Army Perspective on Thermoelectrics

Presented at the

DARPA/ONR/DOE Thermoelectrics Workshop

by

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1990 State-of-the-Art

State-of-the-Art Thermoelectric Materials in 1990 were Semiconductor Alloys based on Bi_2Te_3 with ZT=1.0

e.g. n-type $Bi_2(Te,Se)_3$ p-type $(Bi,Sb)_2Te_3$

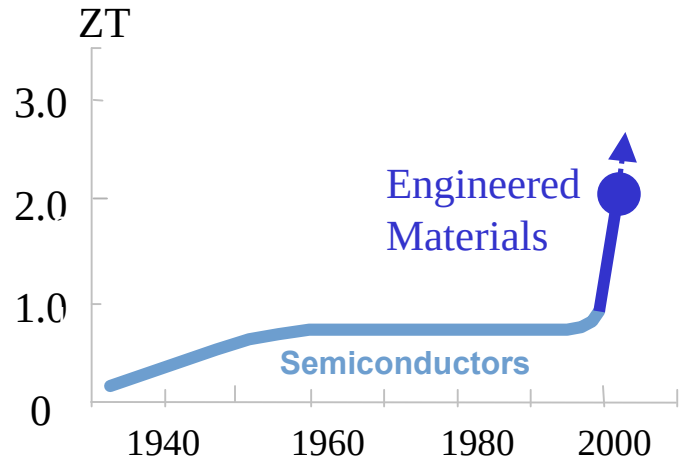
Guiding Principles:

semiconductor materials - single carrier systems
high density of states near the Fermi level (multiple carrier pockets) - high Seebeck coefficient
high carrier mobility - low Joule heating
high carrier effective mass - high Seebeck coefficient
large atomic masses - small phonon group velocity (μ (K/M) $^{1/2}$); low lattice thermal conductivity
alloying - enhanced phonon scattering with little degradation in the electrical conductivity

DoD Thermoelectrics Initiative
(1992-2002)

OBJECTIVES:

Develop and demonstrate new and innovative approaches leading to vastly improved thermoelectric materials for cooling applications



ACCOMPLISHMENTS:

- New approaches to the engineering of thermoelectric materials were investigated and significant breakthrough concepts identified.
- Joint DARPA /Navy/Army initiative has recorded ZT gains over the broad temperature range from 100 - 850 K.

ARMY RELEVANCE:

- Cryogenic Coolers for Night Vision
- Cooling of Microelectronics
- Refrigeration/Air Conditioning
- Low-Power Generation

DoD Thermoelectric Program

1992: ARO (J. Prater) and ONR (J. Pazik) Independently Start Funding MIT-Lincoln Labs to Investigate Bandgap Engineering of BiSb (T. Harman)

ONR Funding of Skutterudite Studies at JPL (J.P. Fleurial)

1993: Theoretical Prediction of Enhanced Thermoelectric Properties via Quantum Enhancement Effects in Superlattice Systems (MIT-M. Dresselhaus)

1995-6: Preliminary Experimental Confirmation of Enhanced Thermoelectric Effects in both Superlattice (MIT-LL) and Skutterudite Systems (JPL)

1997: DARPA (S. Wolf) Initiative in Thermoelectics Launched

ONR Funded MURI Center in Quantum Structure for Thermoelectric Applications was initiated at UCLA (G. Chen)

1999-2000: Efficacy of Quantum-dot (MIT-LL) and Cross-plane Superlattice (R. Venkatasubramanian at RTI) Approaches Demonstrated

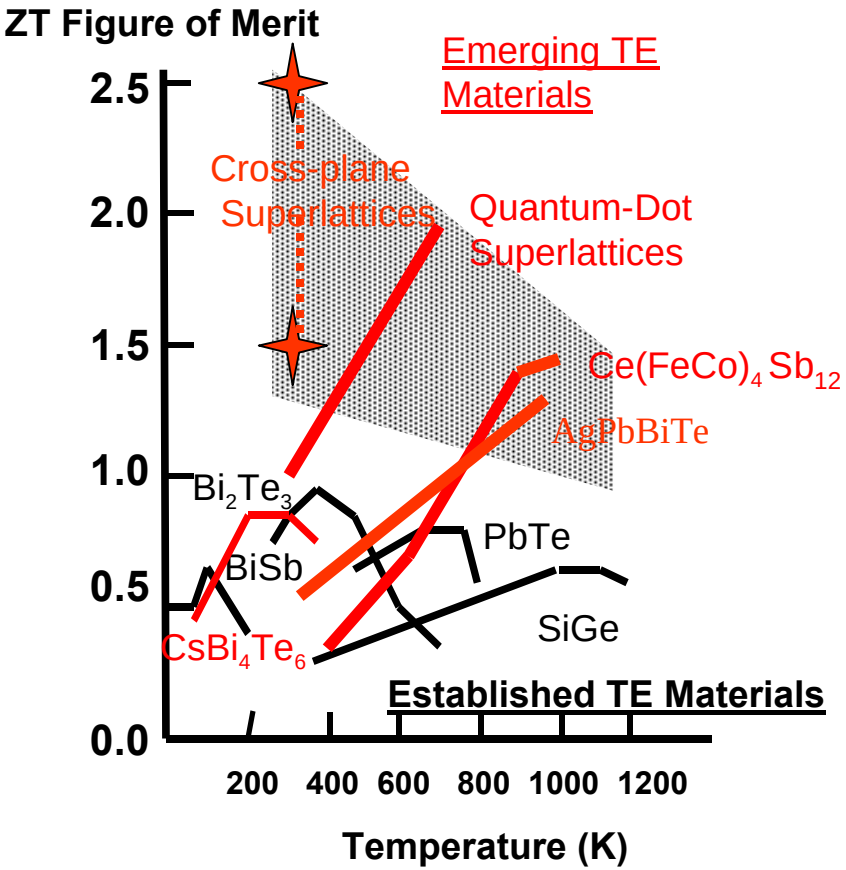
Paradigm-Shifting Concepts for TE Materials

1) Bandgap Engineering of Electrical Properties

- Band Engineering in low-D Systems
- Quantum Confinement Effects on Density of States
- Energy Filtering at Band Offsets
- Mobility Enhancement via Modulation Doping

2) Phonon Engineering

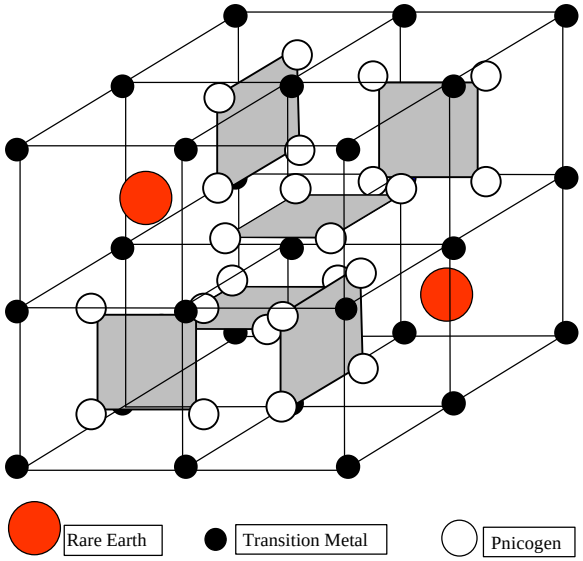
- Phonon Rattlers in Bulk Systems
- Interface Scattering in Superlattices

