Nano-scale Thermoelectric Materials for Solid-State Cooling and Direct Thermal-to-Electric Energy Conversion

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September 15, Washington, D.C.

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Outline

- Thermoelectrics Overview
  - Background
  - Material and Device Results
- Nano-scale Materials Technology Overview
  - Recent Results in Transitioning the Materials Breakthrough
  - Solid-state Cooling Applications
    - Thermal Management for Electronics
    - Advanced System-Level Concepts to further leverage nano-materials advancements
  - Thermal to Electrical Energy Conversion
- Potential with Nano-scale Materials

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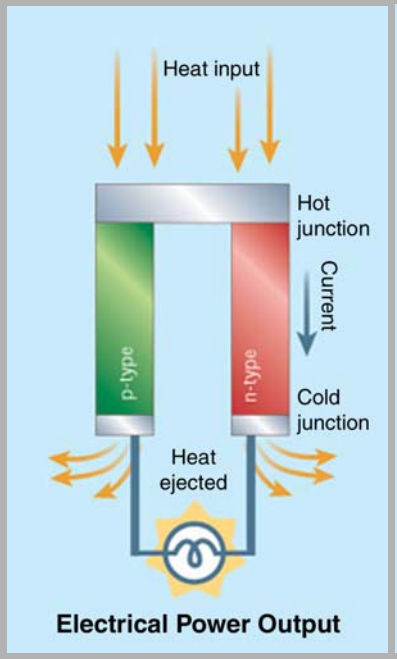
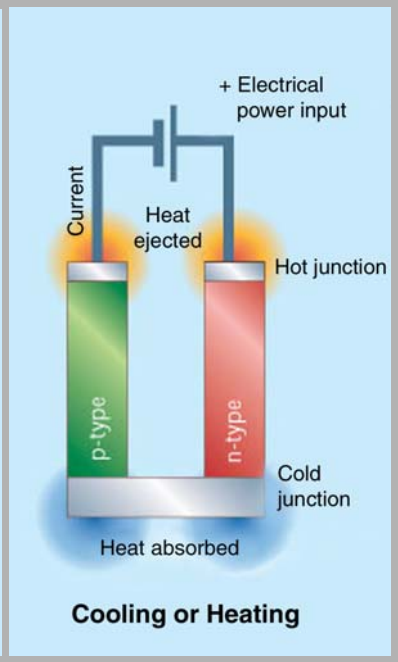
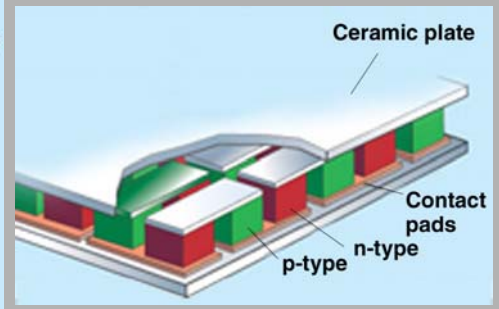
Thermoelectrics







- Solid-State Technology
  - Solid-state Reliability
  - No Moving Parts
  - Vibration/Noise free
  - CFC-free
- Heat or Cool
  - Thermal Management
- Power Generation
- Thermal control functions
  - Chemistry, Biology, Physics

- **In 1960's**, semiconductor thermoelectrics were considered to replace mechanical refrigerators and diesel-generators!!
  - Hope back then – if transistors can replace vacuum tubes for electronics!
  - Biggest problem then – materials efficiency or figure-of-merit (ZT)
    - Had to improve from ~0.9 to 3 or higher
    - **Identified as a Key Military Technology again in 1992**
      - ✓ **New Materials, especially nano-structures to the rescue?**

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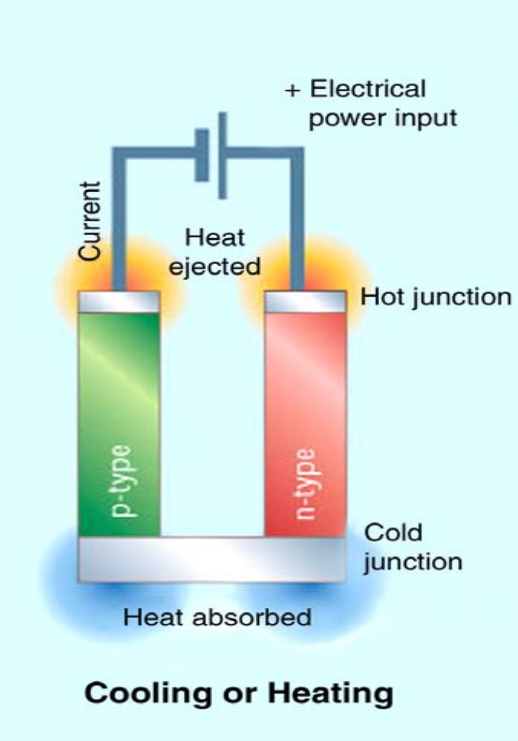
What makes a good Thermoelectric Material?

- Figure of Merit = ZT = $(\alpha^2\sigma/k)T$
  - T = Absolute Temperature
  - α^2 = (Seebeck coefficient)^2
    - Tells how much average thermal energy is transported by each carrier
  - σ = electrical conductivity
    - Tells how much the carriers can transport energy without Joule loss
  - k = thermal conductivity
    - Tells how small is the reverse flow of heat from the cold-side to the hot-side, opposing the electron-transport of heat
- <u>Minimize</u> thermal conductivity and <u>maximize</u> electrical conductivity
  - Has been the biggest dilemma for the last 40 years
    - Can the conflicting requirements be met by nano-scale material design?



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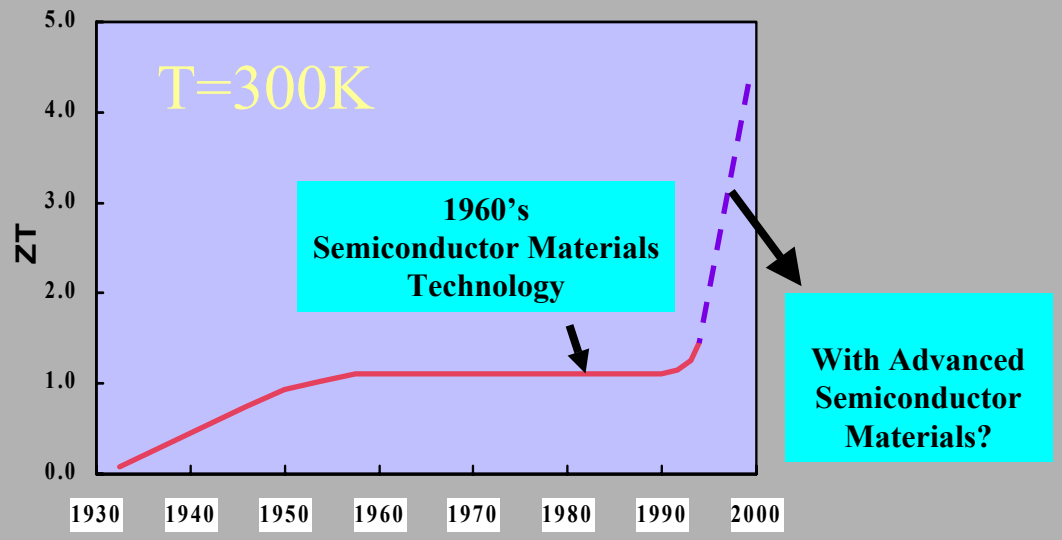
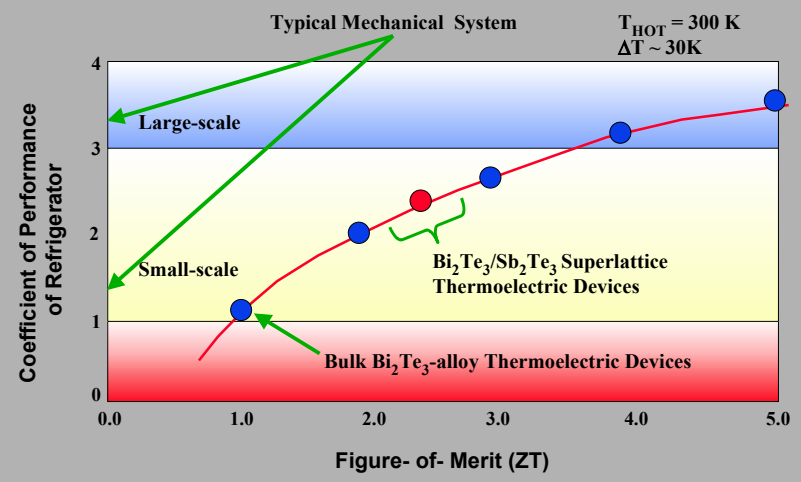
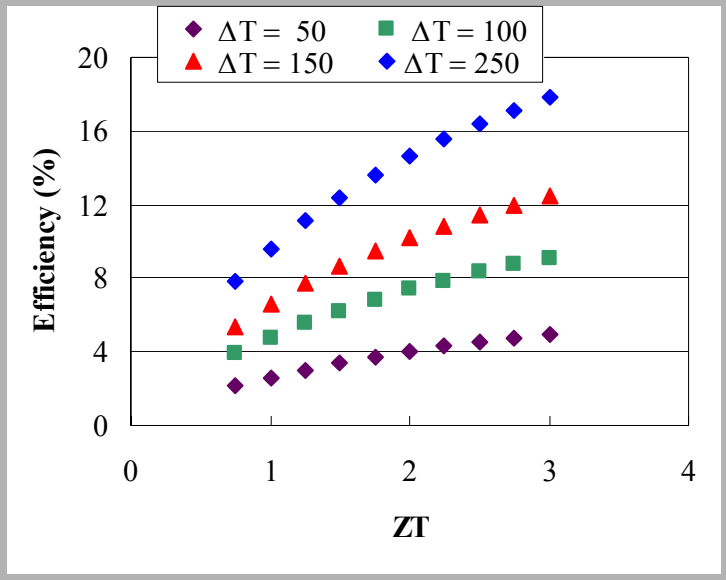
The Big Challenge





- ZT need to improve over 1.3 at 300K for a major impact in electronics cooling and around 2.5 for a revolutionary impact in air-conditioning, and power from waste-heat



Some of the Approaches

- New Bulk Materials
  - Skutterudites (Rensselaer, Oak Ridge, JPL, 1992)
    - Cage-structures with rattling atoms to scatter phonons
  - Novel Chalcogenides and Clathrates (Michigan State and Arizona, 1994)
    - Complex Variations of Bi_2Te_3 to reduce phonon mean-free paths
- Nano-scale Materials
  - Low-Dimensional Structures (MIT, MIT Lincoln Labs, 1992)
    - Quantum-confinement to Enhance Density of states which increase Seebeck coefficient
  - Nano-scale Superlattices (RTI, 1992)
    - **Phonon-blocking** from acoustic mismatch between superlattice components but **electron-transmitting** due to negligible electron-energy offsets
  - Heterostructure Thermionics (UCSB, Oak Ridge, 1996)
    - Thermionic-like effects using energy barriers that can be controlled in hetero-structures

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Some Bulk Material and Nano-Material Progress

- Cs Bi_4Te_6 (Michigan State University)
  - Bulk Materials with a ZT~ 0.8 at 225K but less than 0.8 at 300K (*Science* **287**, 1024-1027, 2000)
- Filled Skuterrudites (JPL)
  - Bulk materials with a ZT ~1.35 at 900K (Proc. Of 15th International Conf. On Thermoelectrics, 1996)
- PbTe/PbTeSe Quantum-dots (Harman, MIT Lincoln Labs.)
  - ZT~ 1.6 at 300K based on cooling data (*Science* 297, Sep. 2002)
- Bi_2Te_3/Sb_2Te_3 Superlattices (RTI)
  - ZT~2.4 at 300K in devices with all properties measured at the same place, same time, with current flowing and verified by two independent techniques (*Nature*, 597-602, Oct. 2001)

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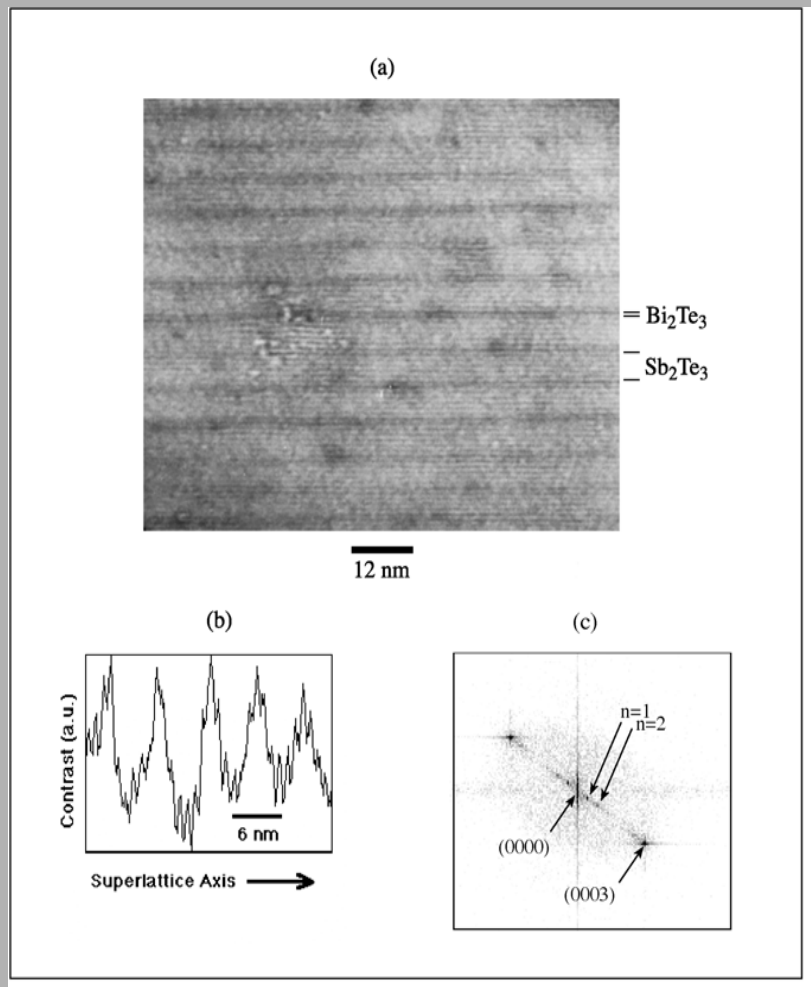
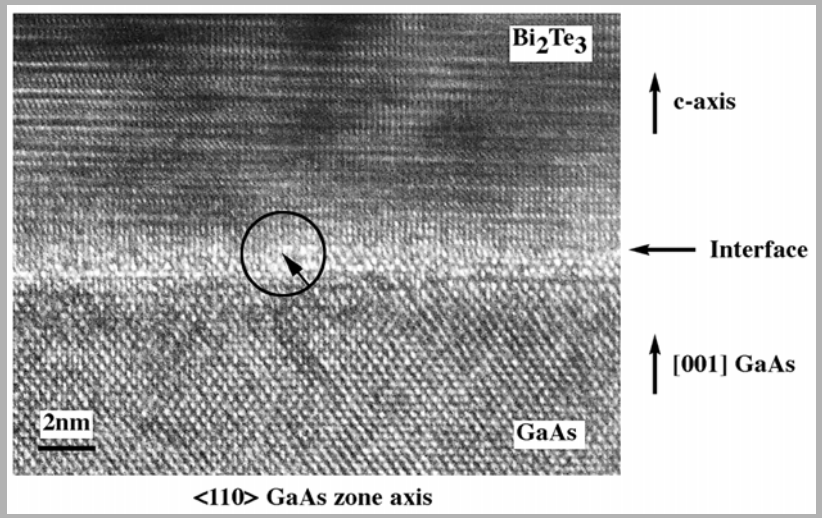
Nano-structured Superlattice Material



