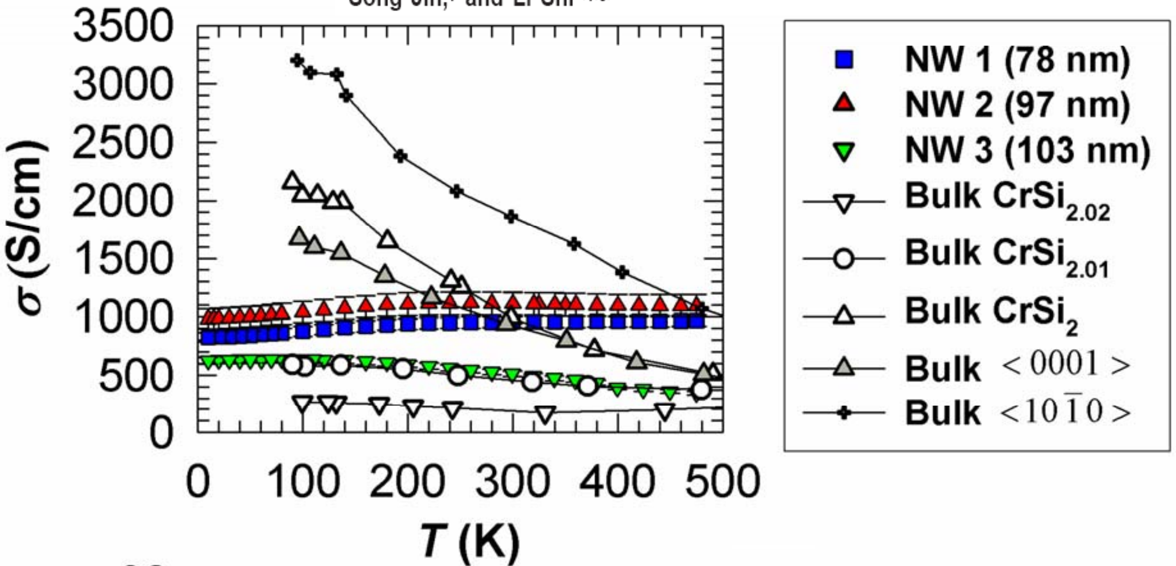
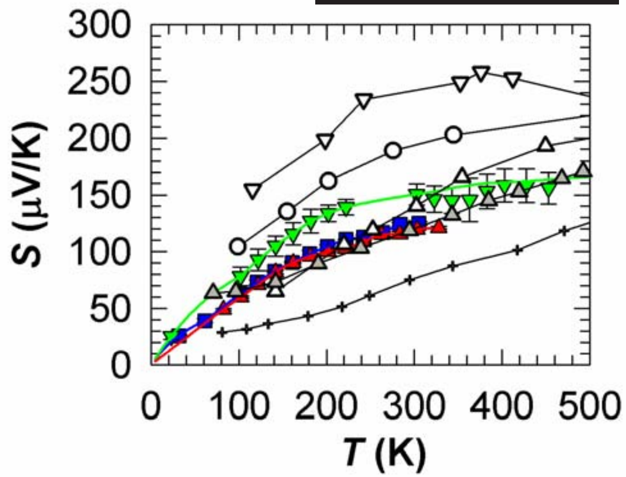
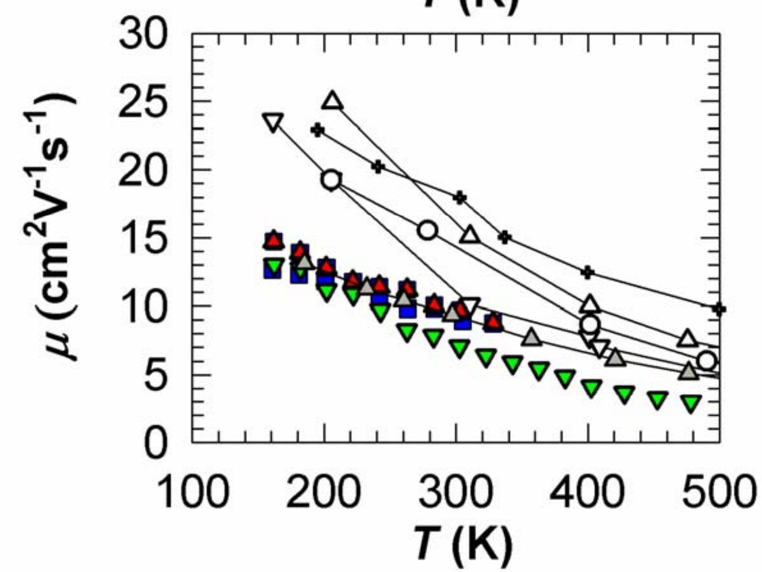
2007
Vol. 7, No. 6
1649−1654