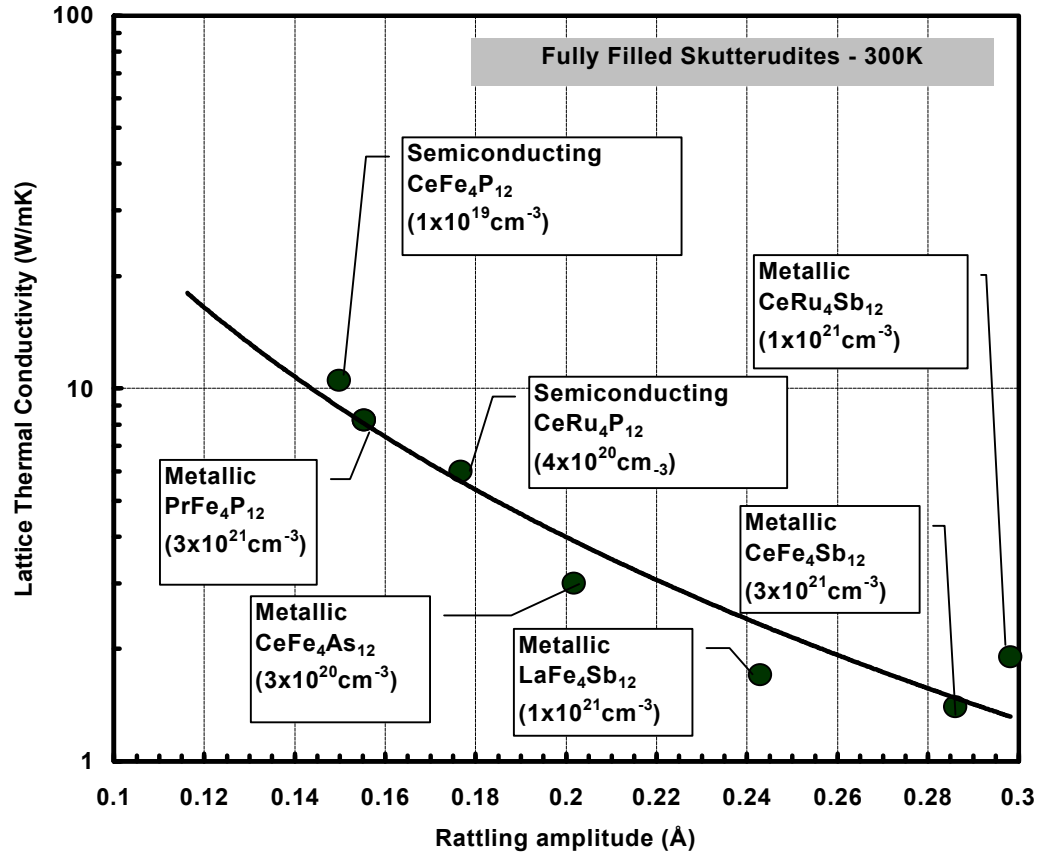


Note: Most of these concepts have yet to be implemented in a bulk material!

Phonon Rattler Concept in the Skutterudite Systems

J.P. Fleurial, JPL





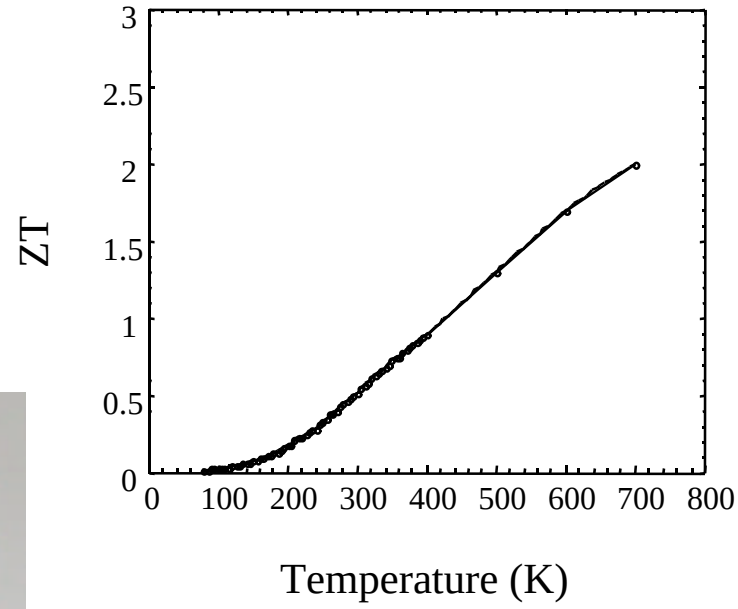
Skutterudite systems were known to have promising electrical properties, but high thermal conductivities. JPL researches demonstrated that the thermal conductivity of the Skutterudite systems could be decreased by an order of magnitude by filling void spaces with Phonon Rattlers

$A_mB_nM_mQ_{2m+n}$ System

Mercouri Kanatzidas, Michigan State Univ.

Segregation at the nanoscale?
High Power Factors between 300-~800 K
Promising new materials for power generation

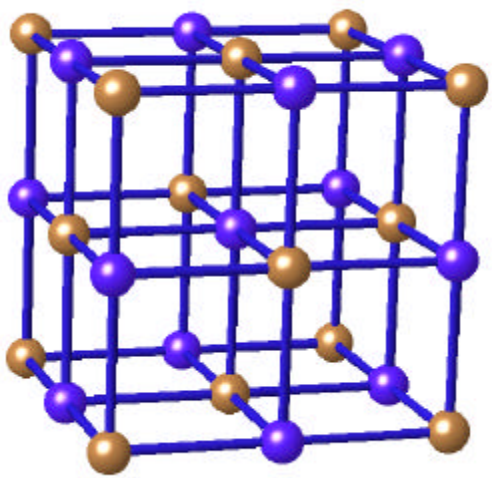
Cubic Pb-Ag-Sb-Te



NaCl structure type: $Fm\bar{3}m$

A,B, M

Q



<u>Cationic positions</u>
A: +1 (K, Ag)
B: +2 (Pb, Sn)
M: +3 (Bi, Sb)

<u>Anionic positions</u>
Q: -2 (S, Se, Te)

MICHIGAN STATE UNIVERSITY

Approaches under Investigation for Realizing Improved Thermoelectric Properties in Bulk Systems

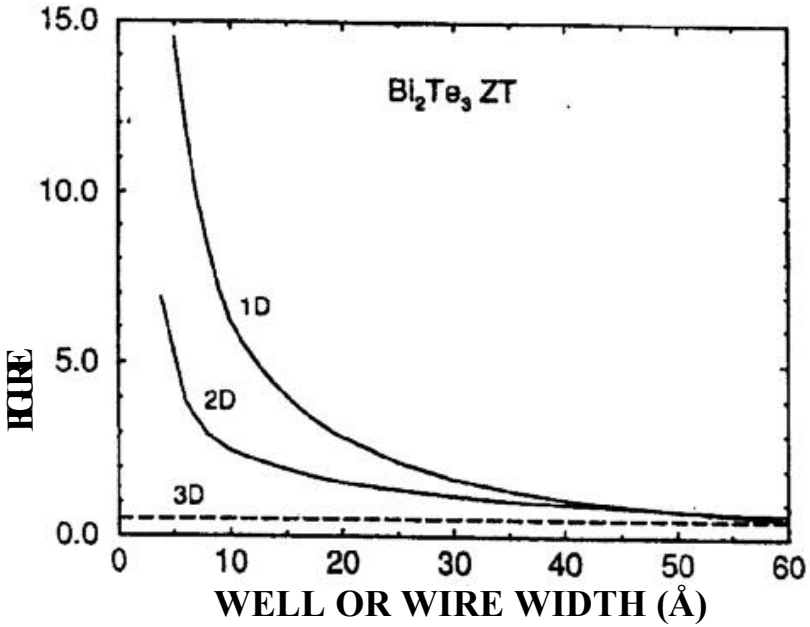
Synthesis and Self-Assembly of Nanoparticles - C. O'Connor at U New Orleans and C. Murray at IBM Watson RC