Applied Physics Letters, 75, 1104 (1999)

- 10Å/50Å Bi_2Te_3/Sb_2Te_3 Structure
- Optimized for disrupting heat transport while enhancing electron transport perpendicular to the superlattice interfaces

Growth of Superlattices

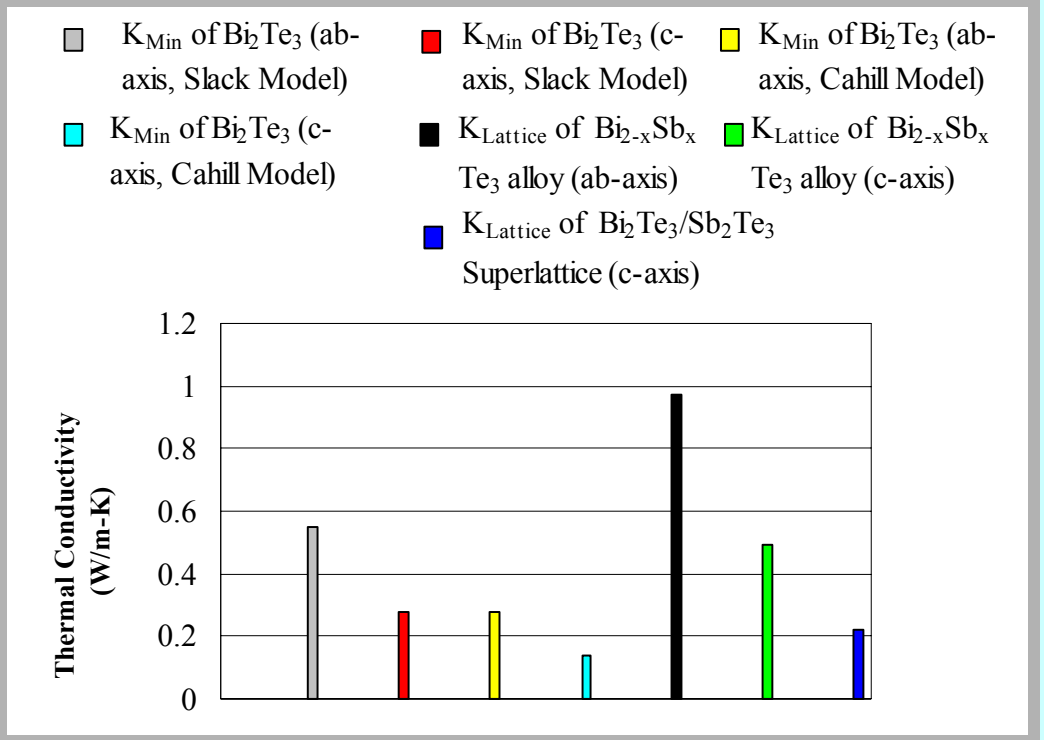


Applied Physics Letters, 75, 1104 (1999)

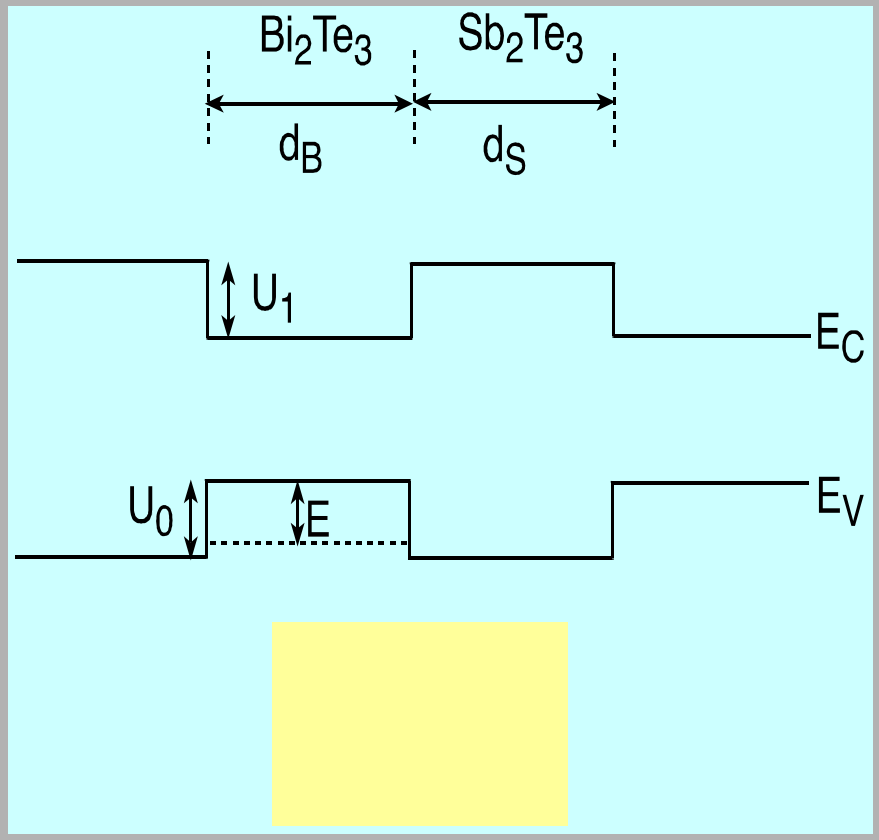
- Low-temperature growth needed
  - To enable formation of low-energy van der Waals bond along the growth direction (c-axis)
    - Allows growth of highly-lattice-mismatched structures without defects that can scatter carriers
      - ✓ **Lattice-mismatch is preferred for acoustic-mismatch**
- In-situ ellipsometry for nanometer-scale control of deposition

Physics Behind ZT Enhancement

Ultra-low Cross-Plane Lattice Thermal Conductivity in Bi_2Te_3/Sb_2Te_3 Superlattices



Efficient Cross-Plane Hole Mini-band Transport in Bi_2Te_3/Sb_2Te_3 Superlattices



Venkatasubramanian, Siivola, Colpitts, O'Quinn, Nature, 413, 597 (2001)

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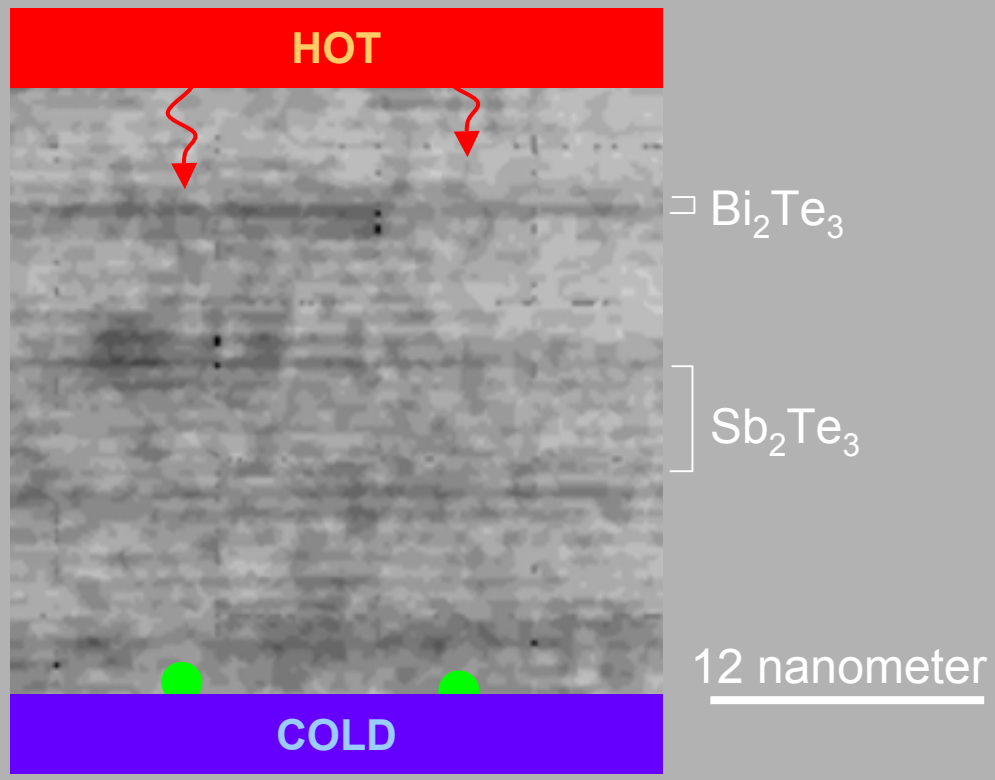
RTI's Superlattice Material



The RTI breakthrough arises from reducing heat transmission without disrupting electron flow

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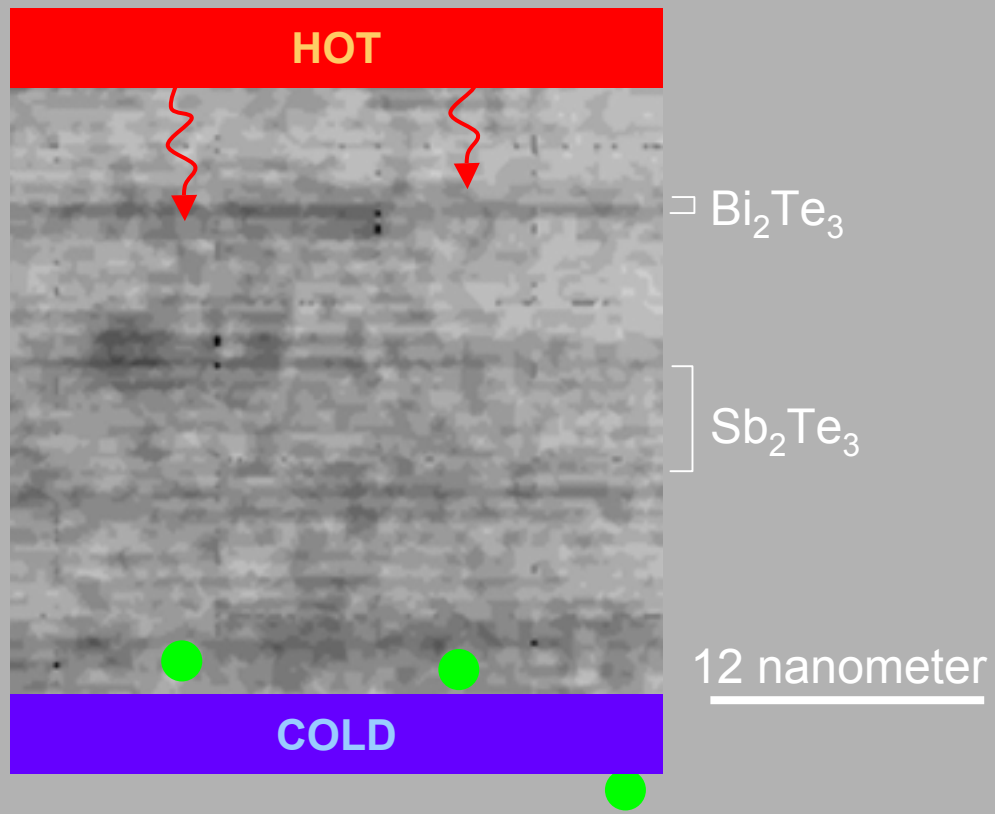

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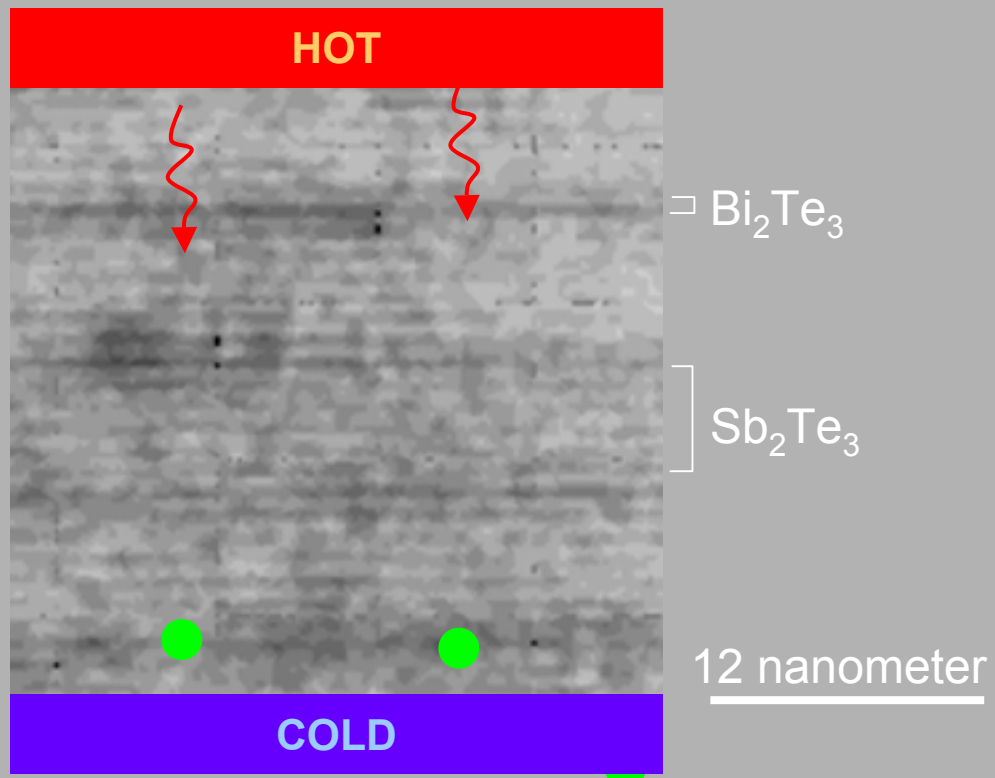