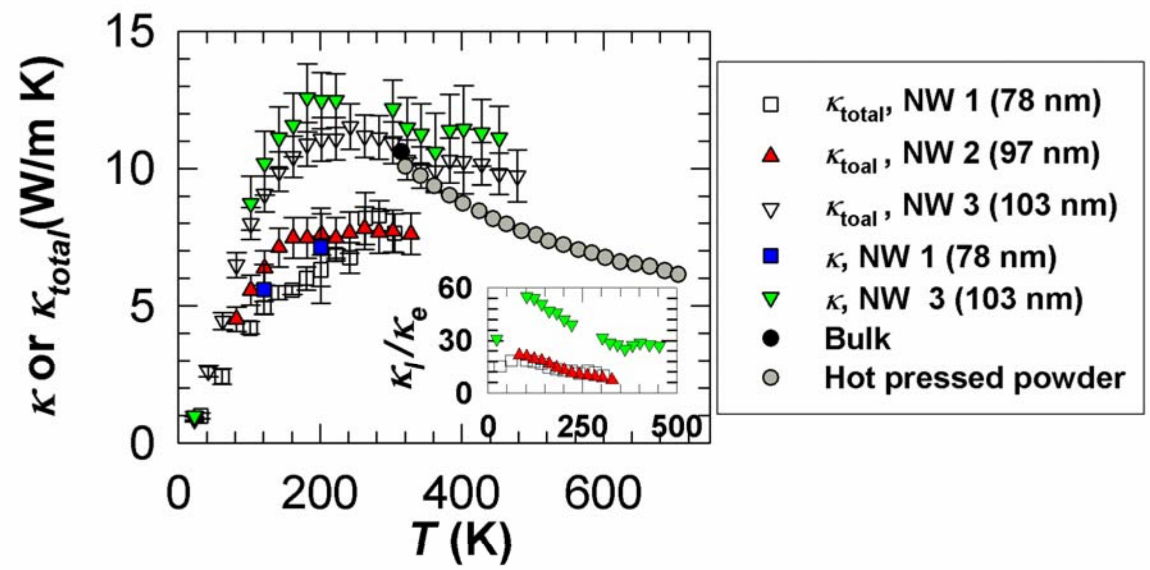


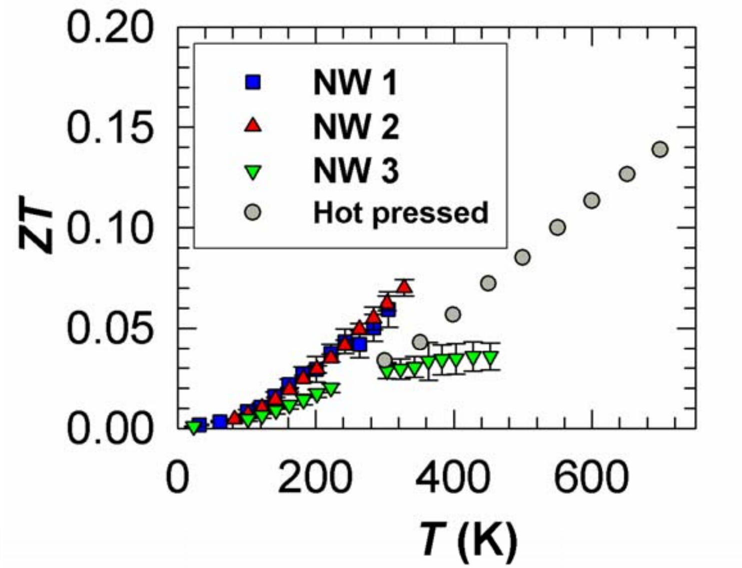




- μ of the NW is close to bulk values along the same direction.
- Hole effective mass $m^*= 5m_0$ → large p & low bulk μ
- σ is high because of a large m^* and p
- μ and τ in NWs were dominated by acoustic phonon scattering instead of boundary scattering.

Thermal Conductivity and *ZT* of $CrSi_2$ Nanowires

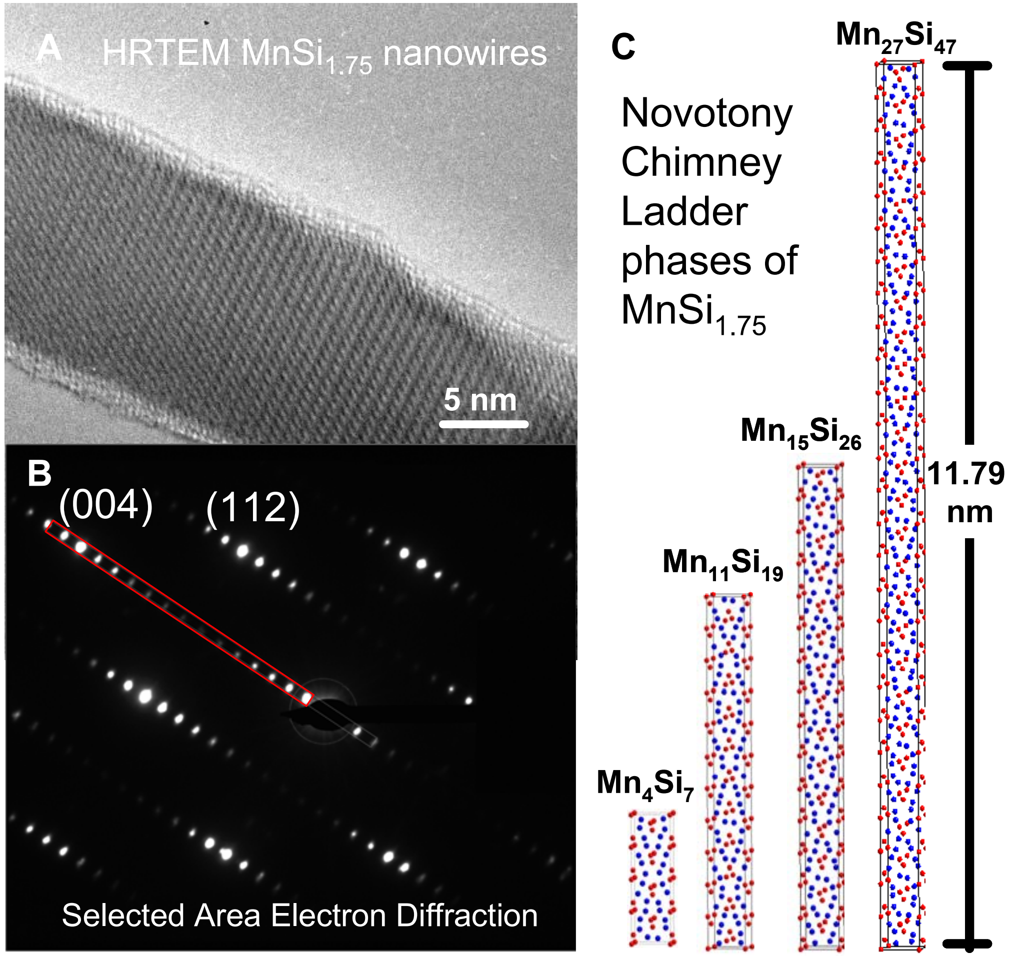


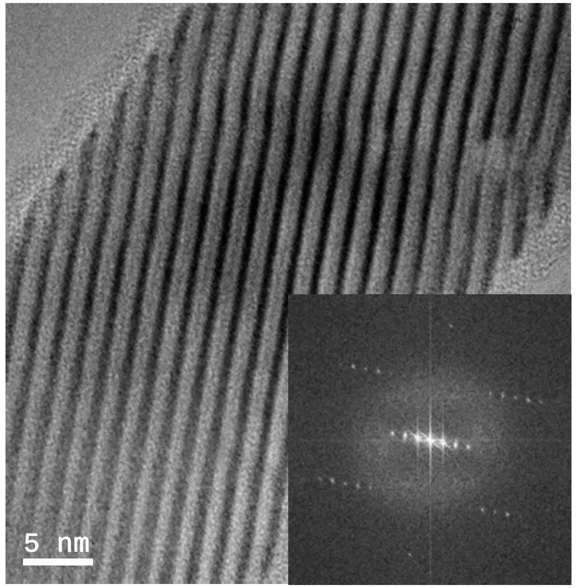


- Phonon m.f.p. in bulk $CrSi_2$ is less than 10 nm < *d.*
- Compared to the hot pressed bulk powder sample, small *ZT* enhancement was found in two NWs of <100 nm diameter mainly because of the slightly suppressed κ without mobility reduction.

- κ_l suppression in a NW is rather small unless *d* ≤ the umklapp scattering m.f.p. (l_u).