Nanowire Composites Prepared by High Pressure Injection into Porous Dielectrics - T. Huber (Howard Univ) ; M. Dresselhaus (MIT)

Vapor Deposition (Sputtering, Pulsed Laser Deposition & Chemical Vapor Deposition) - J. Farmer, LLNL, T. Sands (Berkeley), and R. Venkatasubramanian (RTI)

Electrodeposition and Sol-gel Deposition Approaches - J.-P. Fleurial (JPL), B. Dunn and A. Stacy (UCLA)

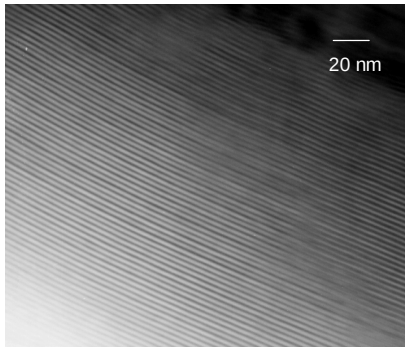
Prediction of Quantum Confinement Effects in Low-D Systems



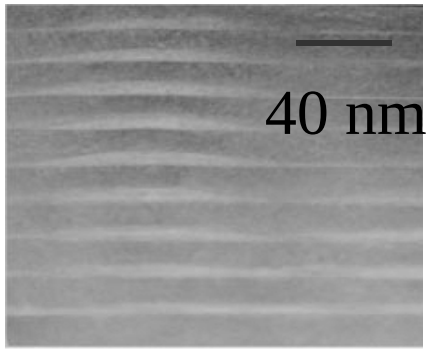
Note: Conduction is assumed to be along the extended dimension

2D, 3D: Hicks and Dresselhaus, Phys. Rev. B47 (1993), p. 12727-31

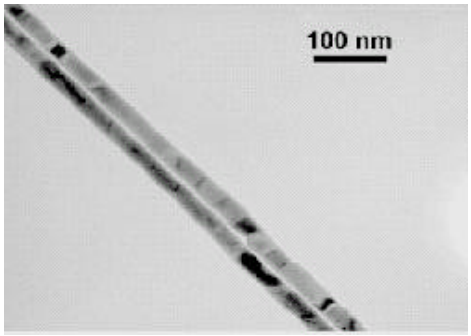
1D: Hicks and Dresselhaus, Phys. Rev. B47 (1993), p. 16631-34



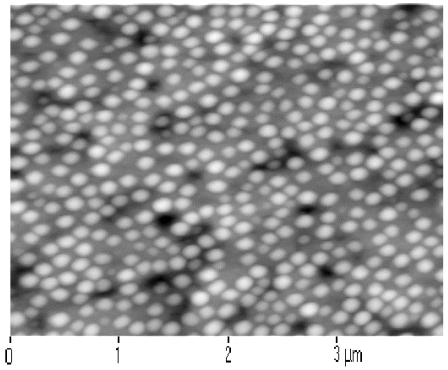
Bulk



Superlattice
2D



Nanowire
1D



Quantum Dots
0D

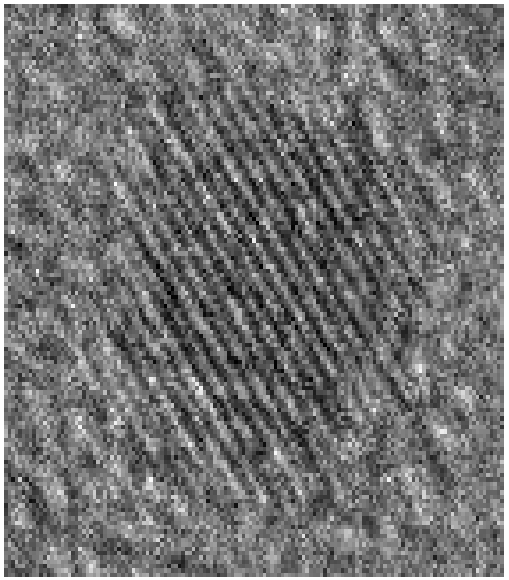
Nanophase Materials for Thermoelectric Applications

C. O'Connor at U New Orleans and C. Murray at IBM Watson RC

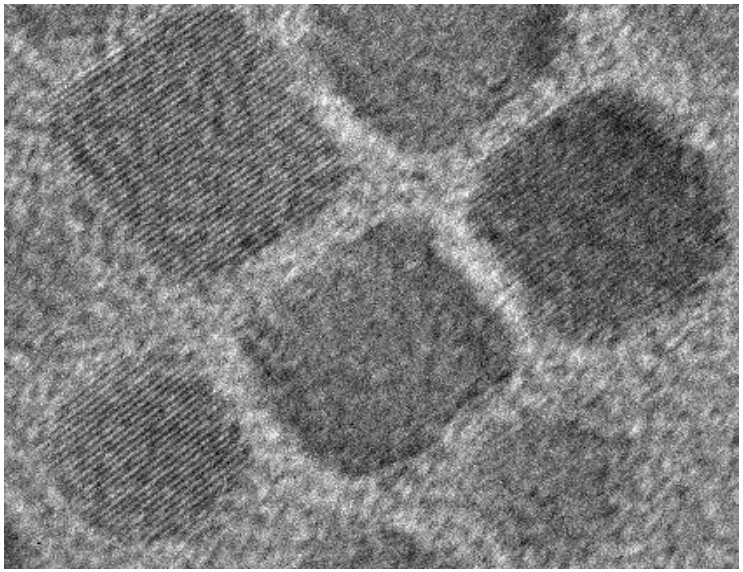
OBJECTIVE: Investigate synthesis and self assembly of nanoparticles for thermoelectric applications

ACCOMPLISHMENT: Synthesized PbSe and Bi nanoparticles (1-30 nm) by various liquid phase chemical techniques. Post synthesis size selection techniques result in nearly monodisperse distributions of particle sizes, which results in well ordered arrays of self assembled dots

HIGH RESOLUTION TEM IMAGES OF PbSe NANOPARTICLES



single 4 nm particle



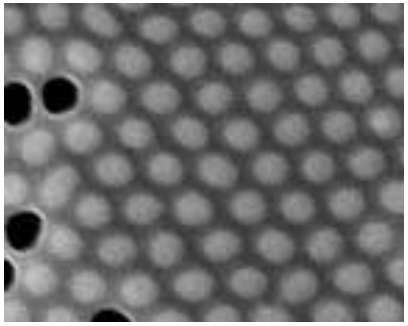
8 nm spherical particle and 12 nm cubic particles

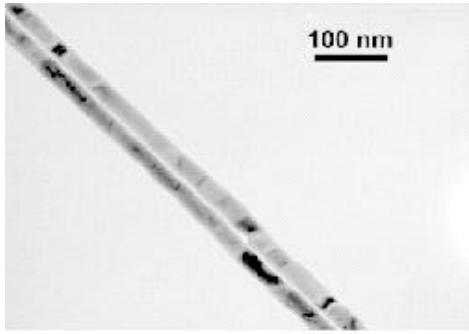
Nanowires

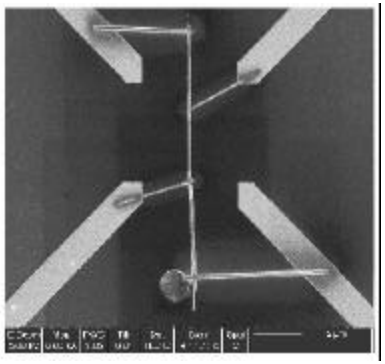
T. Huber at Howard Univ; M. Dresselhaus at MIT

Objective: **Investigate Thermoelectric Properties of Nanowire Composites Prepared by High Pressure Injection into Porous Dielectrics**