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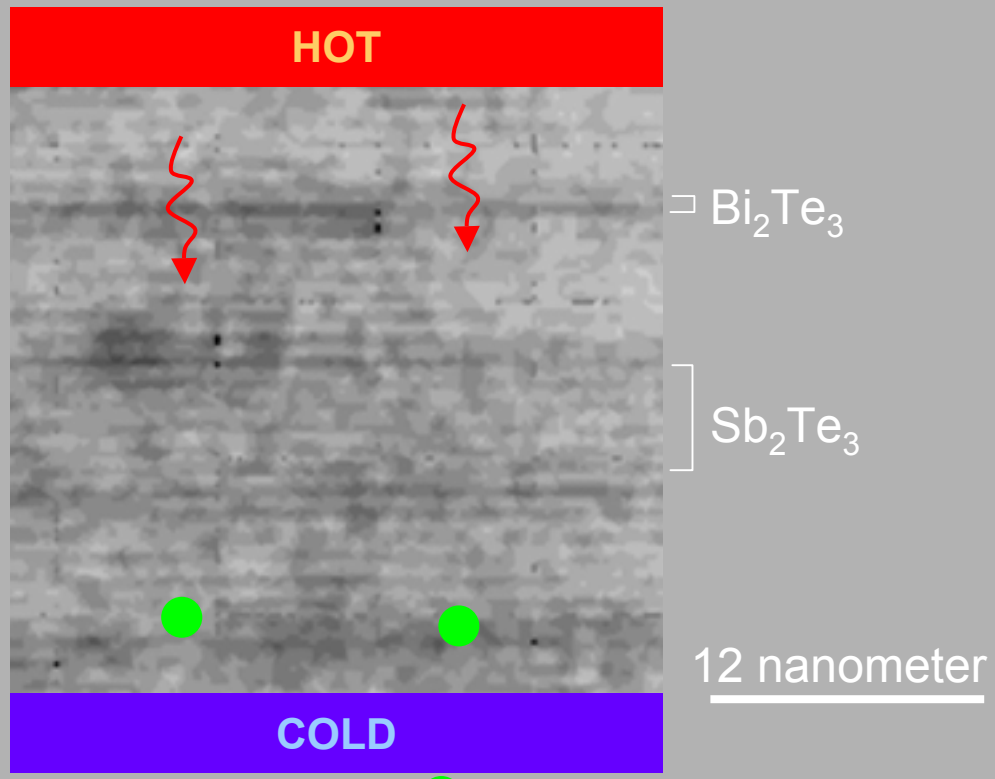

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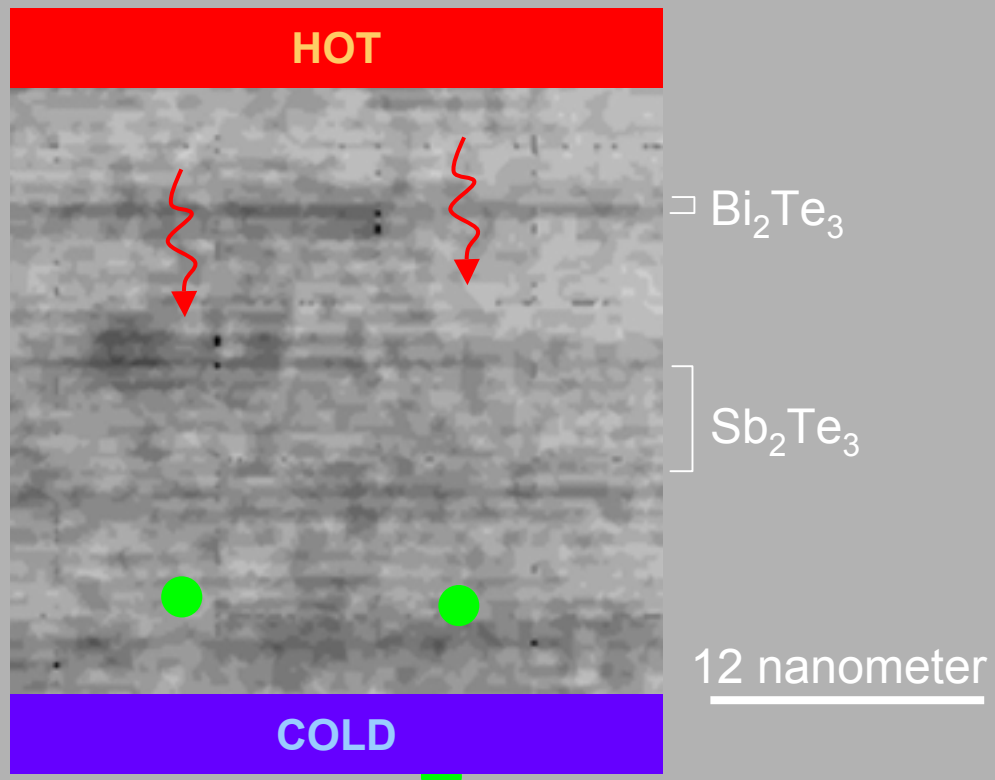

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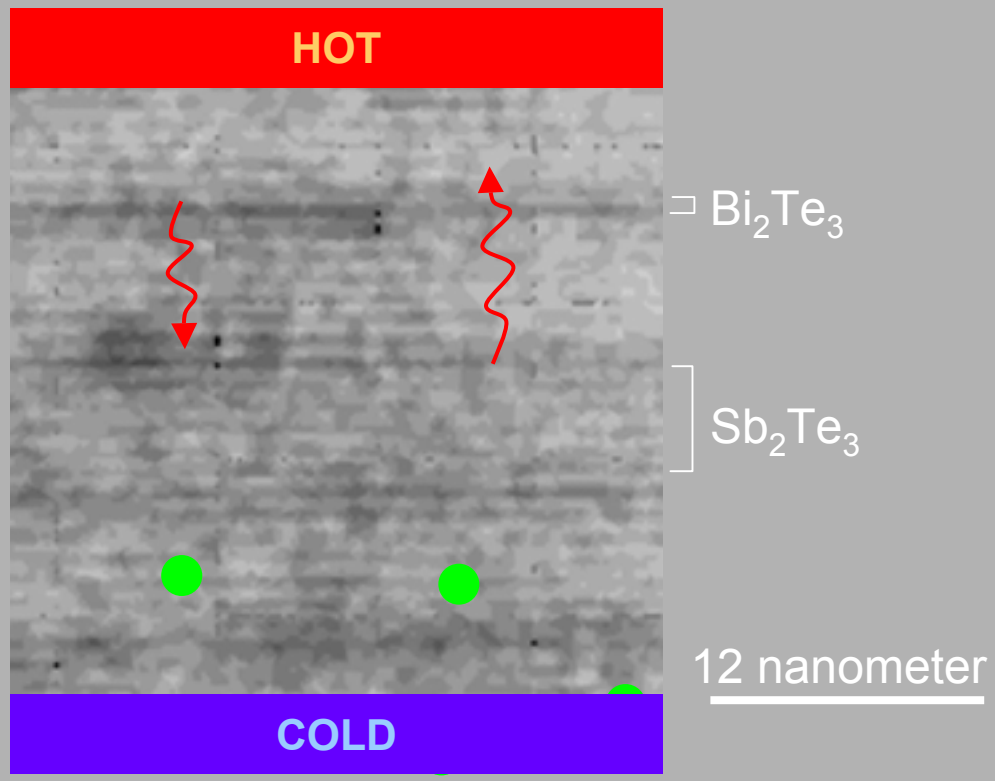

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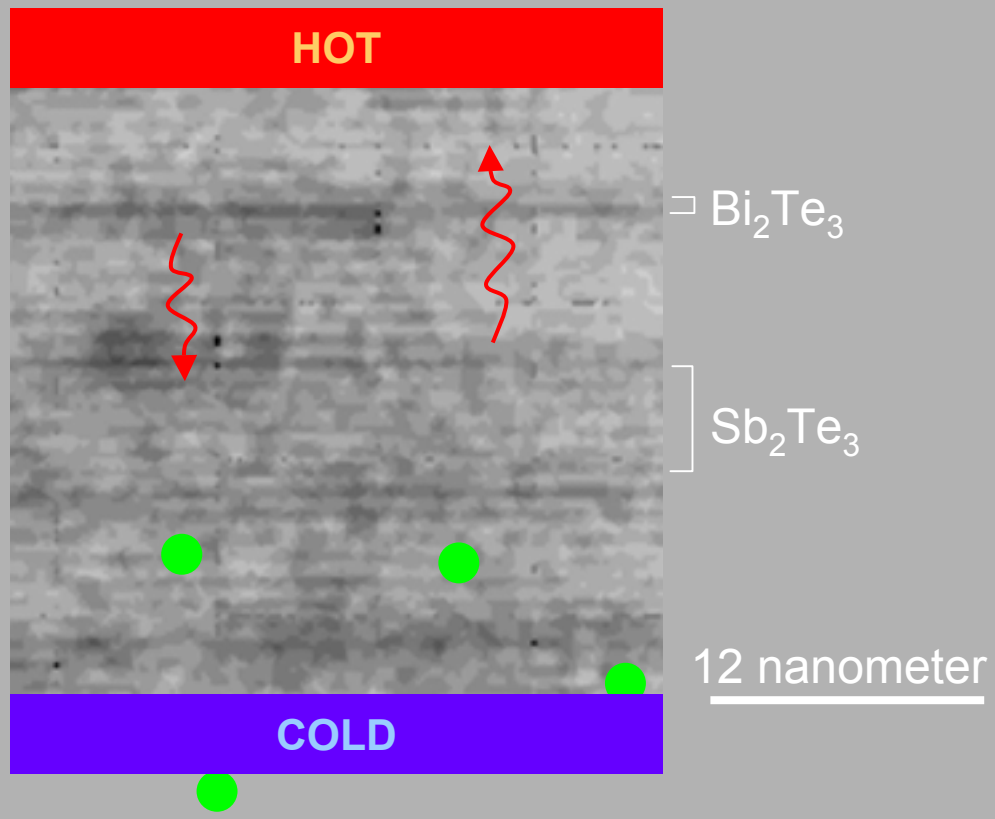

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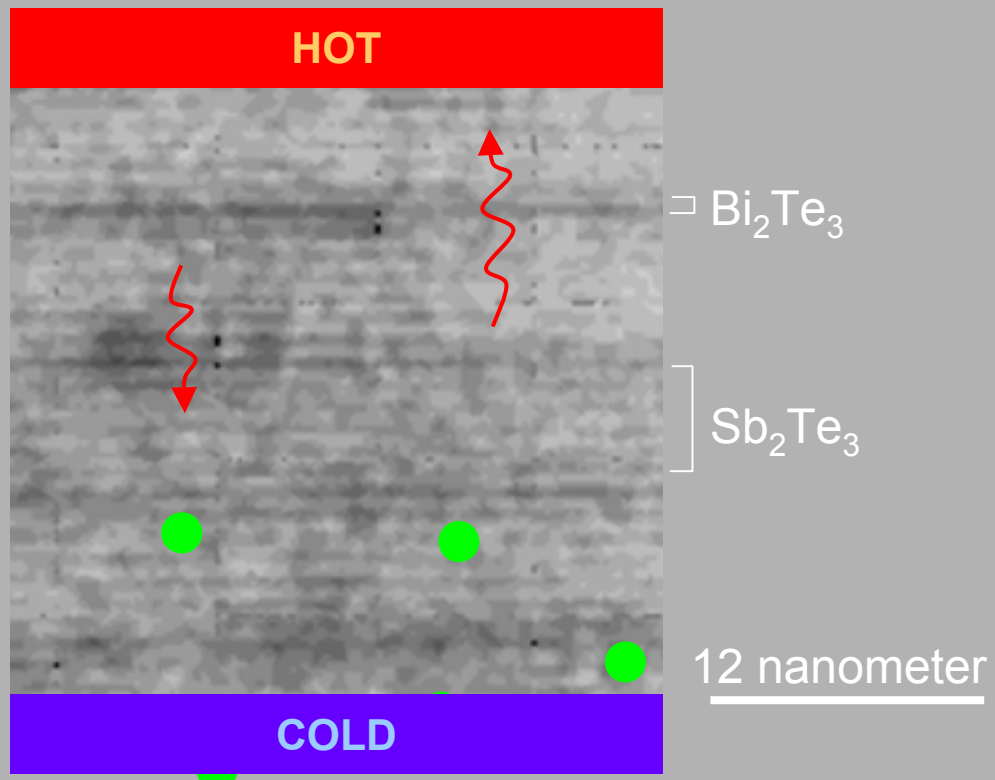

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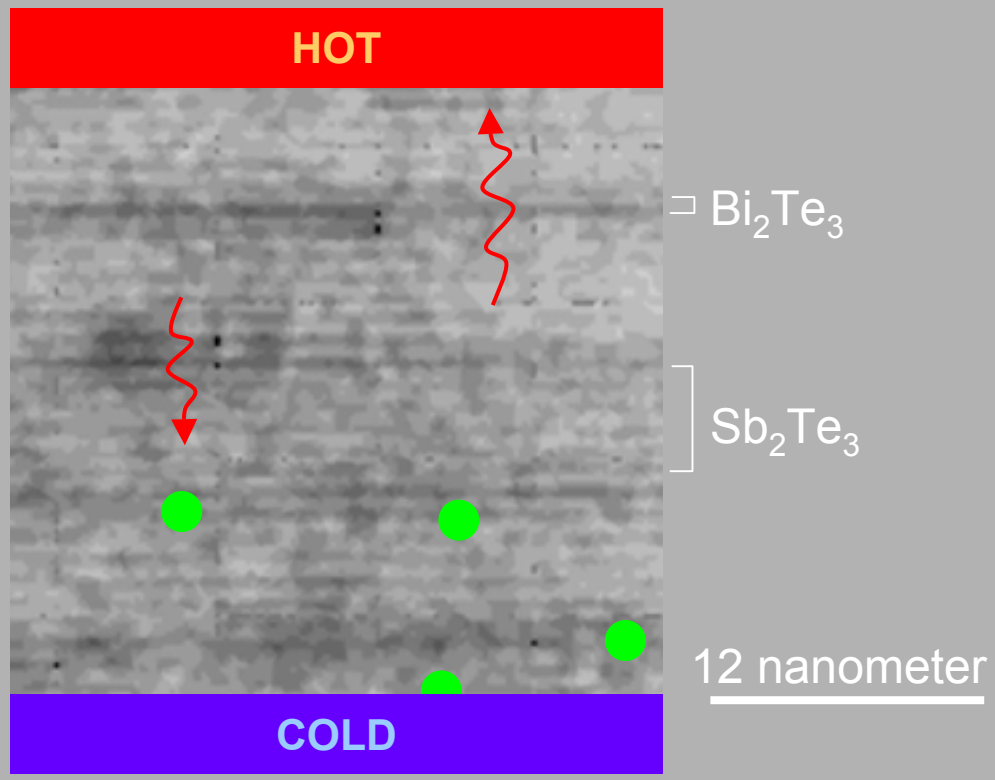