Complex Silicide Nanowires of Large Effective Mass



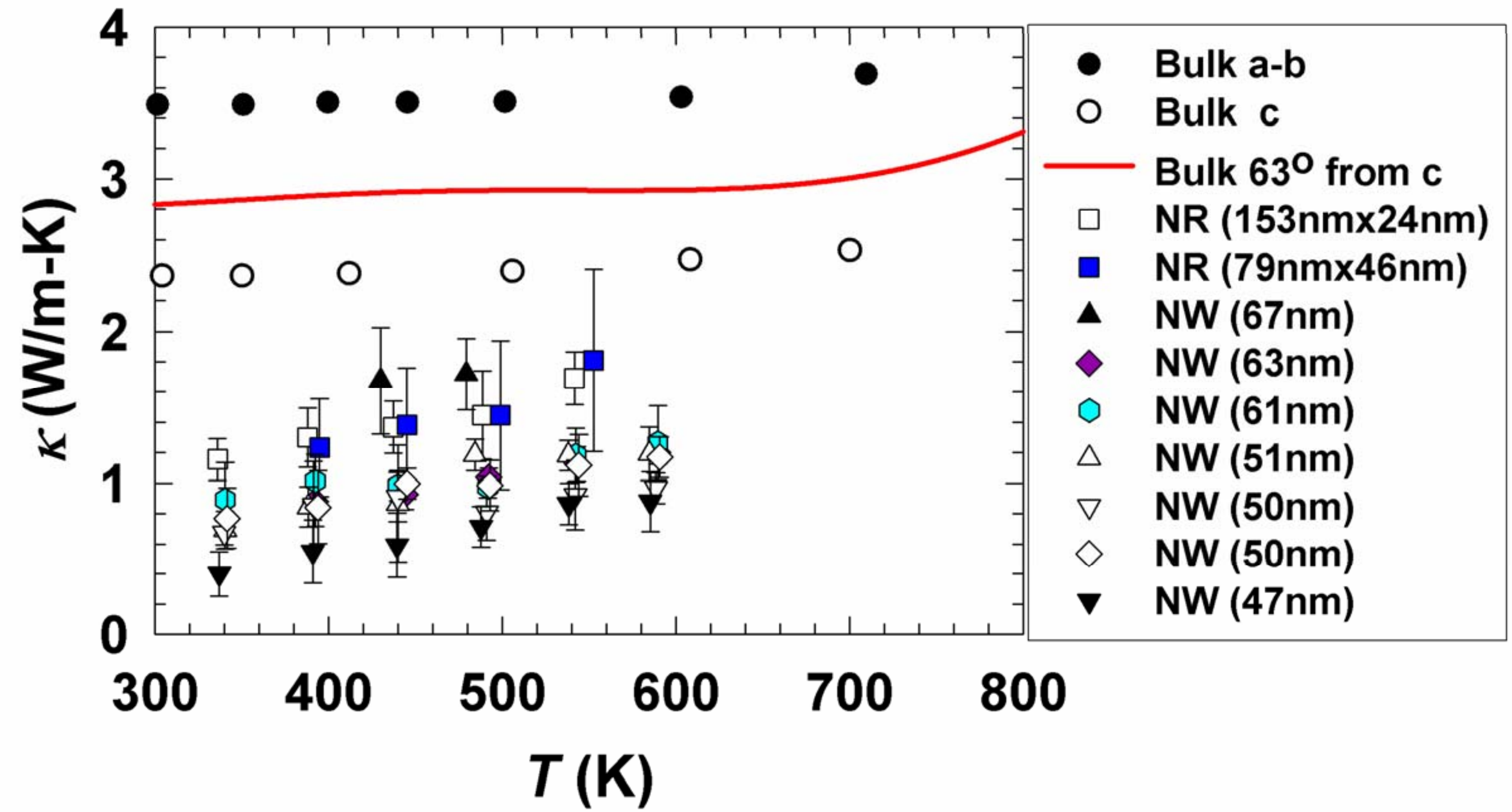


J. M. Higgins, A. Schmitt, S. Jin, JACS (2008)

- Large unit cell size (*c*) along the *c* axis of a $MnSi_{1.75}$ NW

- Numerous phonon modes of low group velocity and enhanced phonon-phonon scattering results in low $\kappa = 2–4$ W/m-K and $ZT = 0.7$ at 800 K in bulk $MnSi_{1.75}$.

Phonon-Glass Behavior in $MnSi_{1.75}$ NRs and NWs



- For $MnSi_{1.75}$ NWs and NRs, $\kappa \sim \kappa_{\alpha} = 0.7$ W/m-K calculated with $l = \lambda/2$ and v = speed of sound.
- The group velocity of the numerous optical phonons is much smaller than the speed of sound.
- The m.f.p. of acoustic phonons could be still quite long in bulk $MnSi_{1.75}$, and is reduced by diffuse surface scattering in the nanostructure.

Summary

• It appears to be possible to achieve phonon-glass, electron-crystal behavior in silicide NWs of complex crystals that have a large effective mass and abundant on earth.

• In such NWs, κ_l can be suppressed to κ_α via the combination of numerous low-velocity optical phonons with a small fraction of acoustic phonons of suppressed m.f.p.

• While it remains to be verified, the large effective mass can potentially lead to large carrier concentration and low-medium bulk mobility that is not reduced much in a NW, so that the power factor is not reduced as much as κ_l suppression.

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Research Sponsors:

NSF

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Department of Energy United States of America

Texas Higher Education Coordinating Board

NASA

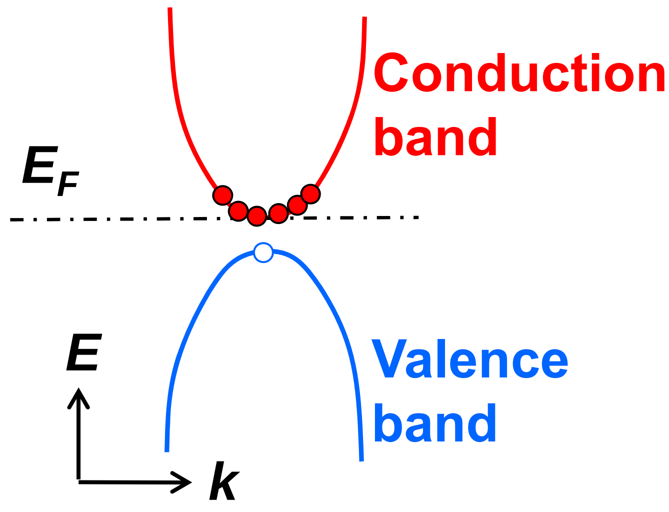
Power Factor ($S^2\sigma$)