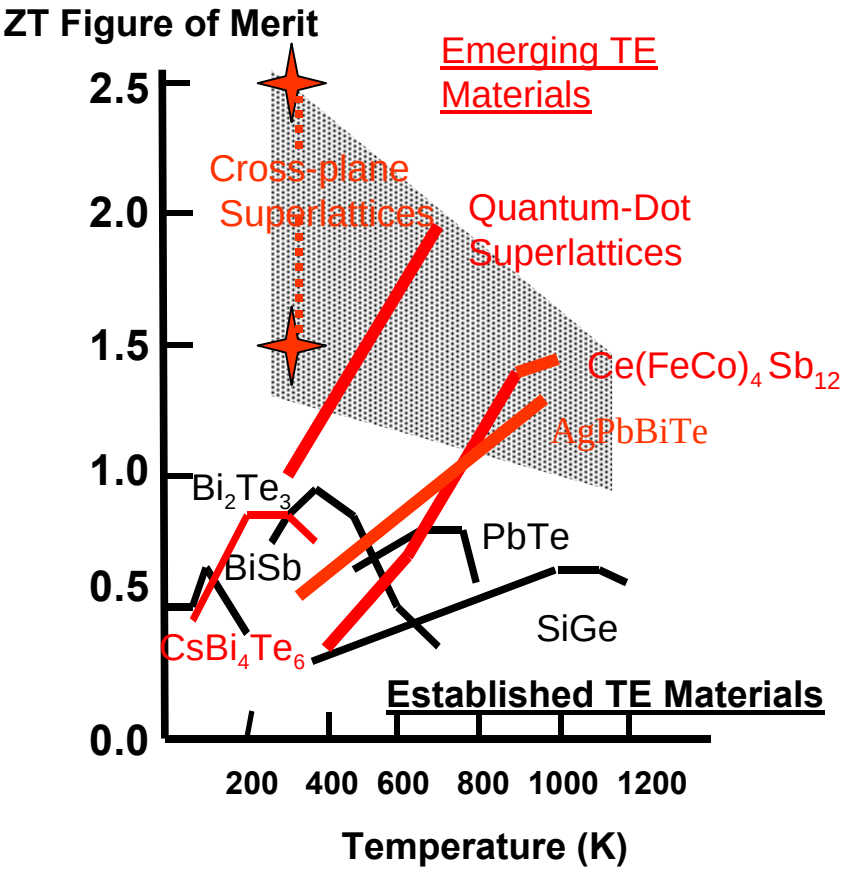
Results: **High pressure injection of molten Te, Bi and BiPb into the cylindrical channels (20-200nm) of anodized aluminum (porous Al_2O_3) has produced densely packed, highly oriented, crystalline nanowire composites. However, preliminary ZT values have been disappointing, apparently due to nanowire oxidation.**