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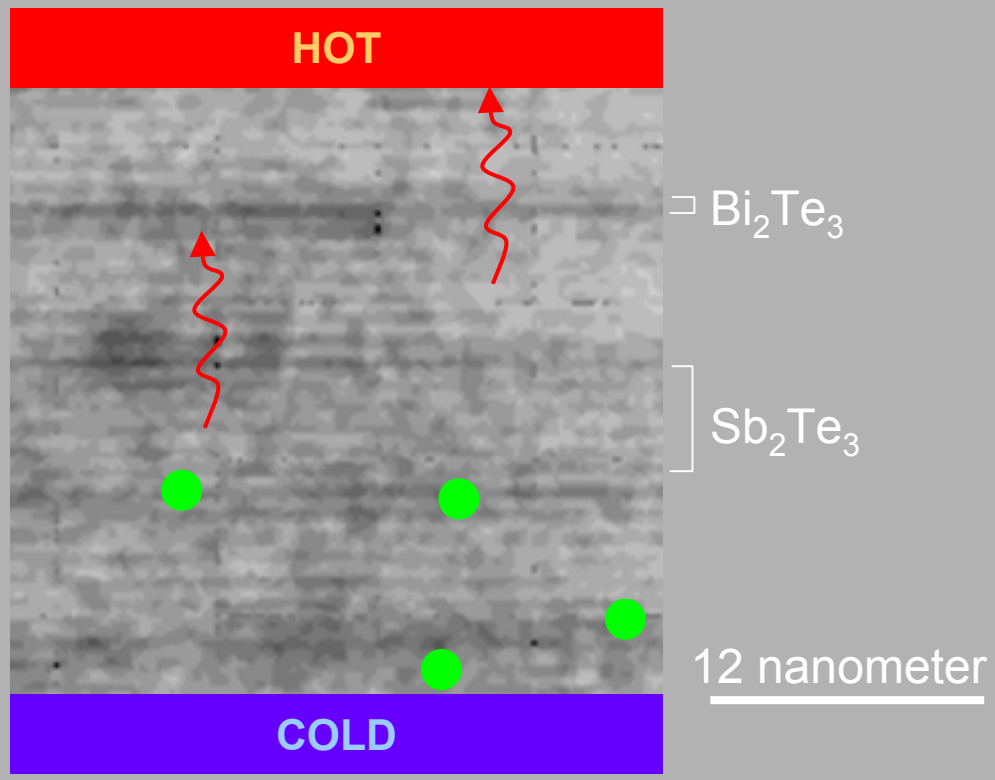

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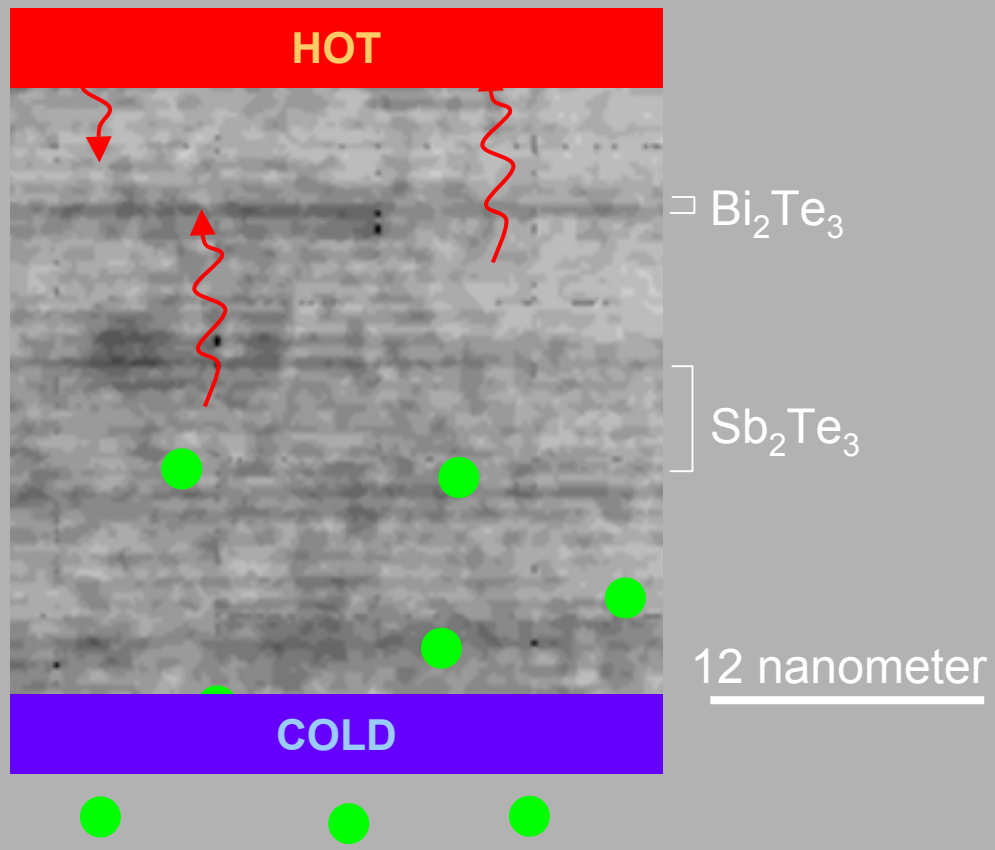

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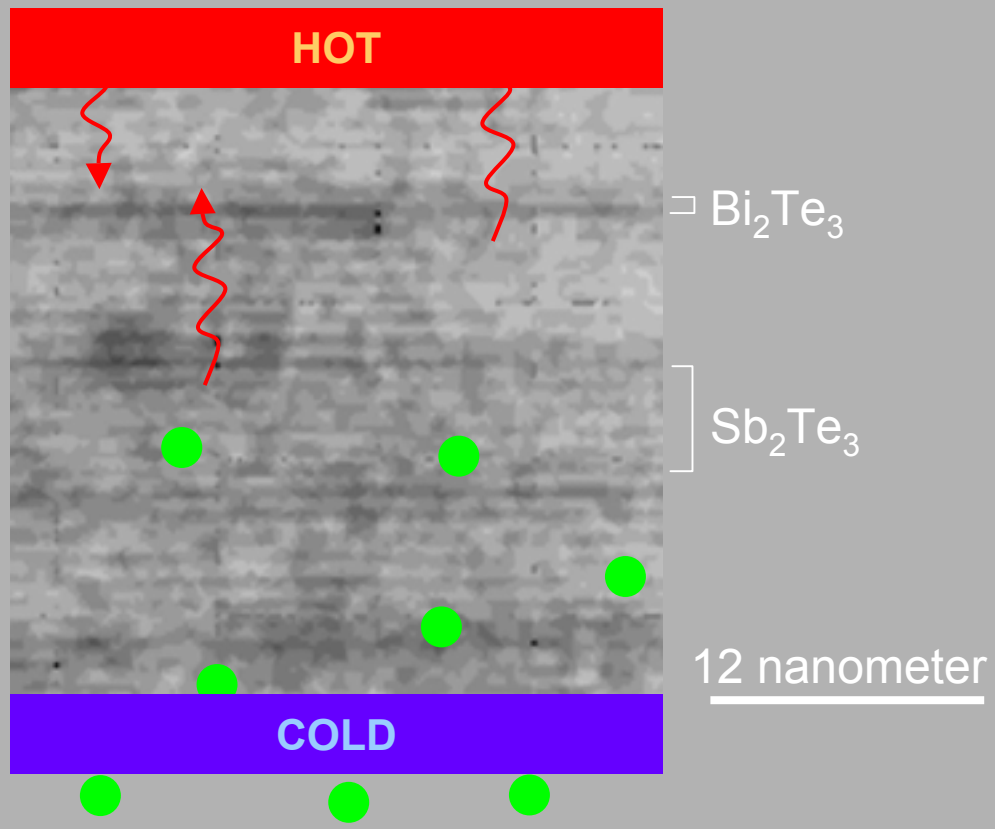

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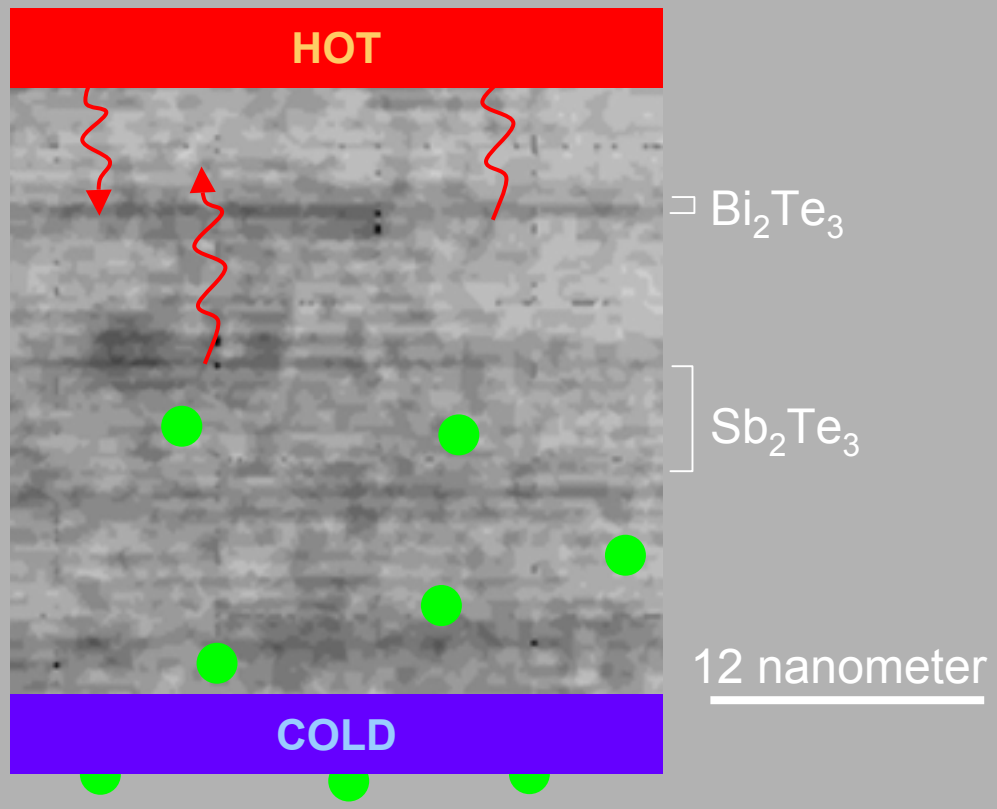

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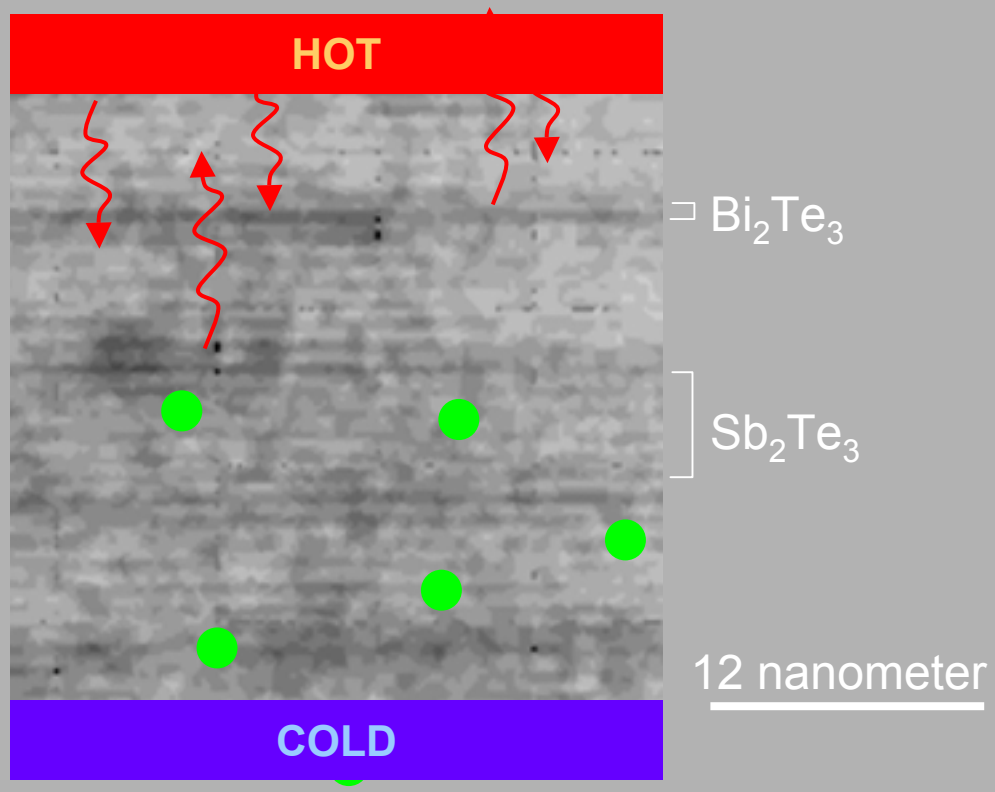

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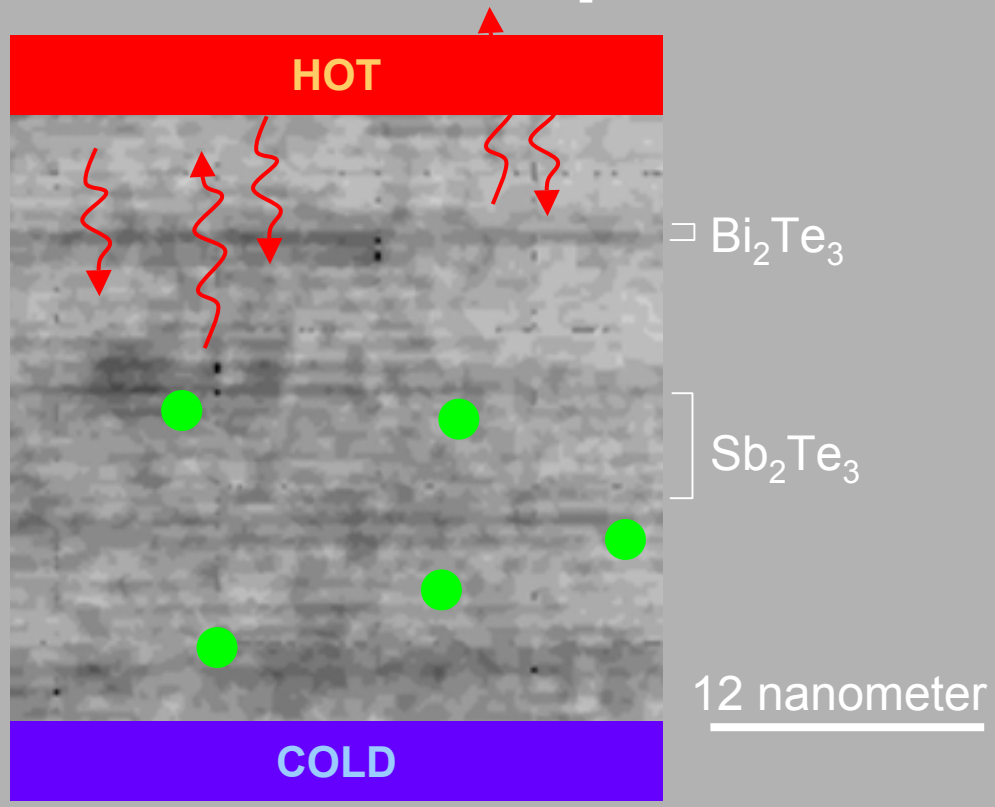