- **Electrical conductivity:**

$$\sigma = \int \sigma_E \, dE \propto \sqrt{m^*}$$

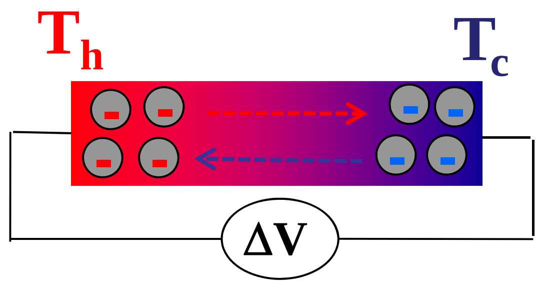
Differential conductivity

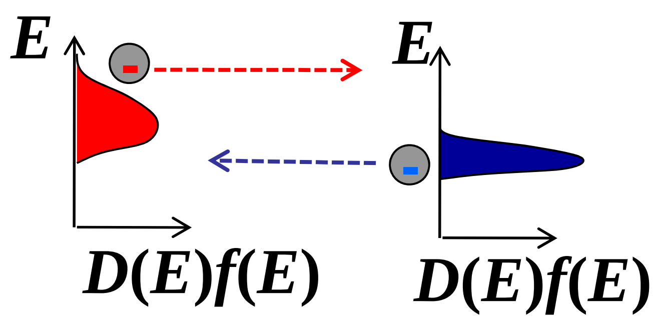
Effective mass



- **Seebeck coefficient:**

$$S = \frac{\Delta V}{\Delta T} \propto \frac{\partial \sigma_E}{\partial E}$$



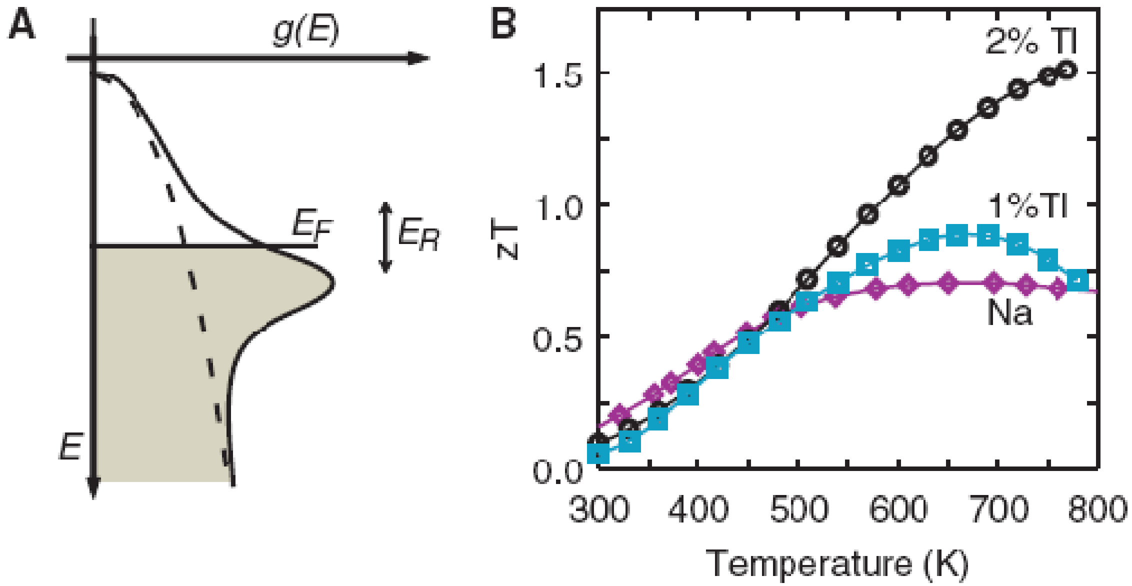


Enhancement of Thermoelectric Efficiency in PbTe by Distortion of the Electronic Density of States

Joseph P. Heremans,[1,2]* Vladimir Jovovic,[1] Eric S. Toberer,[3] Ali Saramat,[3] Ken Kurosaki,[4] Anek Charoenphakdee,[4] Shinsuke Yamanaka,[4] G. Jeffrey Snyder[3]*

25 JULY 2008 VOL 321 SCIENCE

$$S \propto \frac{\partial \sigma_E}{\partial E} \propto \left(\frac{\partial D(E)}{\partial E} \right)_{E_F}$$



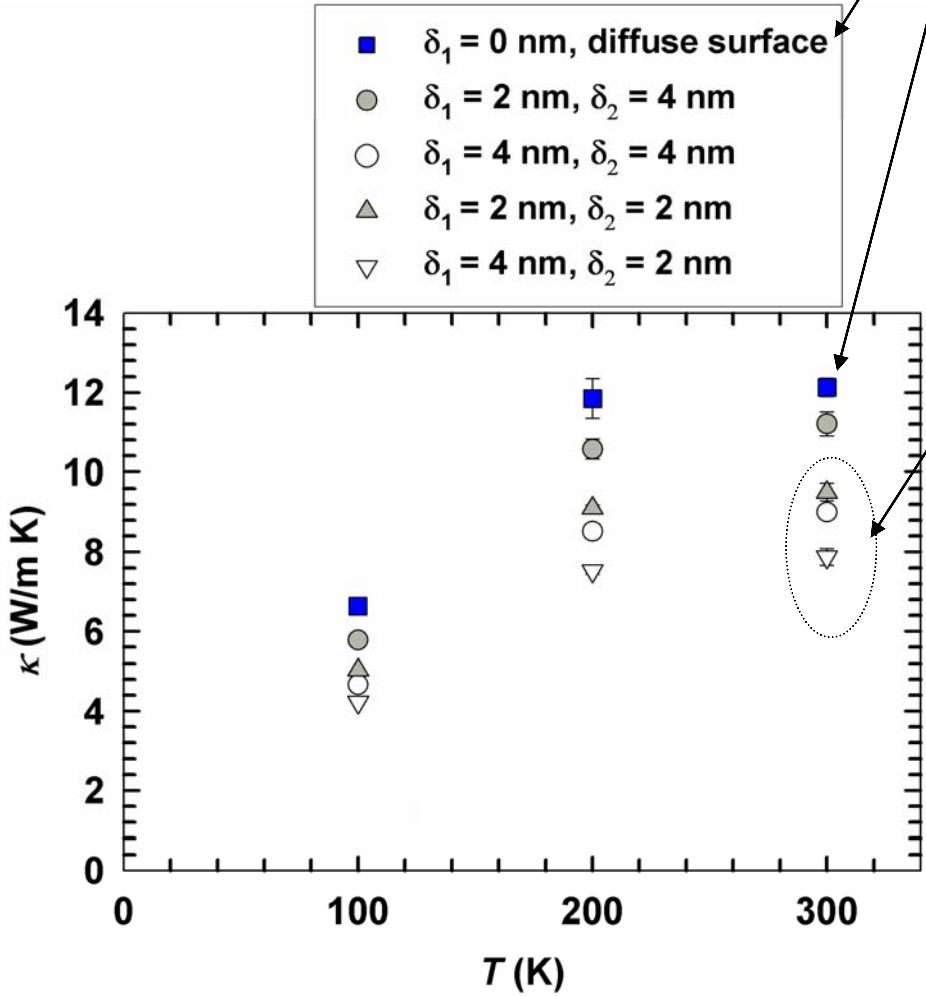
•**Thallium (Tl) doping in PbTe distorts the density of states, increasing $S^2\sigma$ and ZT.**

Phonon backscattering and thermal conductivity suppression in sawtooth nanowires

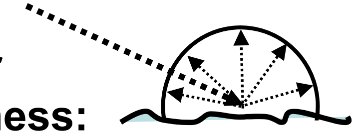
APPLIED PHYSICS LETTERS 93, 083112 (2008)

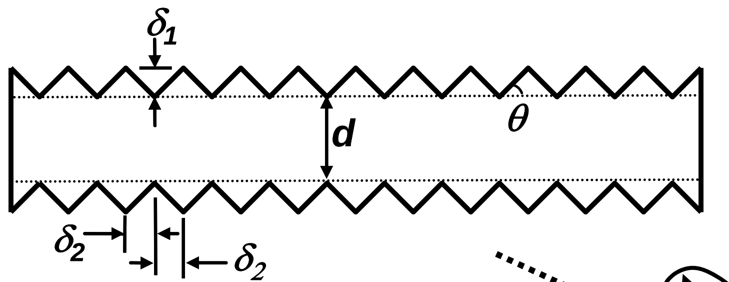
Arden L. Moore,[1] Sanjoy K. Saha,[2] Ravi S. Prasher,[2,3,a)] and Li Shi[4,a)]

- Monte Carlo phonon transport simulation.