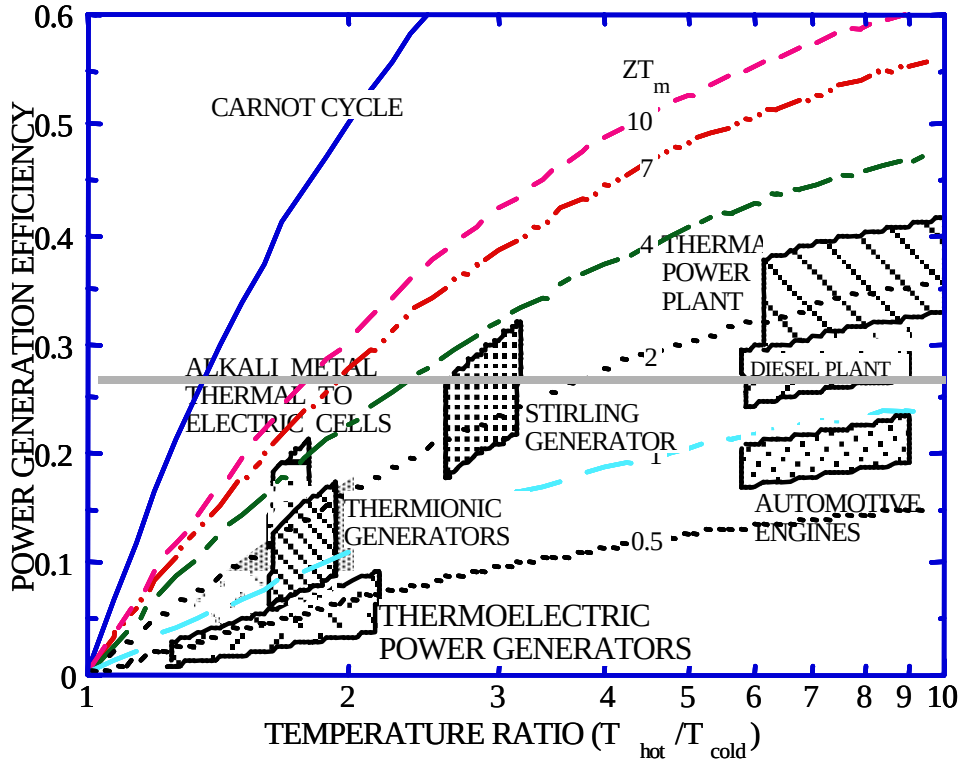




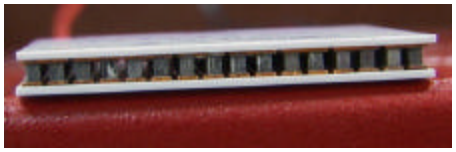


State-of-The-Art

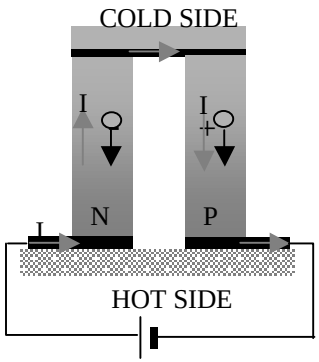




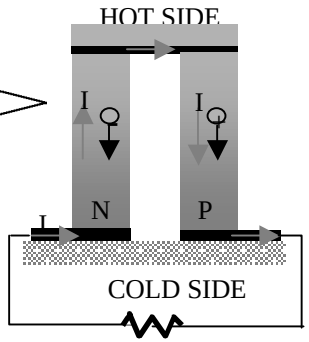
Segmented Thermoelectrics Legs



Heat Pumping

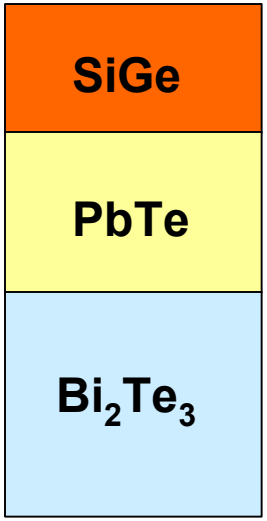


Power Generation

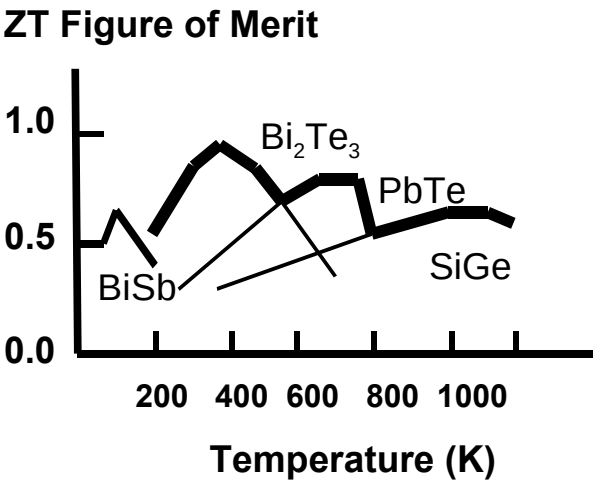


Optimized Leg

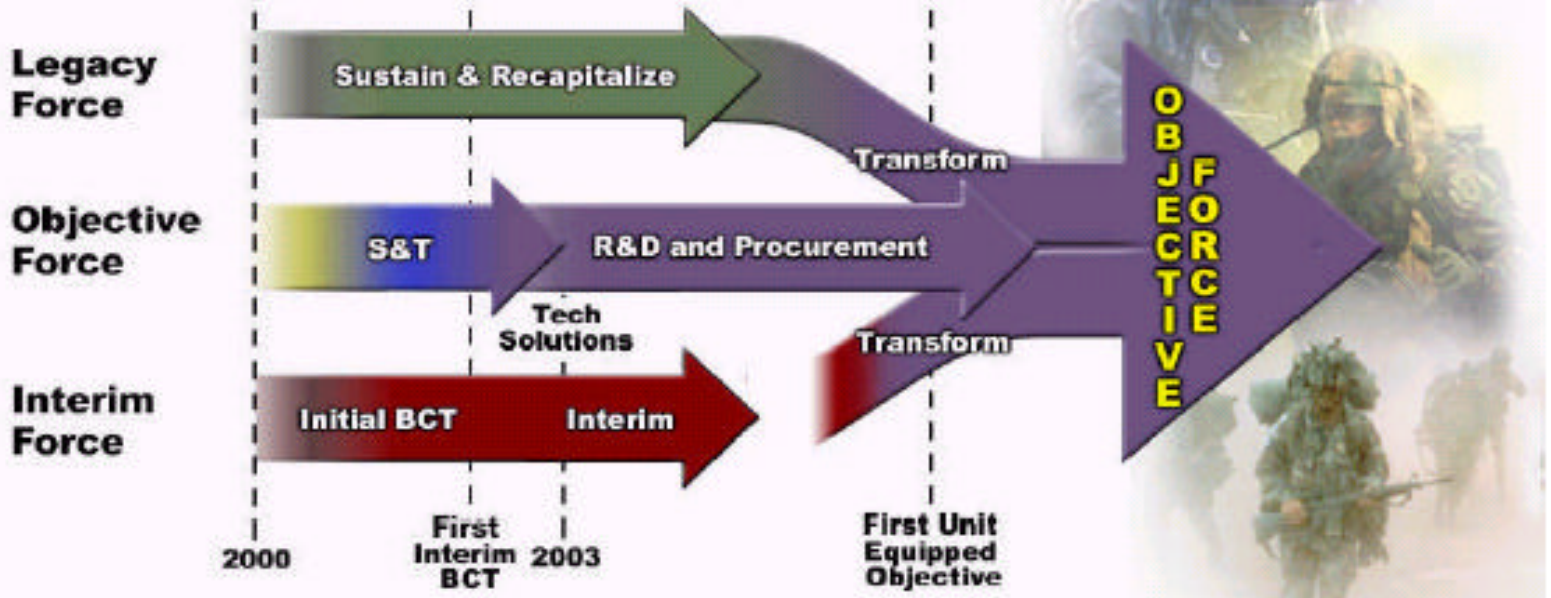
1000 K



270K



The Army Transformation



. . . Responsive, Deployable, Agile, Versatile, Lethal, Survivable, Sustainable.

S&T Strategy

ARO Materials Sciences

THE CHALLENGE: "We must provide early entry forces that can operate jointly, without access to fixed forward bases, but we still need the power to slug it out and win decisively. Today our heavy forces are too heavy and our light forces lack staying power. We will address those mismatches." GEN Shinseki, CSA, 23 June 1999.

THE SOLUTION: The Future Combat System ... the Objective Force

Characteristics:

Comprehensive Situational Awareness

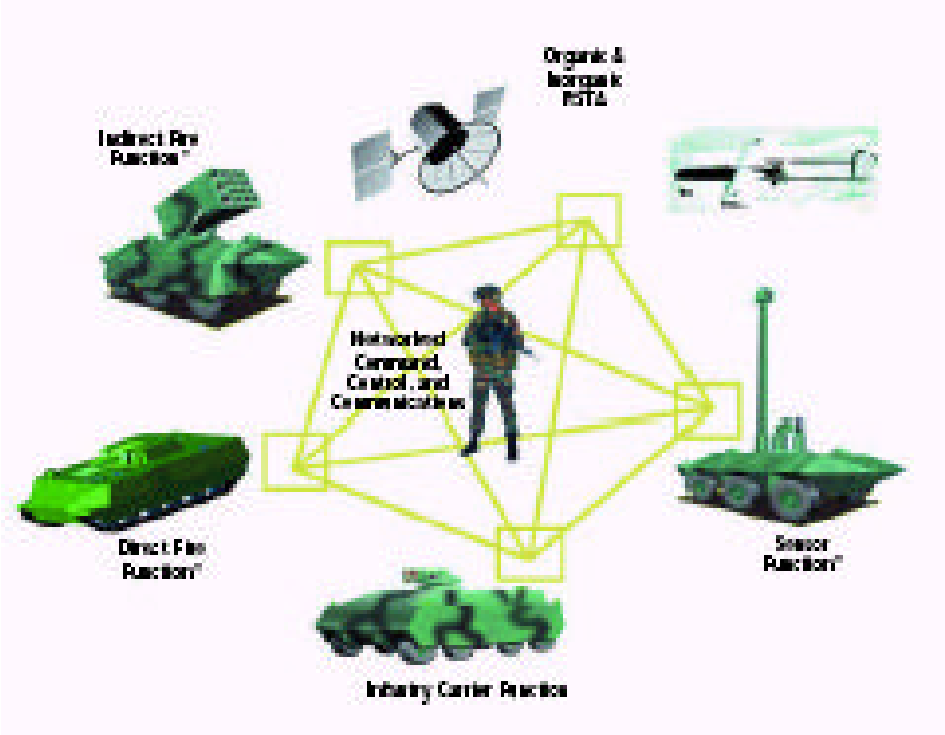
Networked Fires & Extended Range Lethality

Survive First Engagement

Manned/Unmanned Integration

C-130 Transportable

Reduced Logistics



Army Applications for Thermodynamics

Cooling of Electronics a & Optics

- Microelectronics / Communications
- IR Detectors for Night Vision (Cryogenic Cooling & Temperature Stabilization)
- Temperature Stabilization of Optics

Soldier Body Cooling

- Tank & Helicopter Crews
- Protective / Survival Suits

Refrigeration & Air Conditioning

- Medical Supplies

Power Generation from Waste Heat (Vehicles / Shelters / Kitchens)

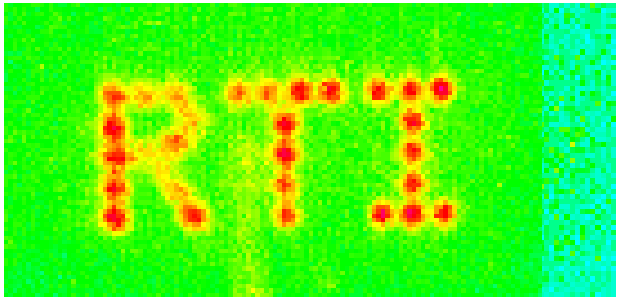
- Remote Power
- Battery Recharging
- Blowers for Heating Units