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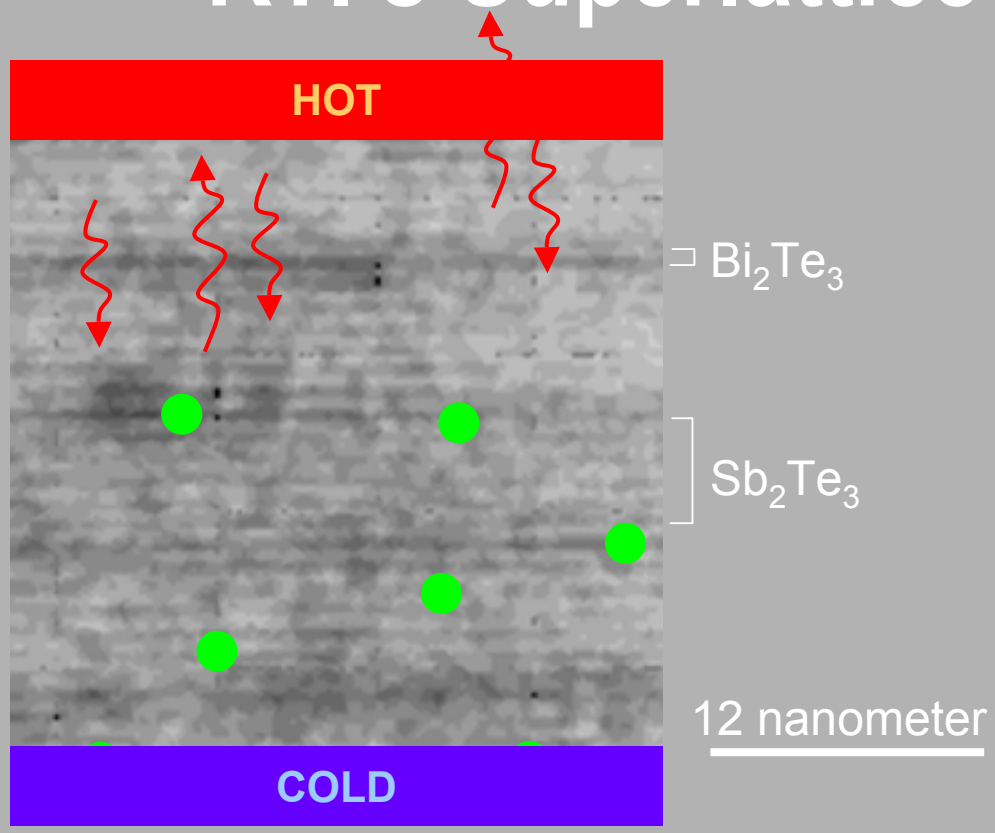

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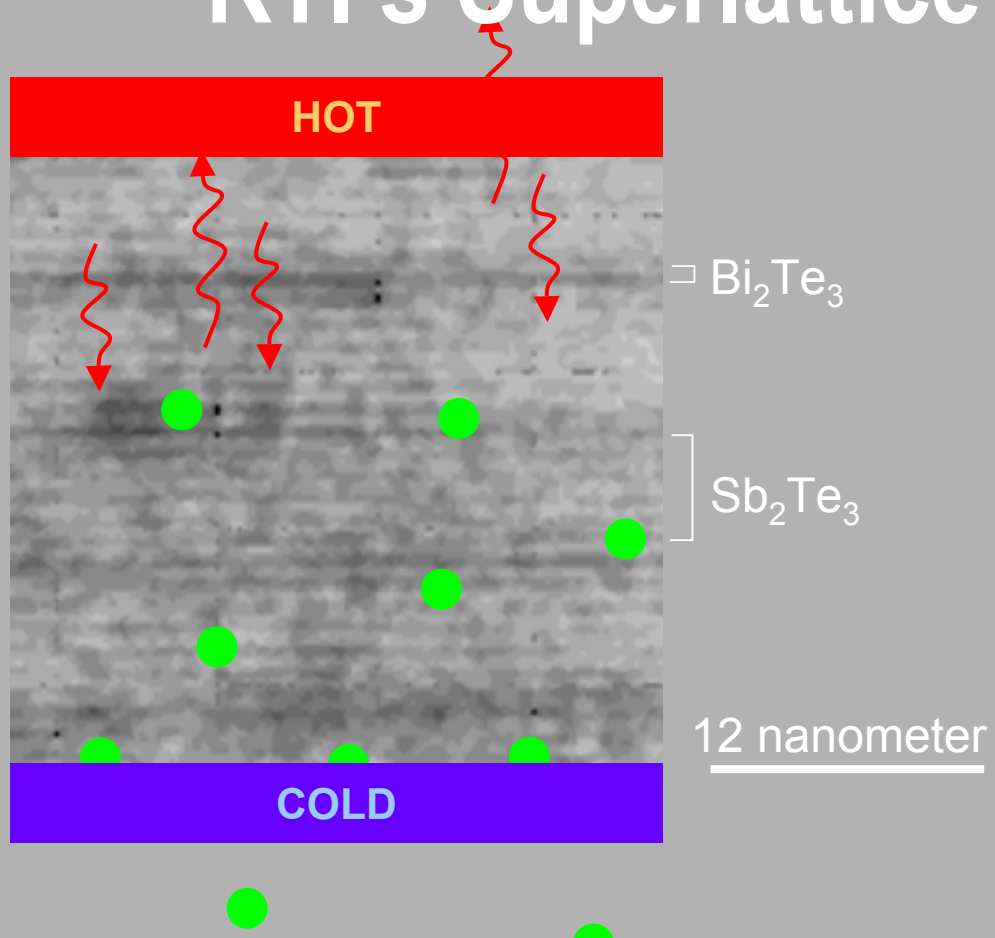

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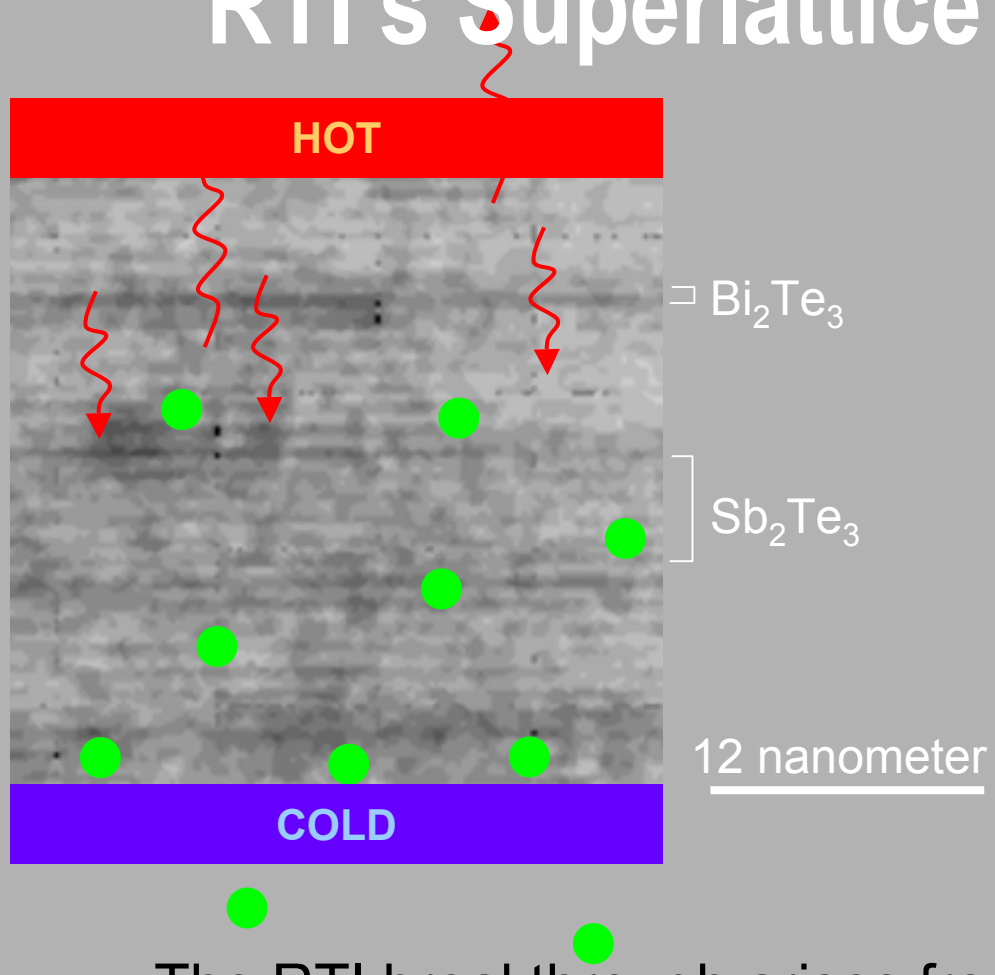

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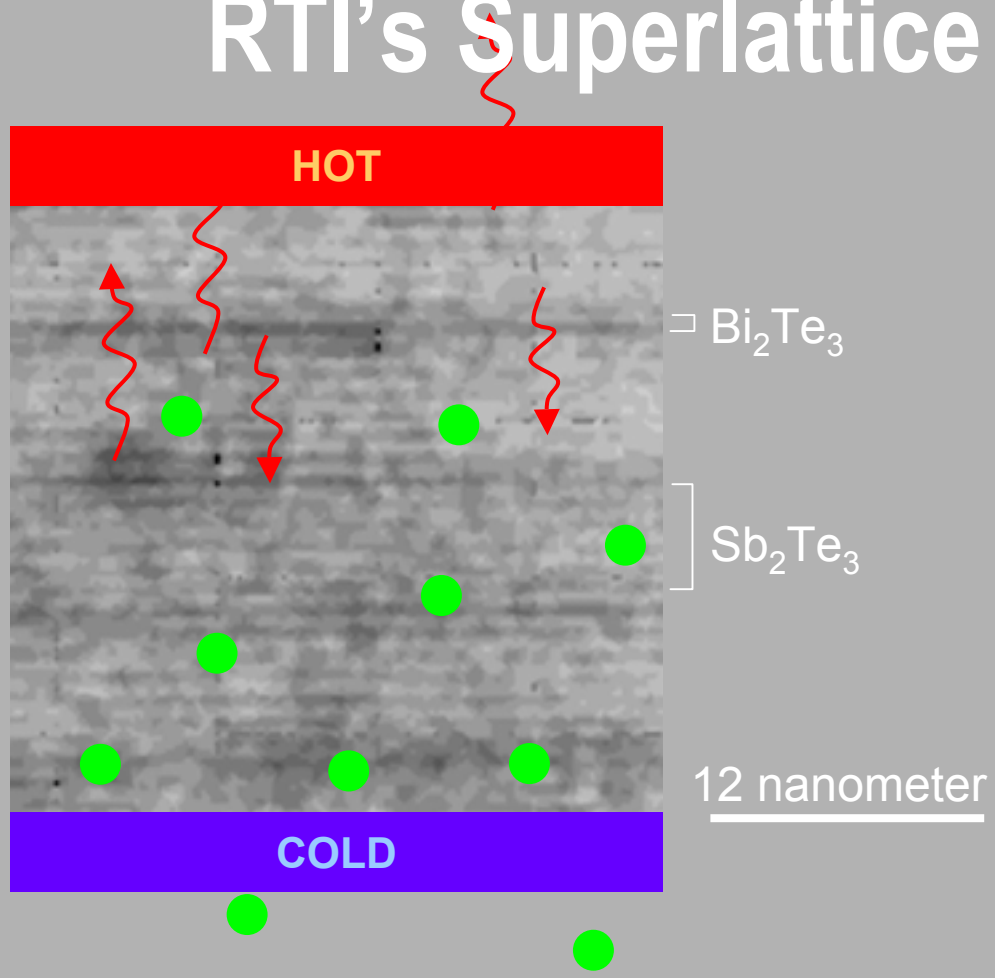

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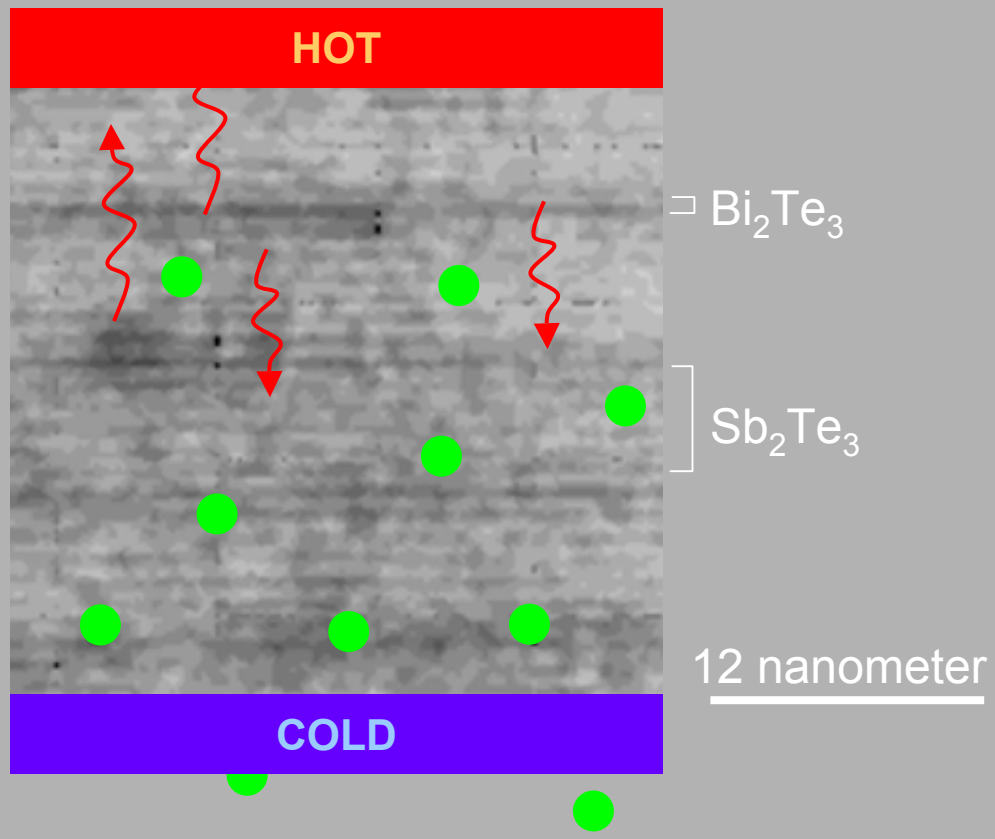