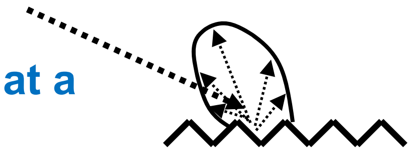


Diffuse surface limit for random surface roughness: $l \rightarrow d$ = 22 nm

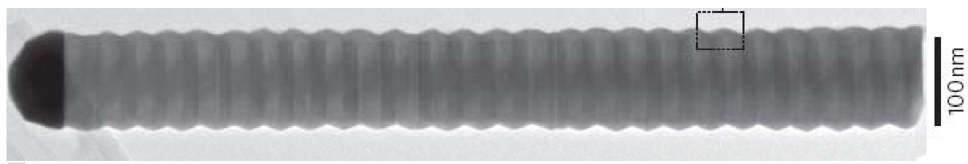




Phonon backscattering at a sawtooth surface: $l < d$



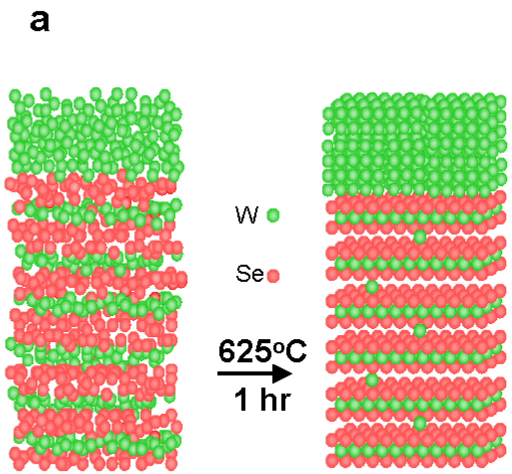
- κ can be decreased by the sawtooth roughness, but is still considerably higher than κ_α.

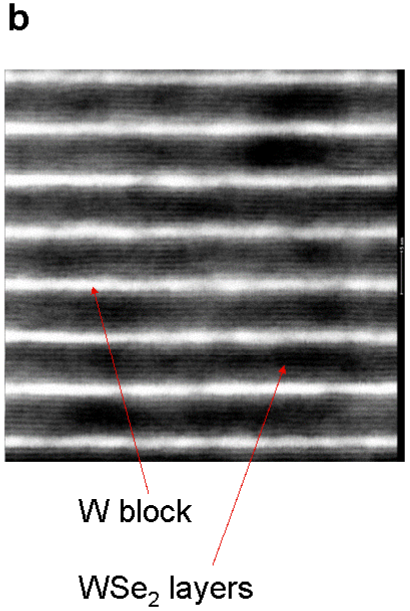


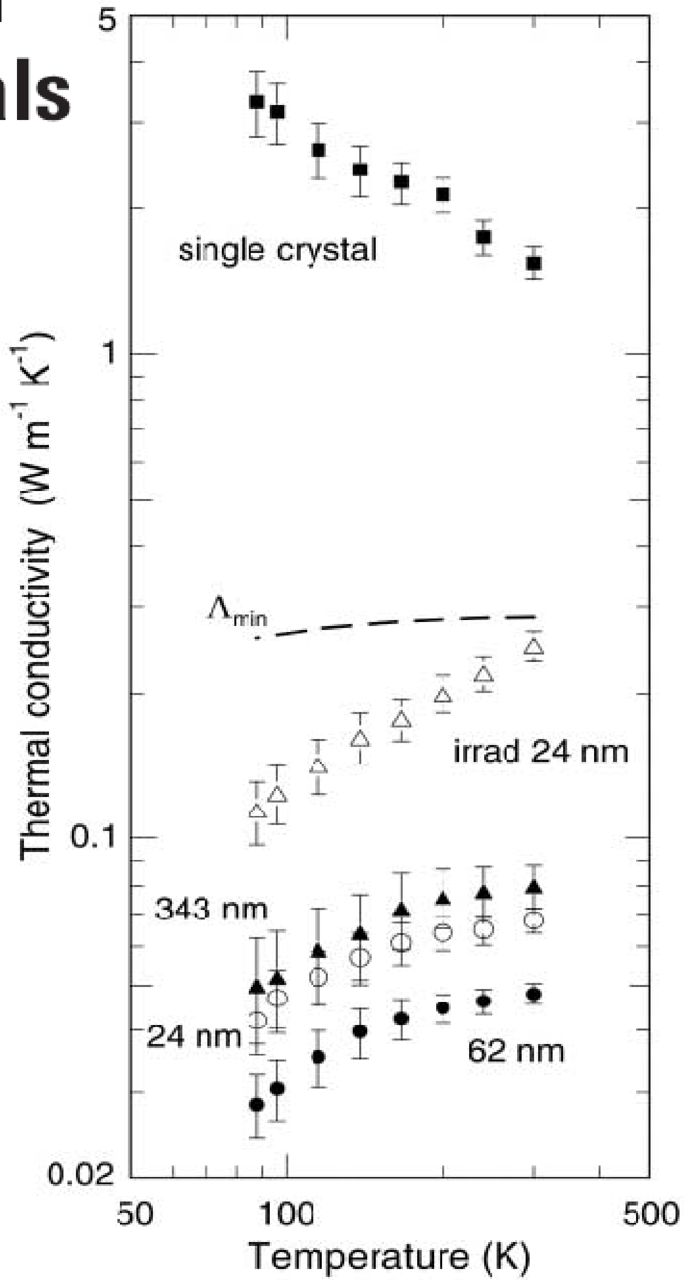
Johansson et al. Nature Nanotech 4, 50 (2009)

Ultralow Thermal Conductivity in Disordered, Layered WSe_2 Crystals

Catalin Chiritescu,[1] David G. Cahill,[1*] Ngoc Nguyen,[2] David Johnson,[2] Arun Bodapati,[3] Pawel Keblinski,[3] Paul Zschack[4]