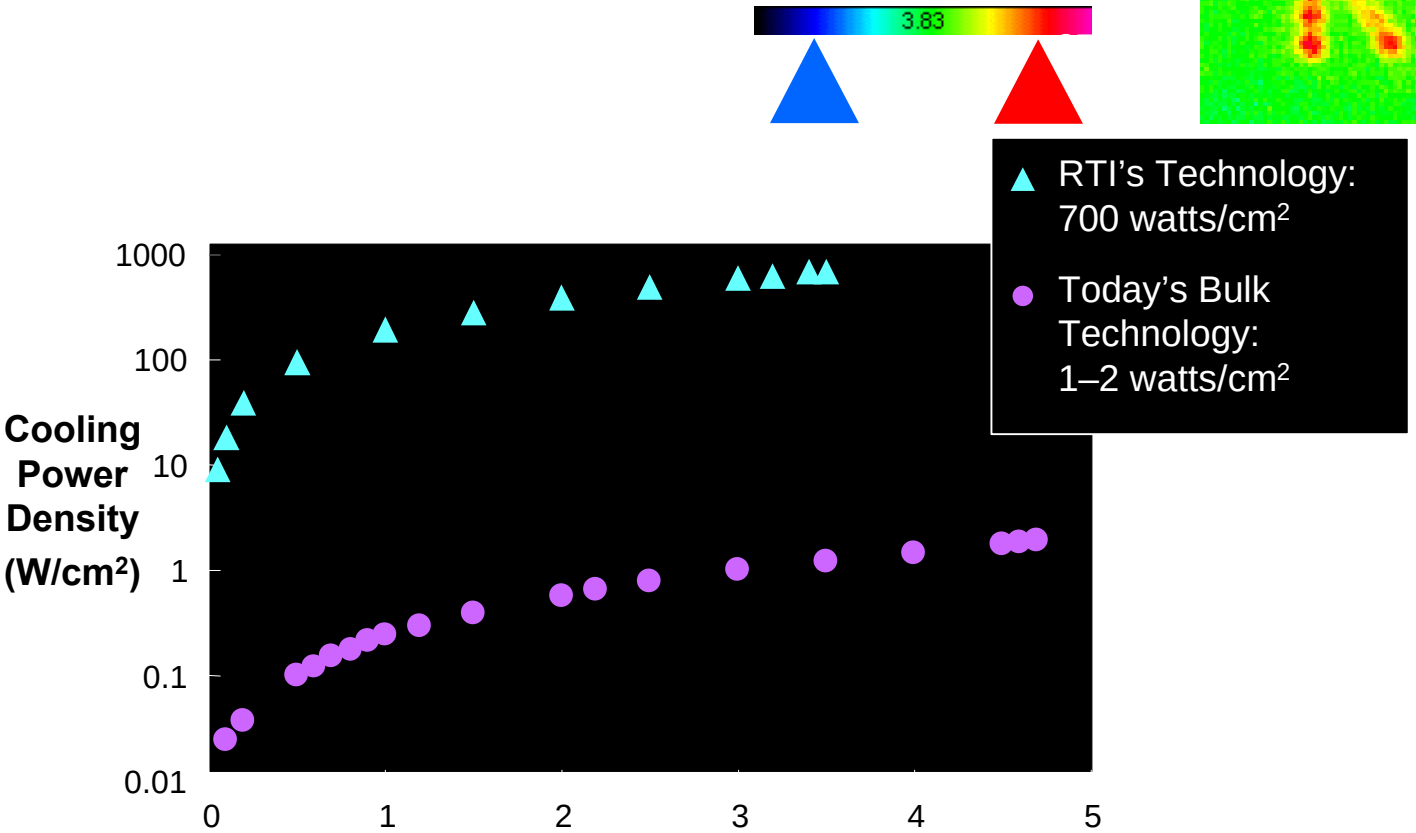
Chameleon IR Surfaces

Cross-Plane Superlattice Thin-film Thermoelectrics

Dr. Rama Venkatasubramanian, Research Triangle Institute

- Enhanced cooling
- Super-fast cooling and heating
- Enhanced power density

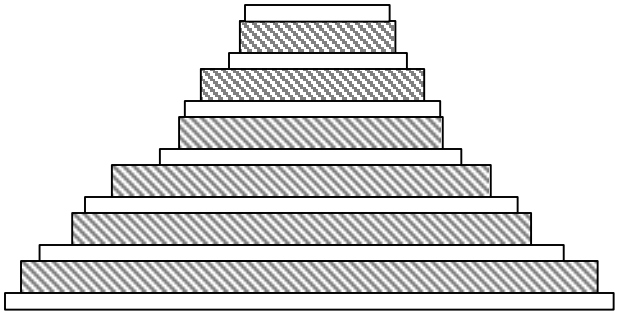




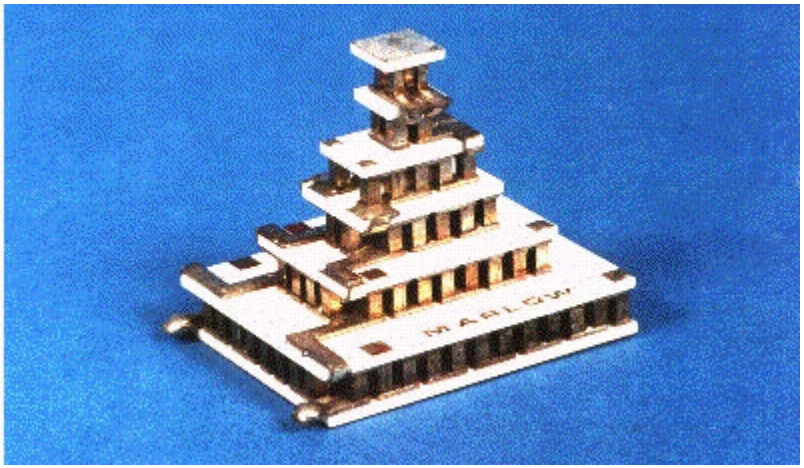
Cryogenic Cooling

Present Technology, ZT=0.7

6-stage:



20 mW pumped with 3.5 W



Marlow Ind.

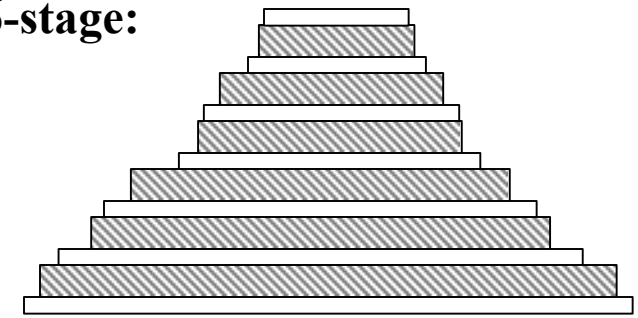
ZT=3

2-stage:

20 mW pumped with 0.15 W

OR

6-stage:



20 mW pumped with 3.5 W

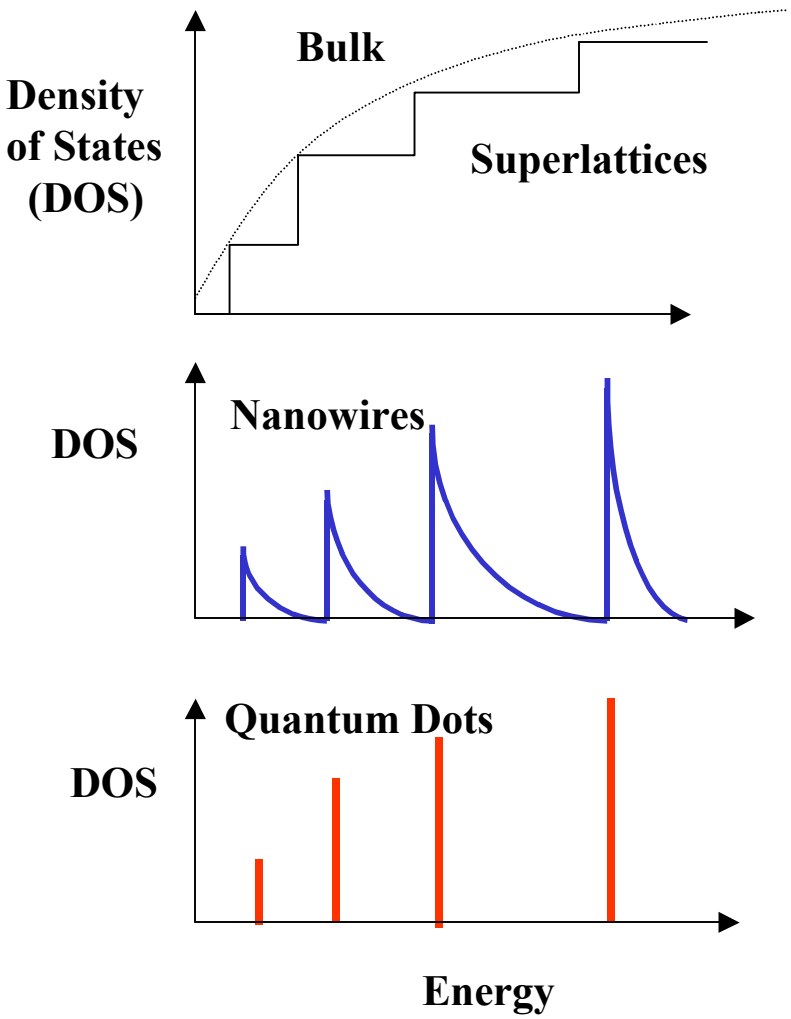
Acknowledgements

- DARPA (Dr. Stu Wolf and Dr.Valerie Browning)
- ONR (Dr. John Pazik)
- Dr. Ted Harman (MIT Lincoln Labs)
- Dr. Rama Venkatasubramanian (RTI)
- Dr. Gang Chen (MIT)
- Dr. Jean-Pierre Fleurial and Dr. Terry Caillat (JPL)

SUMMARY

- Significant increase in thermoelectric figure-of-merit has been reported in recent years, in thin films and some bulk materials.
- New insights have been gained on thermoelectric behavior using a combination of theory and experimental data. However, there are still unexplored ideas and challenges in characterization, particularly for low-dimensional materials.
- With recent demonstration of high ZT materials the potential exists for realizing systems with efficiency of 20%. Continued material development will be required to actually translate these into practice.

Quantum Confinement Effects in Low-D Systems



THERMOELECTRIC PROPERTIES OF SUPERLATTICES

DR. TED HARMAN - MIT LINCOLN LABS

OBJECTIVE: Investigate Thermoelectric Properties of Superlattice Structures

APPROACH: Prepare BiSb/PbTeSe and PbTe/PbEuTe Superlattices by MBE and Investigate Effects of :

- Quantum confinement
- Enhanced carrier mobility by modulation doping
- Band-gap engineering (drop T_v hole band in BiSb)
- Decreased lattice thermal conductivity in superlattice structures

Harman's BiSb/PbTeSe and PbTe/PbEuTe Superlattice Proposal

- **Combine two excellent thermoelectric materials**
  BiSb: b ~ 40,000, ZT~0.6
  PbTeSe: b ~ 7,000, ZT~0.3
  Lattice match to <0.25% in (111) growth plane

- **Potential for bandgap engineering to obtain Eg~0.1 eV and remove losses introduced by the TV hole band in BiSb.**

- **Reduce thermal conductivity by phonon scattering at the interfaces and incorporation of many different atomic masses**

- **Enhance carrier mobility through modulation doping**

Goal: Enhanced TE properties of b ~ 100,000, ZT ~ 2.0

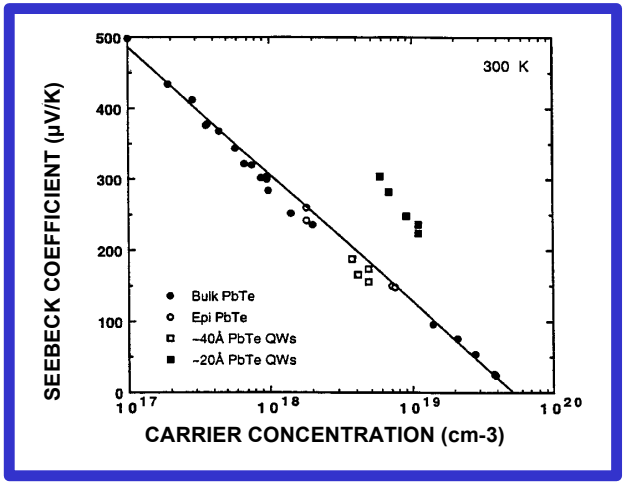
But Material Compatibility Issues Prevented Successful Realization of the Proposed Approach

THERMOELECTRIC PROPERTIES OF SUPERLATTICES
DR. TED HARMAN - MIT LINCOLN LABS

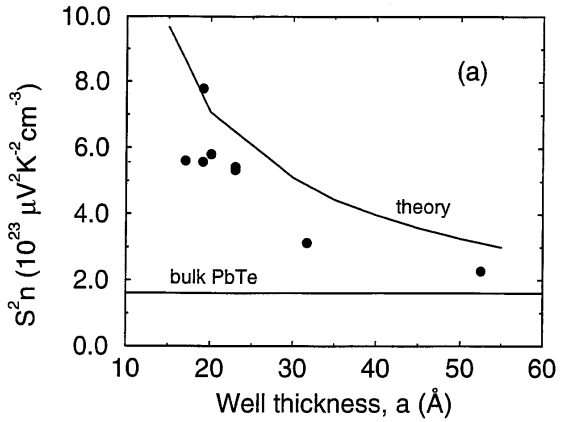
1996: Theoretically predicted enhancements* in $Z_{2D}T$ confirmed in PbEuTe/PbTe multiple quantum wells.

***Hicks and Dresselhaus, Phys. Rev. B47(1993), p. 12727**

Seebeck Coef.



S^2n



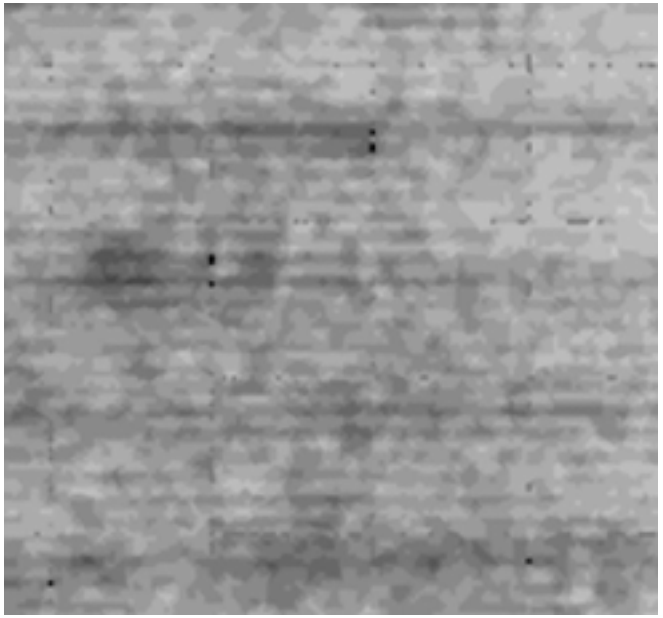
Projected ZT(quasi-2D) value of 1.2 (vs. 0.45 for PbTe) calculated assuming a modest lattice thermal conductivity of the equivalent mixed alloy. Actual thermal conductivity values could be much lower, leading to even higher ZT values