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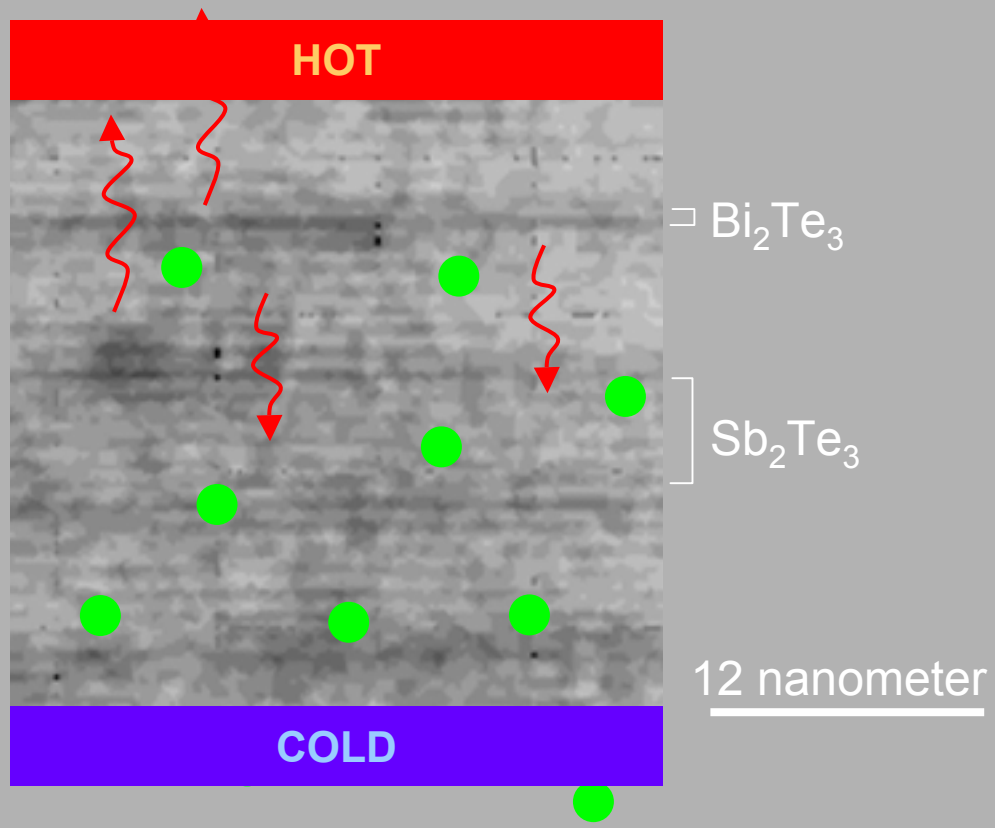

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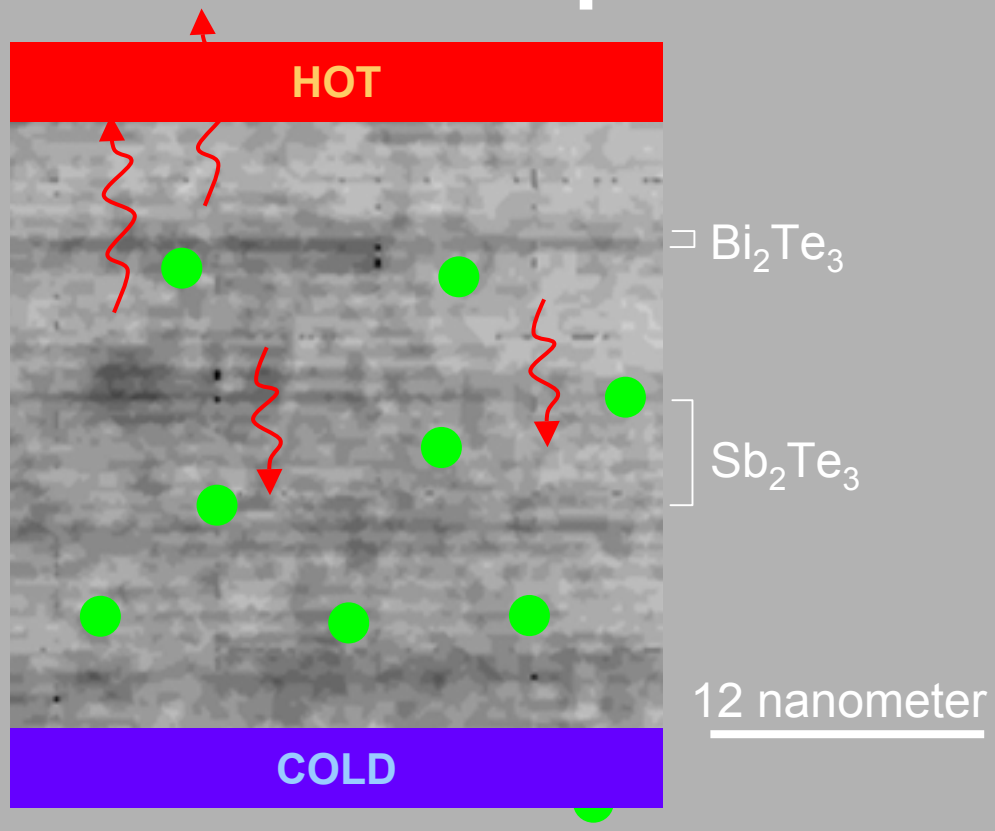

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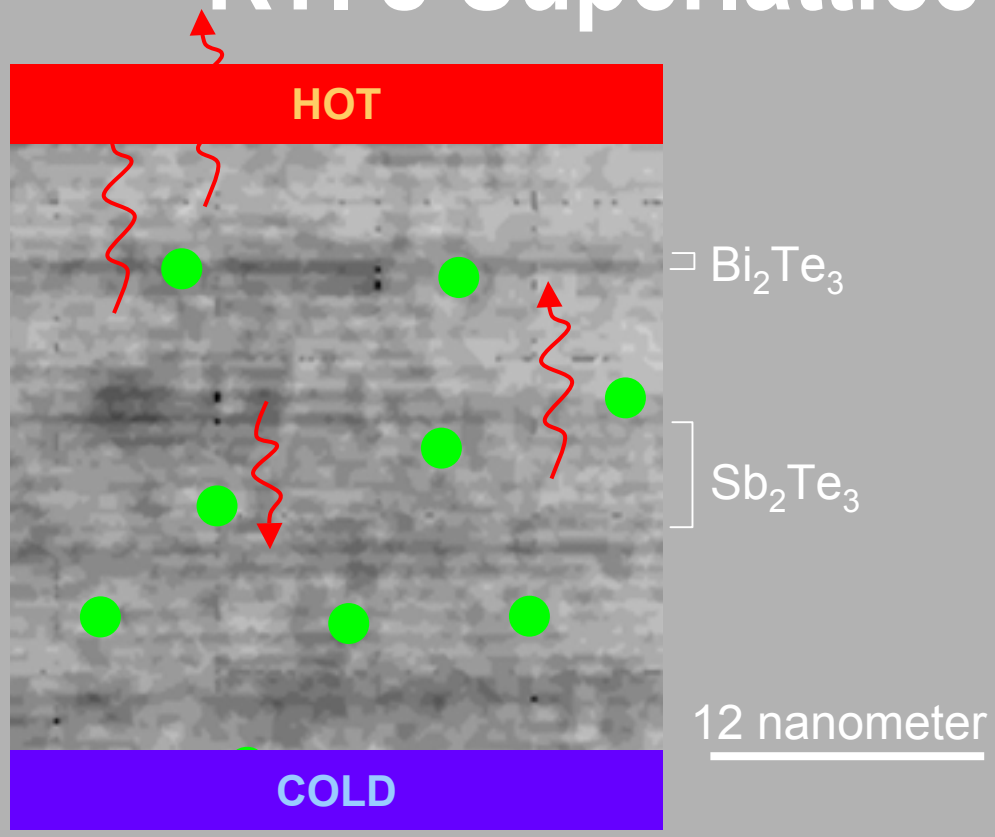

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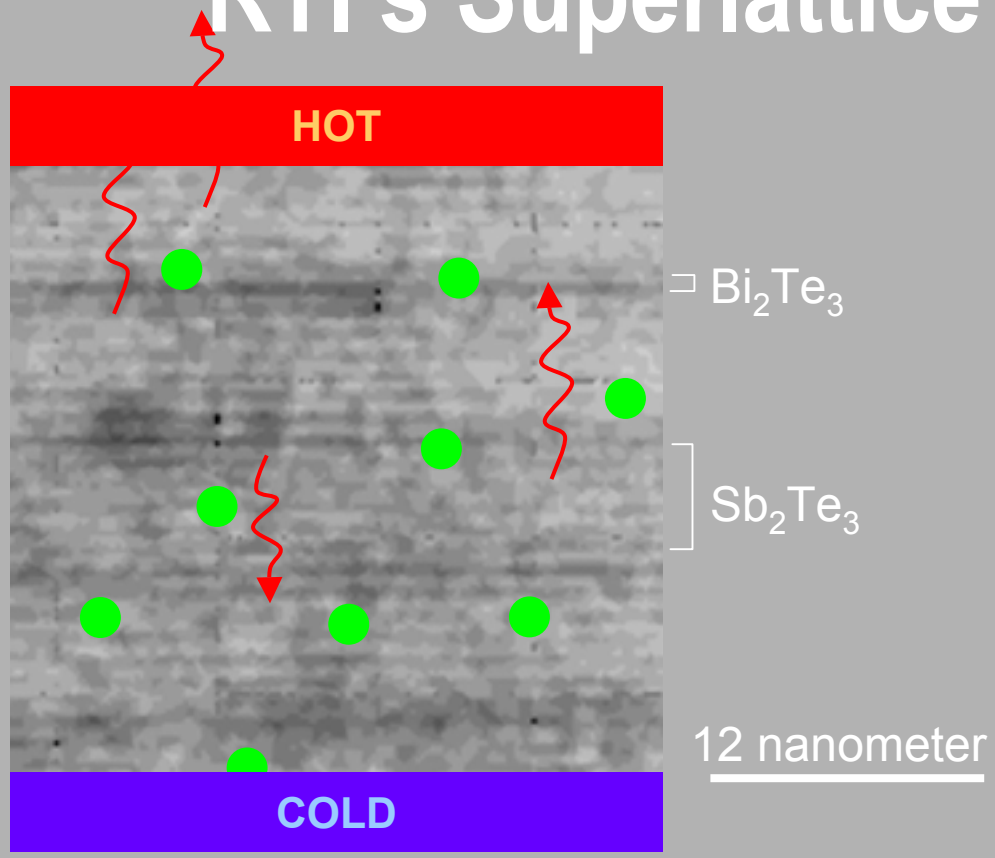

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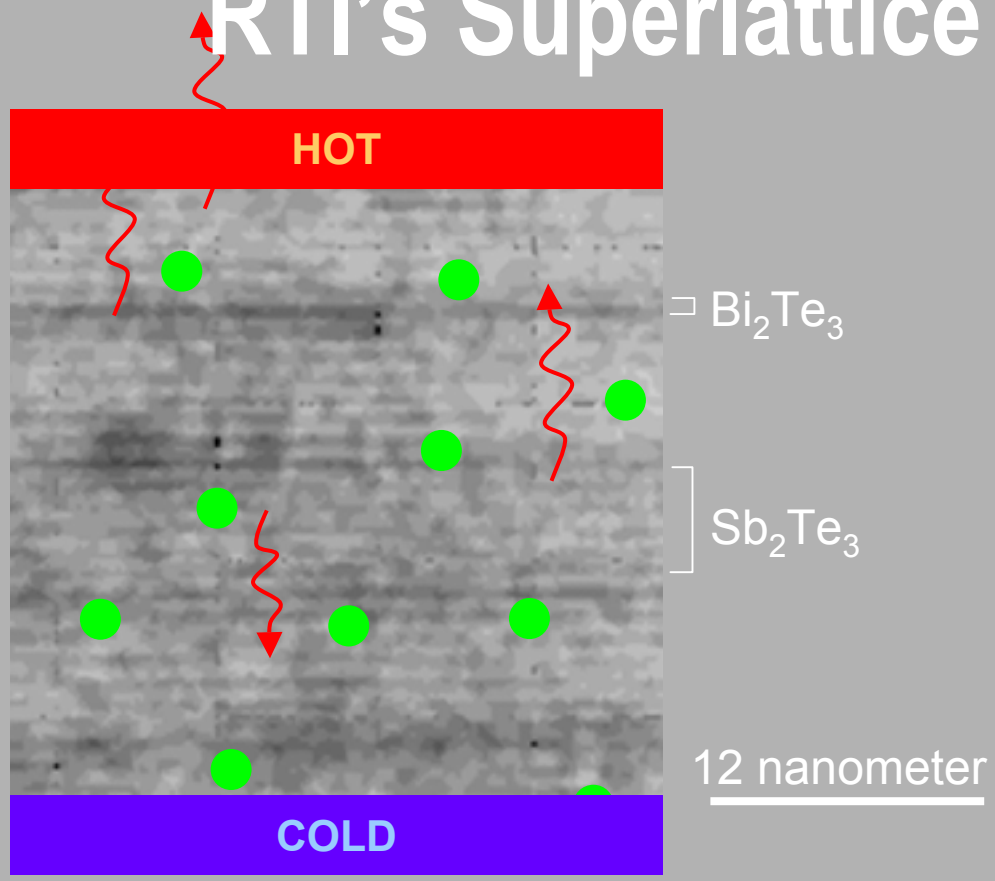