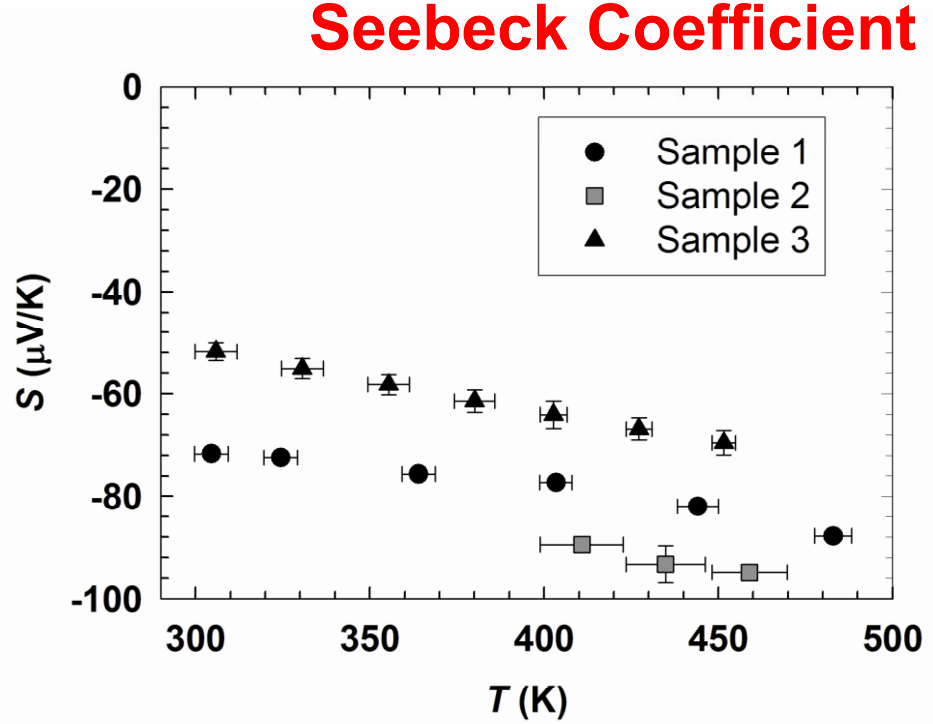


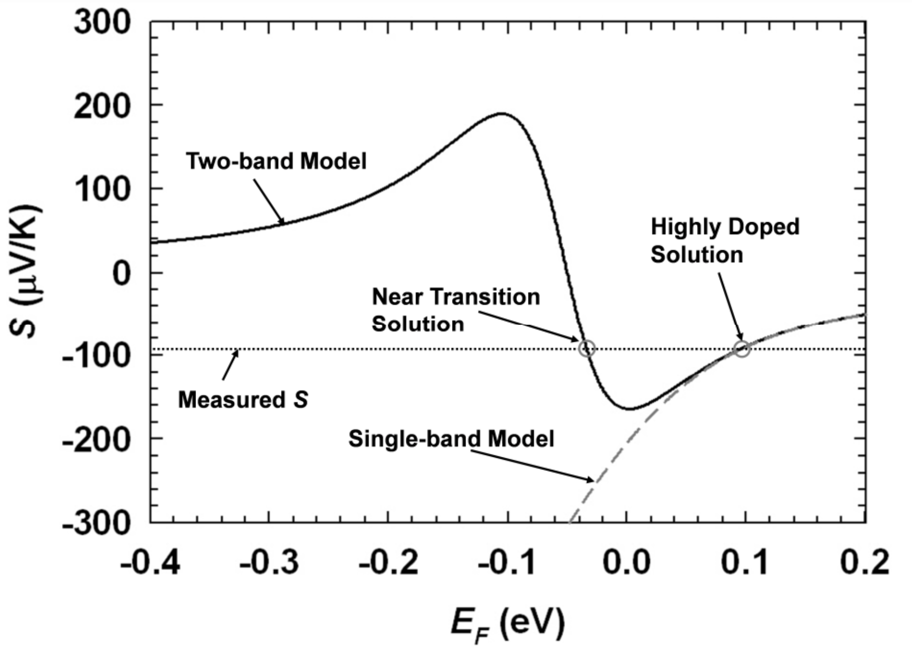




- κ_l << κ_α has been demonstrated.
- The question is how much κ_l can be lowered without considerable reduction of the charge mobility.
- We use nanowires as model systems to investigate this question because of the simple and well-characterized structure and interface.

Seebeck Coefficient and Fermi Level (E_F)





- Hall measurements cannot be used to obtain carrier concentration & mobility in NWs.
- Two-band model: $S = \dfrac{S_e\sigma_e + S_h\sigma_h}{\sigma_e + \sigma_h}$
- Single conduction band model:

$$S_e = -\frac{k_B}{e}\left(\frac{(r_e + \frac{5}{2})F_{r_e+3/2}(\zeta_e)}{(r_e + \frac{3}{2})F_{r_e+1/2}(\zeta_e)} - \zeta_e\right)$$