Cross-Plane Superlattice Thin-film Thermoelectrics

Dr. Rama Venkatasubramanian

Bi_2Te_3 - Sb_2Te_3 Superlattice

Current Flow



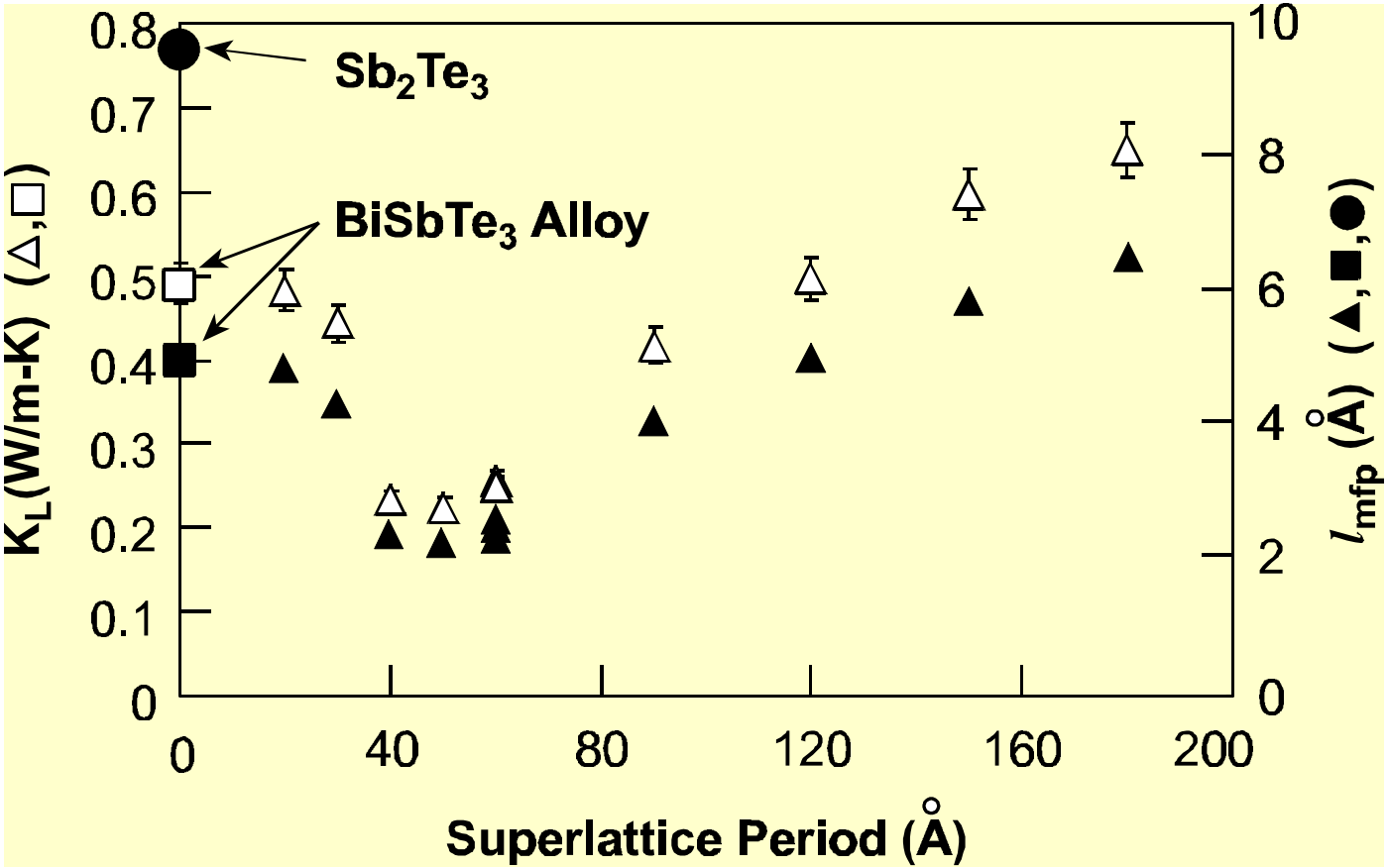
← Bi_2Te_3 layer is about 1 nanometer thick

} Sb_2Te_3 layer is about 5 nanometer thick

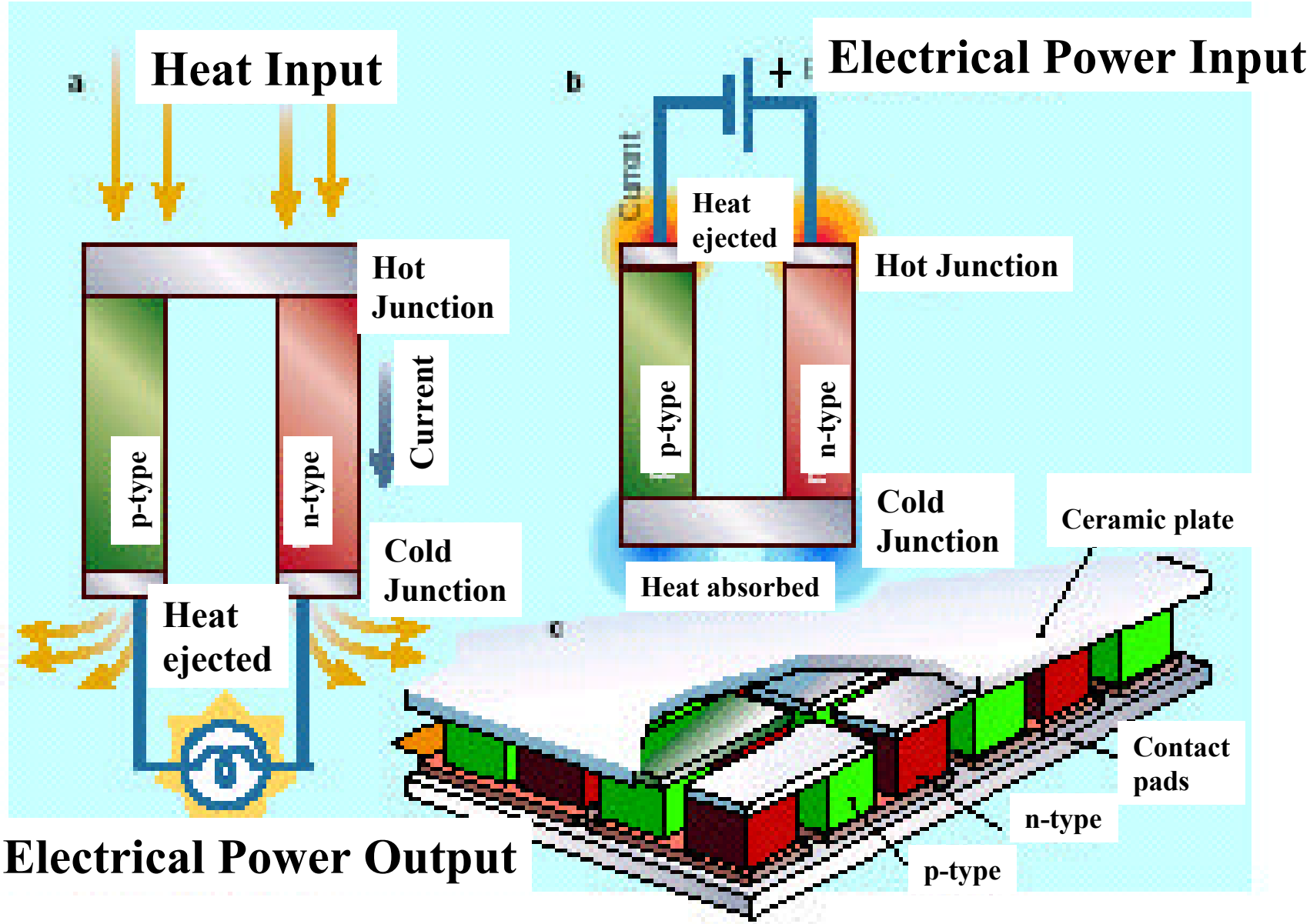
In-situ ellipsometry diagnostics for controlling superlattice deposition

Thermal Conductivity Reduction in p -type Bi_2Te_3/Sb_2Te_3 Superlattices (Cross Plane Geometry)

Superlattice interfaces can significantly reduce thermal conductivity!



Phys. Rev. B, 61, 3091 (2000)



Nature 413, 577 (2001)