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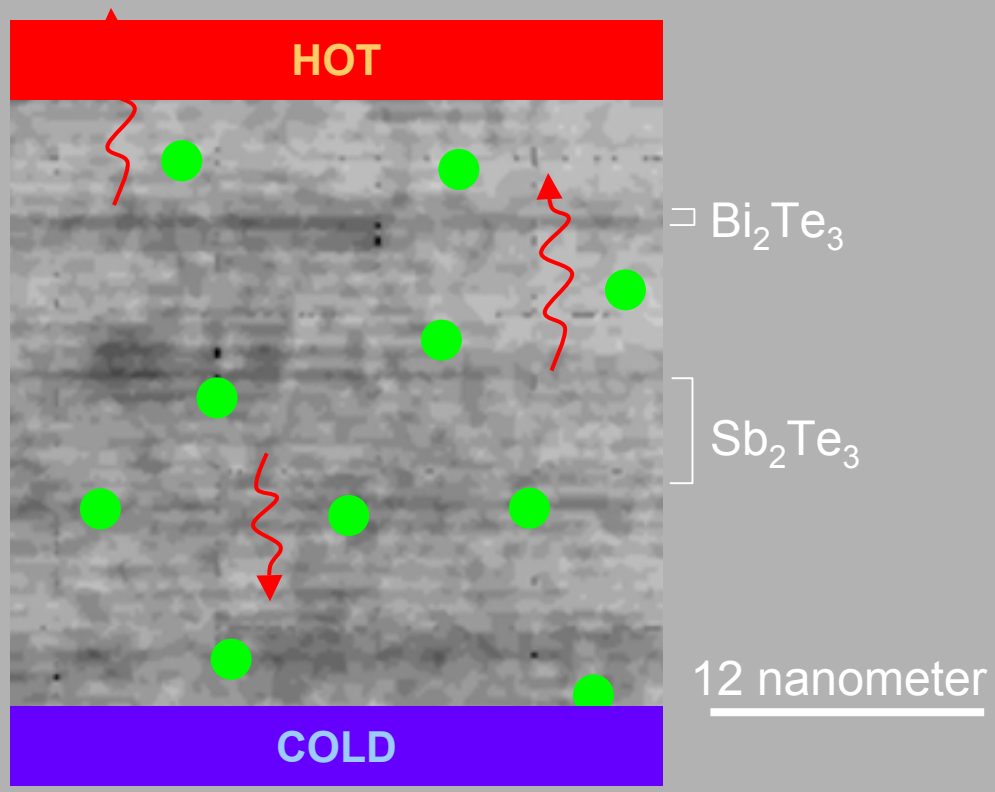

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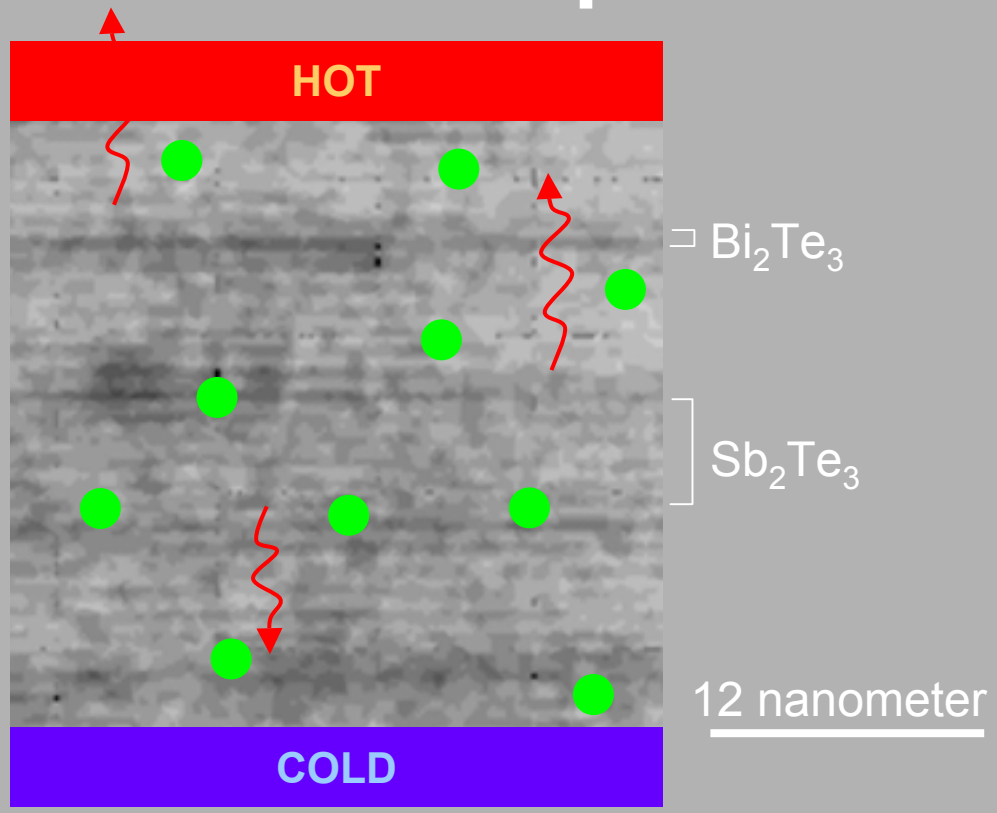

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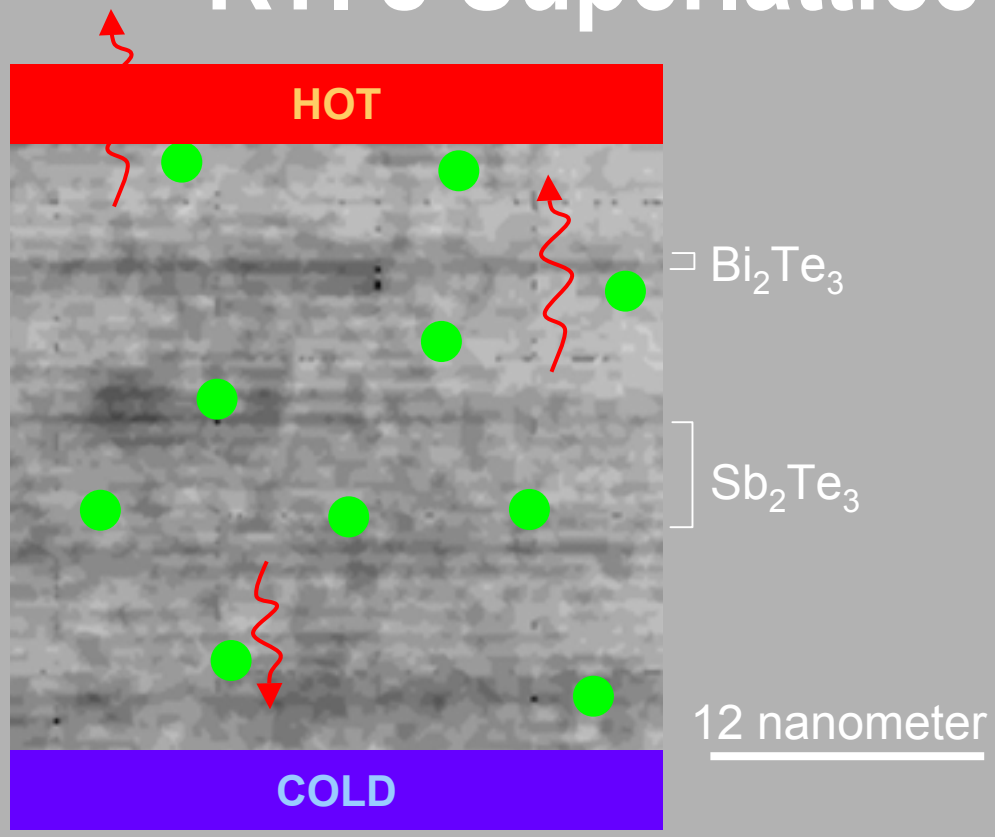

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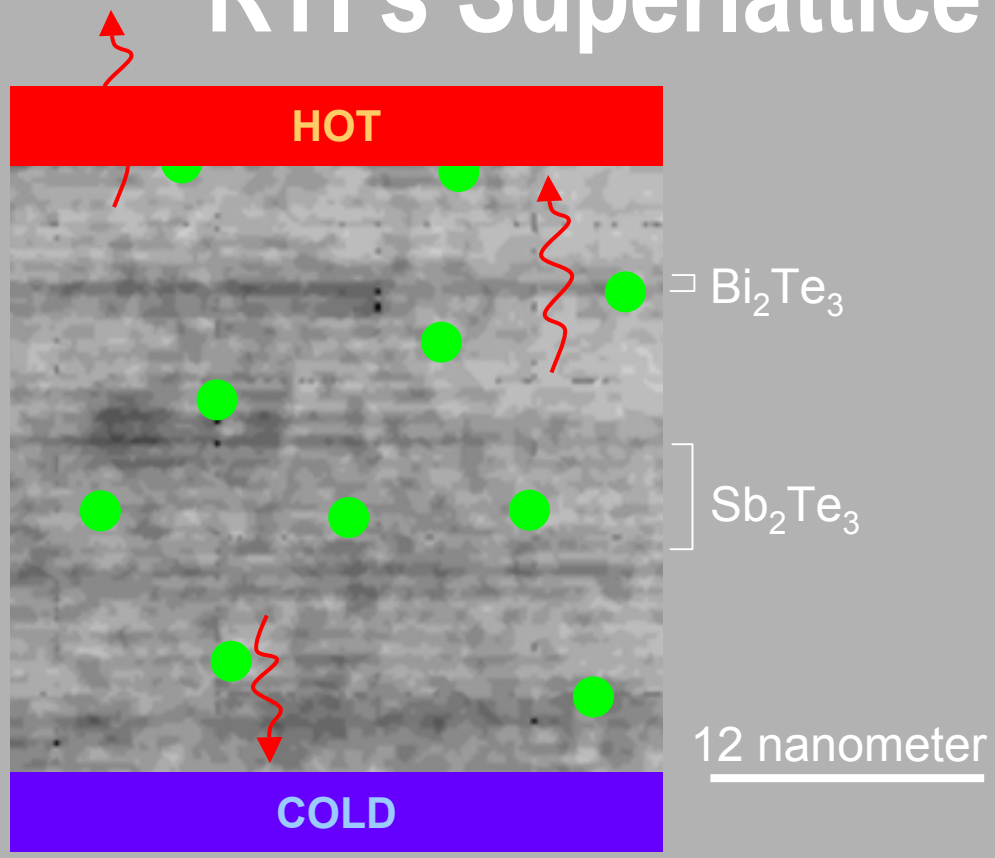

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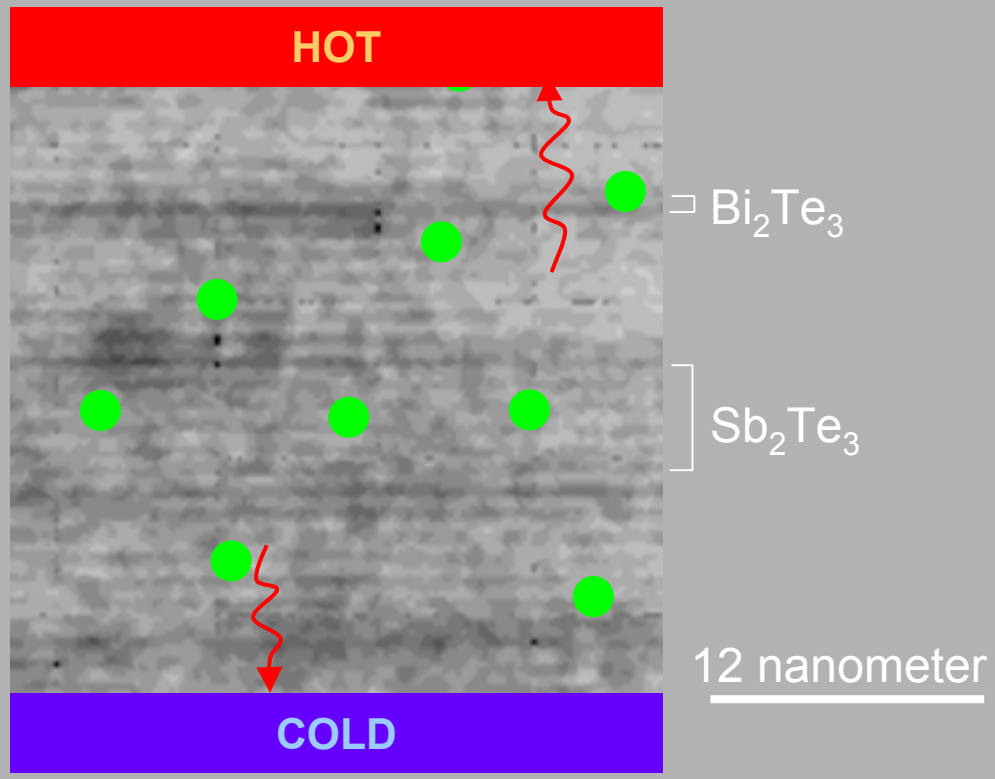

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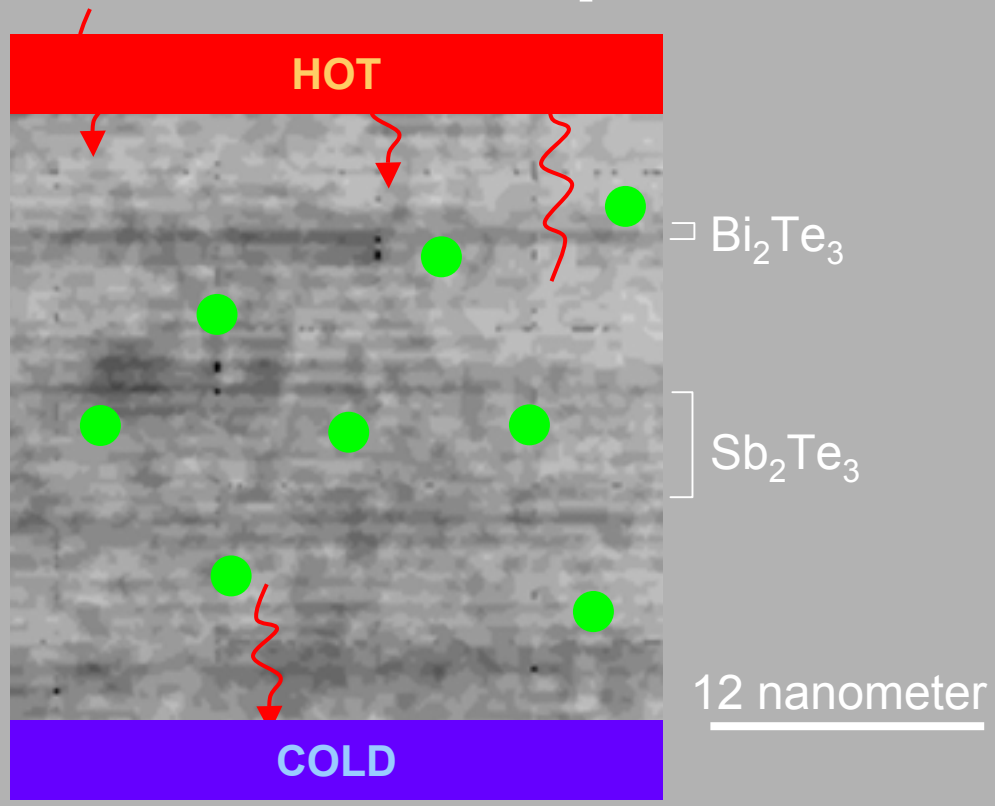