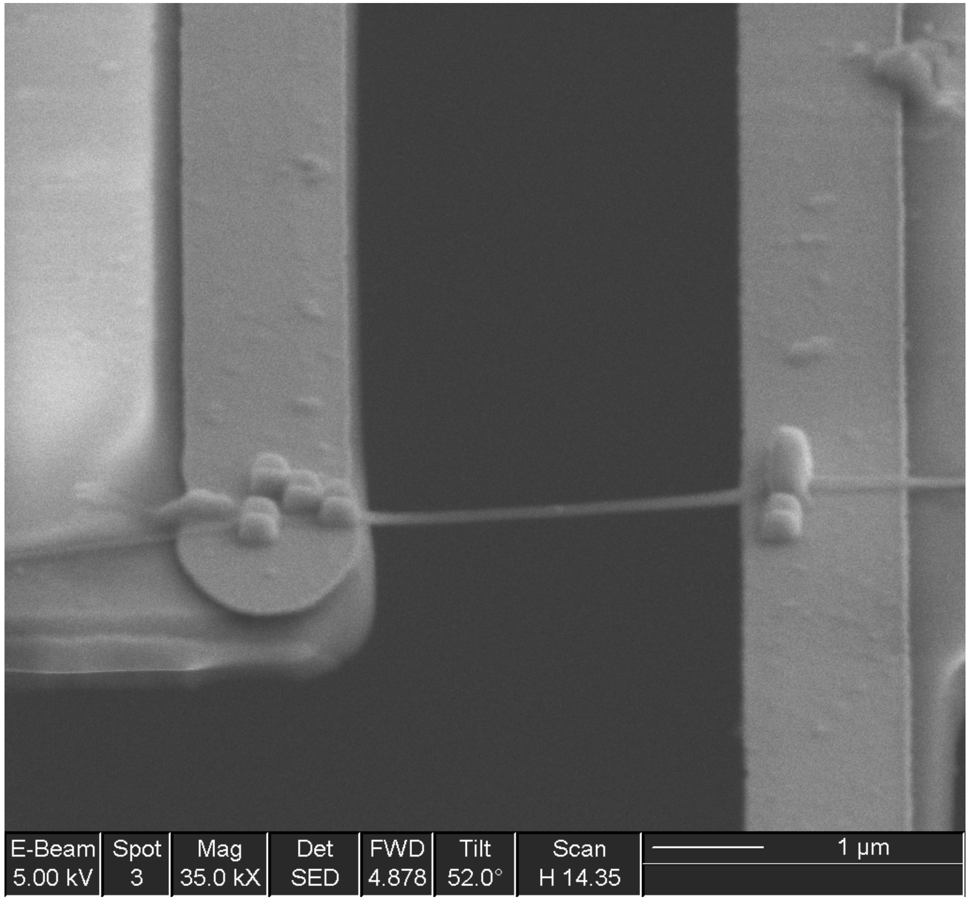
$$\xi_e = \frac{E_F}{k_B T}$$

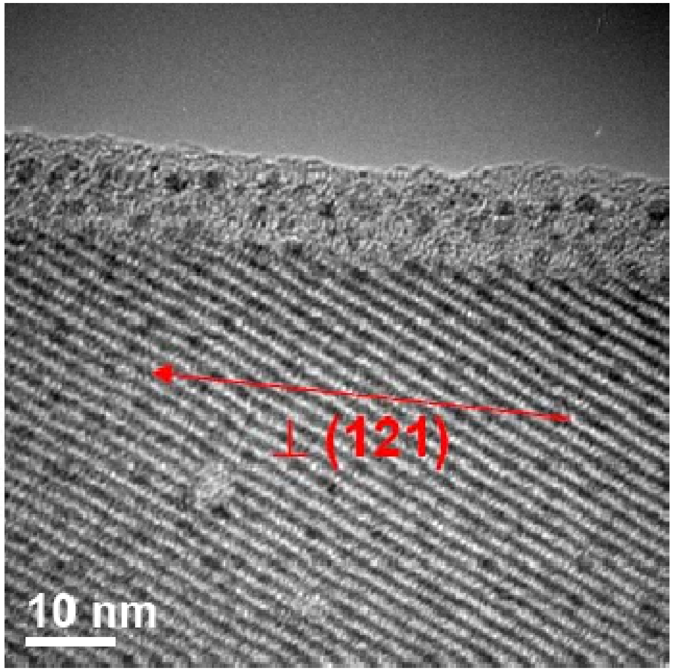
- Relaxation time:

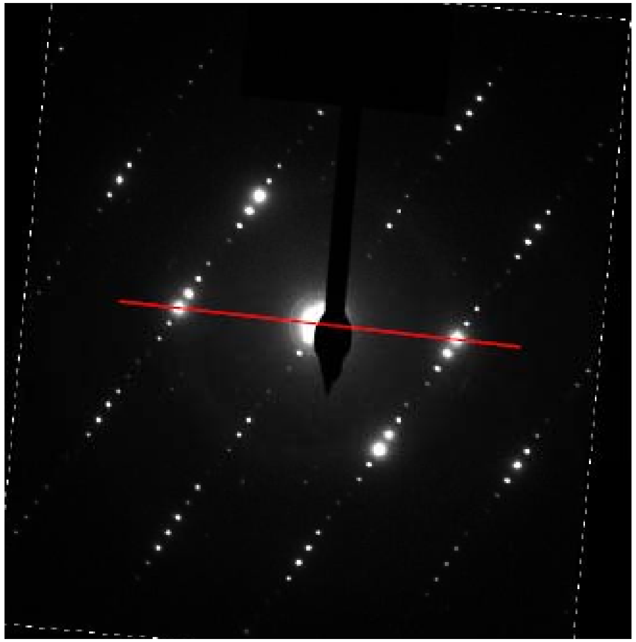
$$\tau = \tau_0 E^{r_e}$$

r_e = -0.5
for phonon and boundary scattering

Structural &Thermal Characterization of $MnSi_{1.75}$ NWs







- $Mn_{39}Si_{68}$ nanoribbon (NR)
- c ≈ 17 nm
- Growth direction perpendicular to {121} planes, or 63° from the c axis

Two-Dimensional Phonons in $MnSi_{1.75}$ NWs?

- If the *c* axis is along a radial direction, $\mathbf{2}\boldsymbol{c} < \lambda_c = 2\boldsymbol{d}/\boldsymbol{n} < 2\boldsymbol{d}$:

  → only one or several phonon wavevectors allowed in the *c* direction.

  → modulation in *d* and thus in λ_c can enhance phonon scattering.

  → κ is reduced.

Determination of Transport Properties in Chromium Disilicide Nanowires via Combined Thermoelectric and Structural Characterizations

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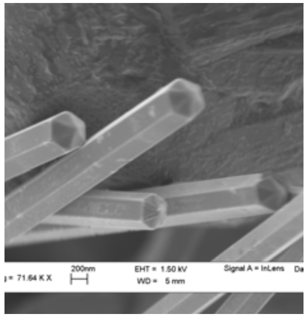
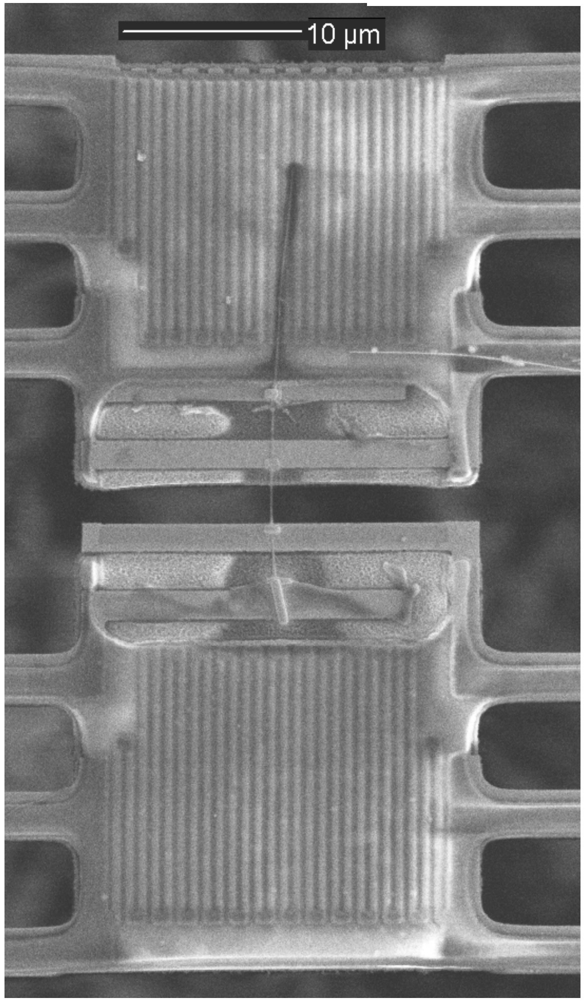
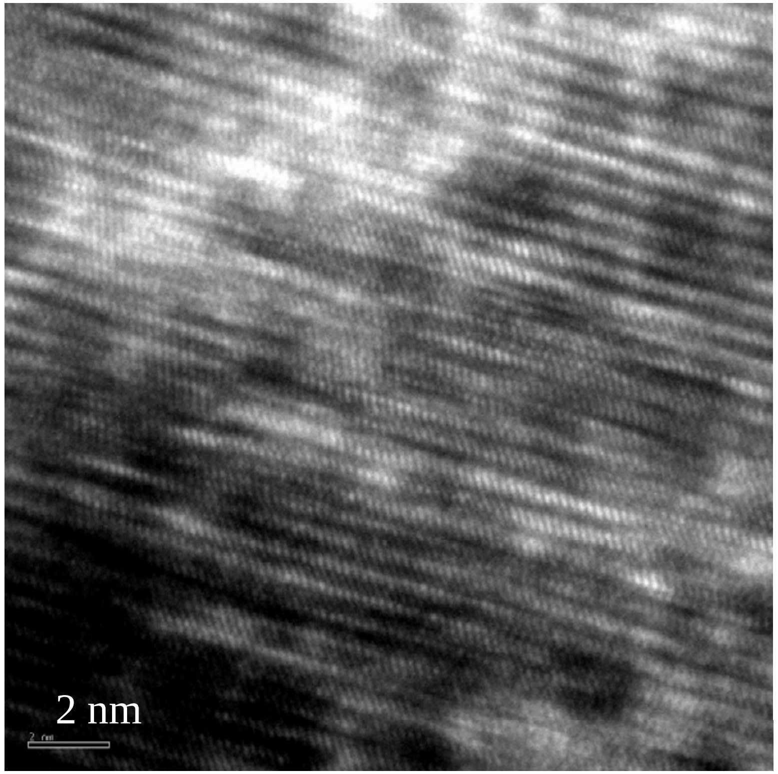
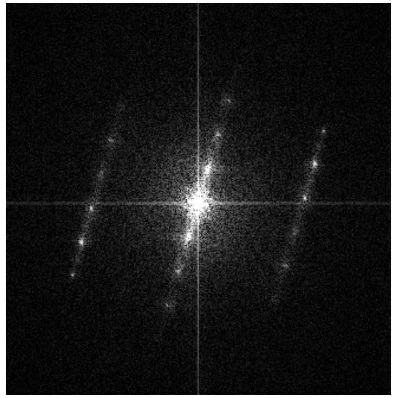


Feng Zhou,[†] Jeannine Szczech,[‡] Michael T. Pettes,[§] Arden L. Moore,[§]
Song Jin,[‡] and Li Shi*,[†,§,||]



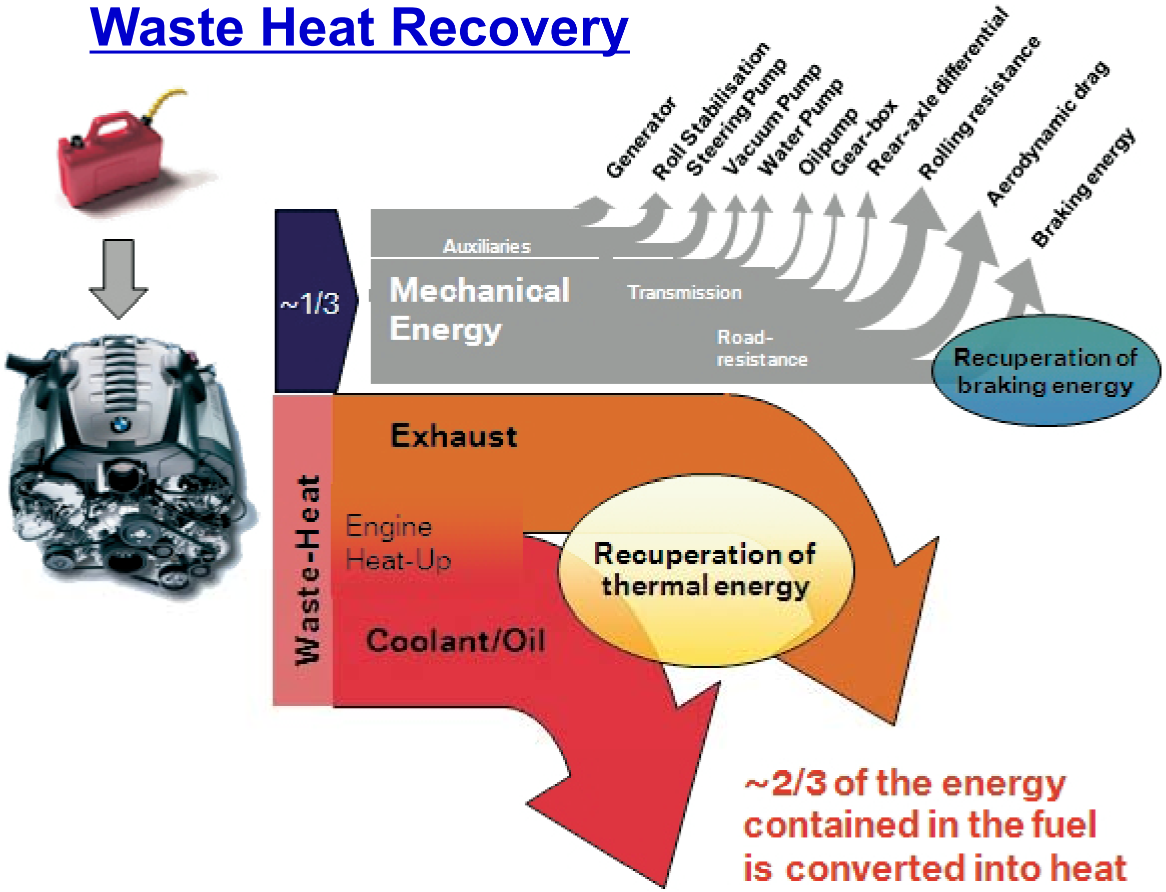




• NW growth direction found to be <0001>

Thermoelectric Energy Conversion

Waste Heat Recovery



Thermoelectric Generator

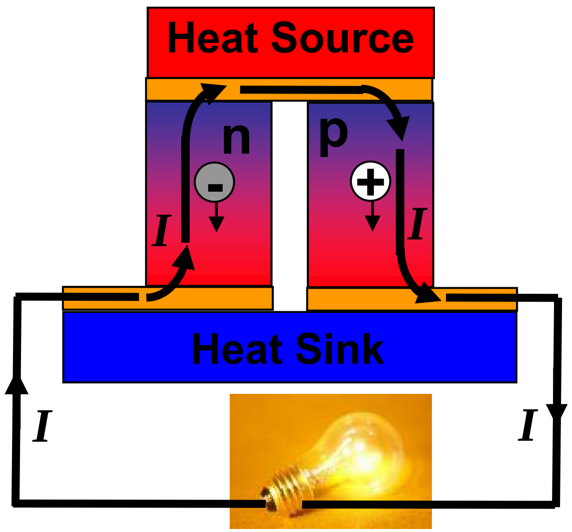


Figure of Merit (*ZT*)

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

Seebeck coefficient

Electrical conductivity

Thermal conductivity