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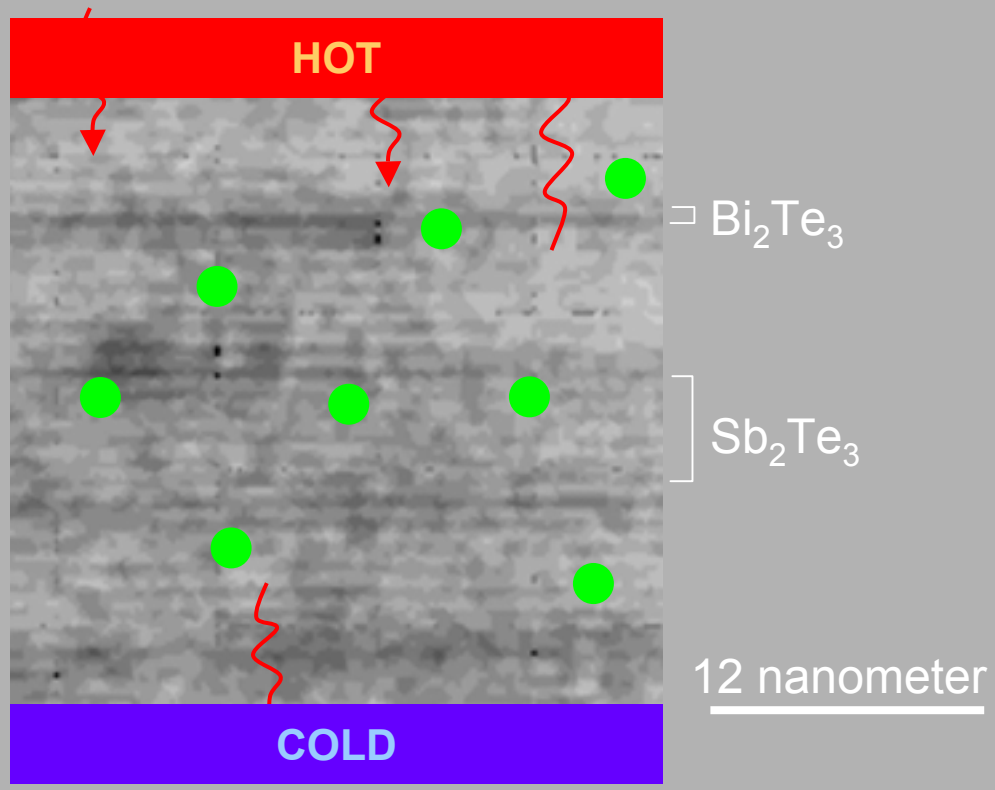

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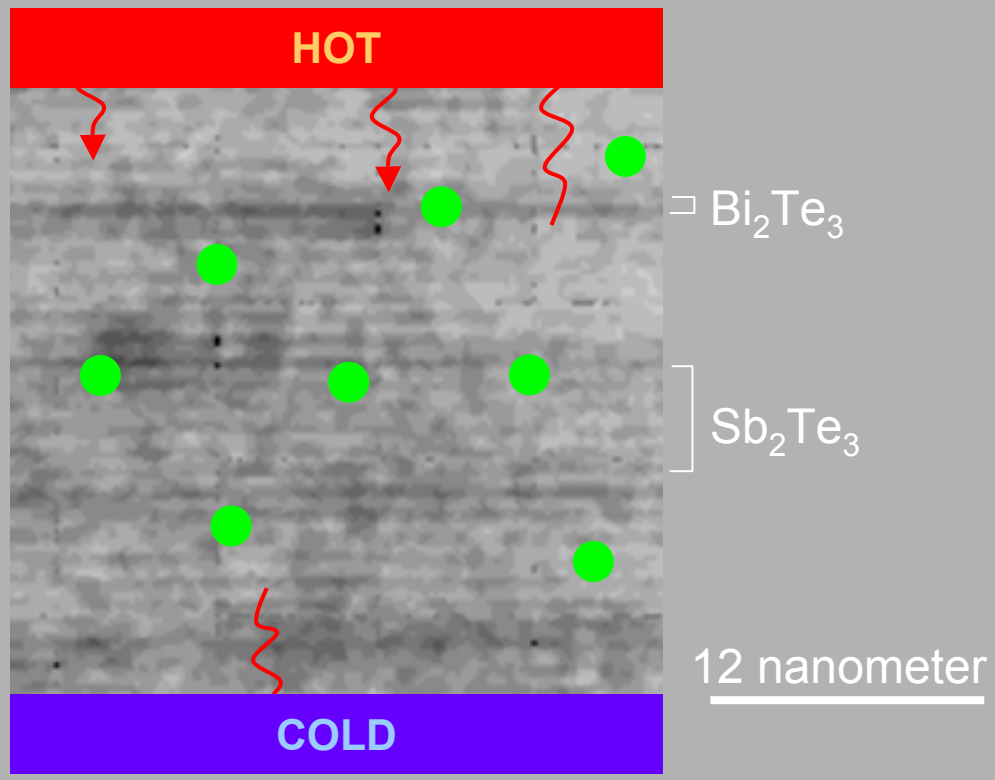

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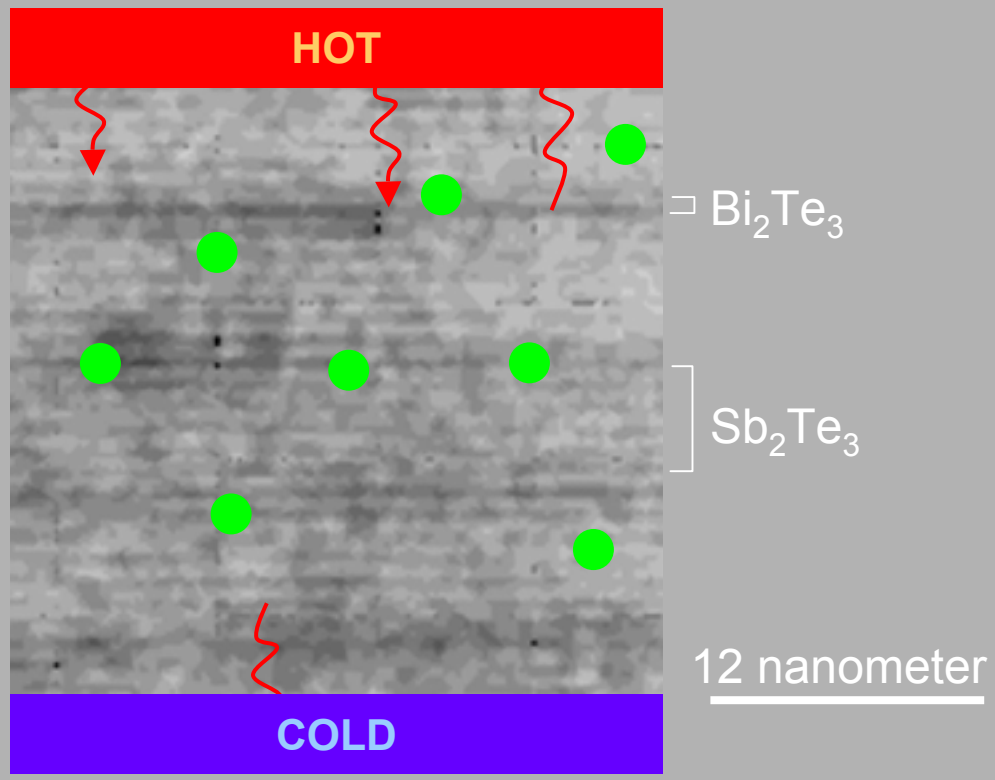

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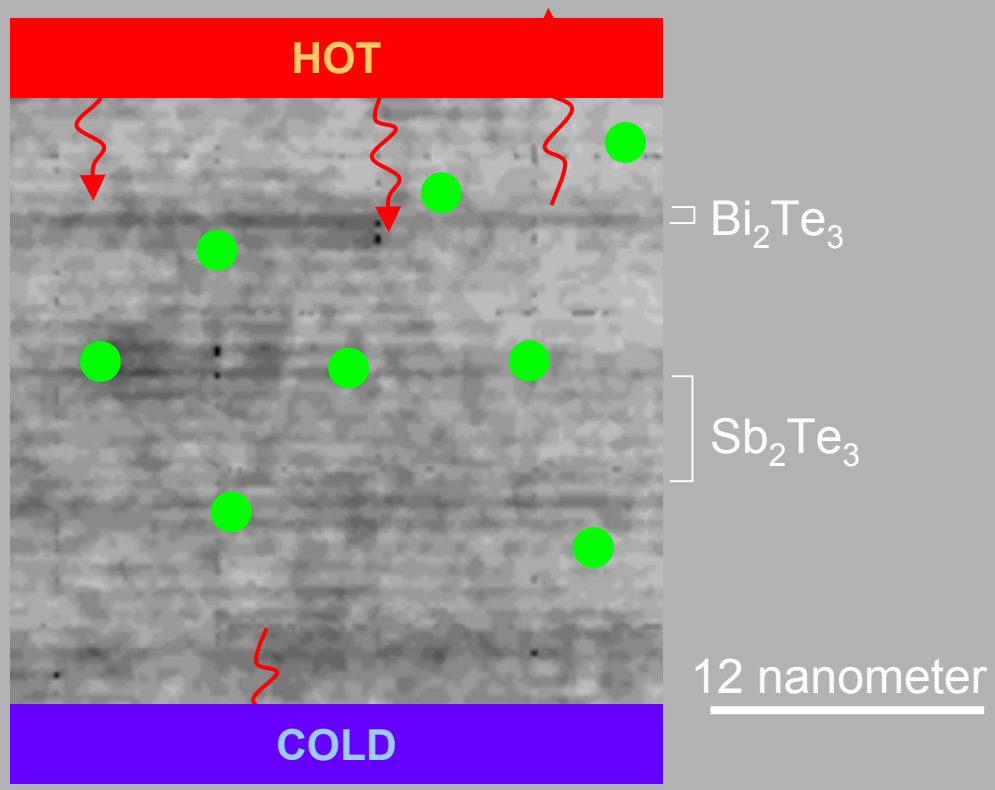

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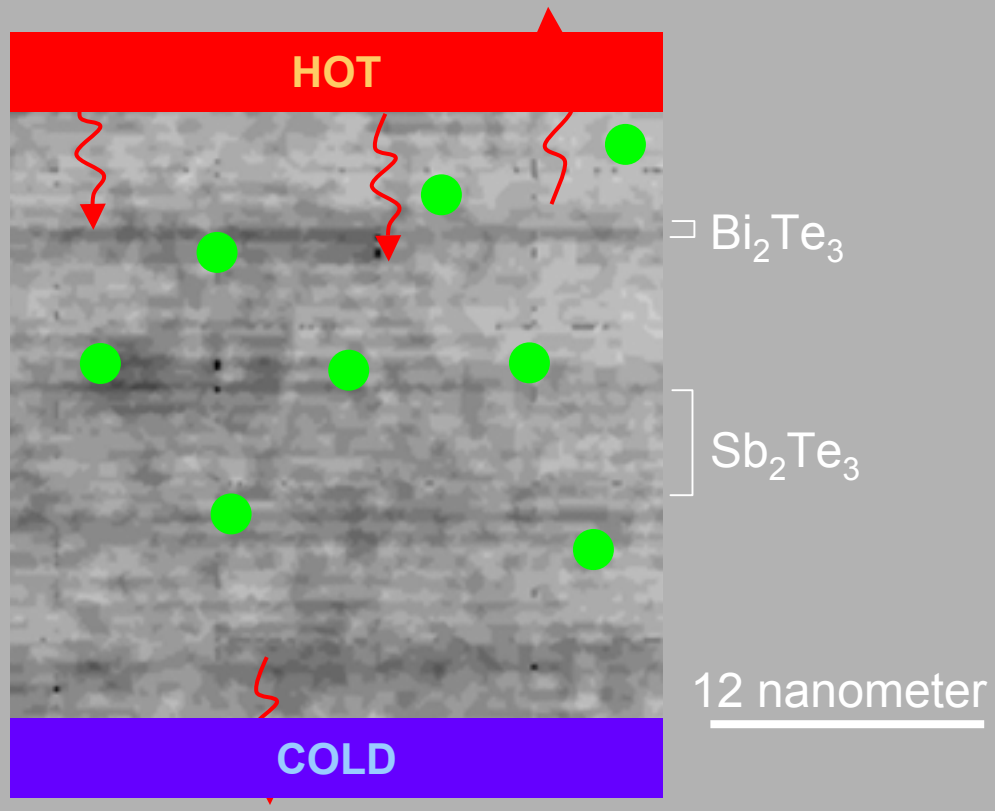

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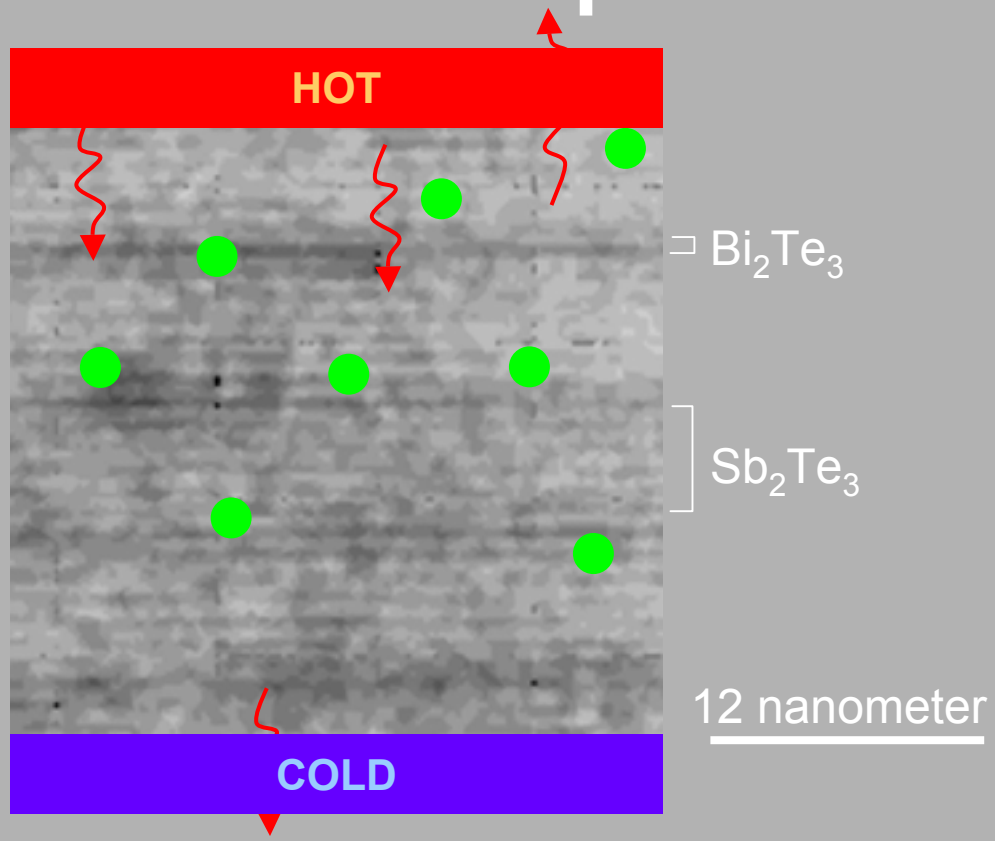

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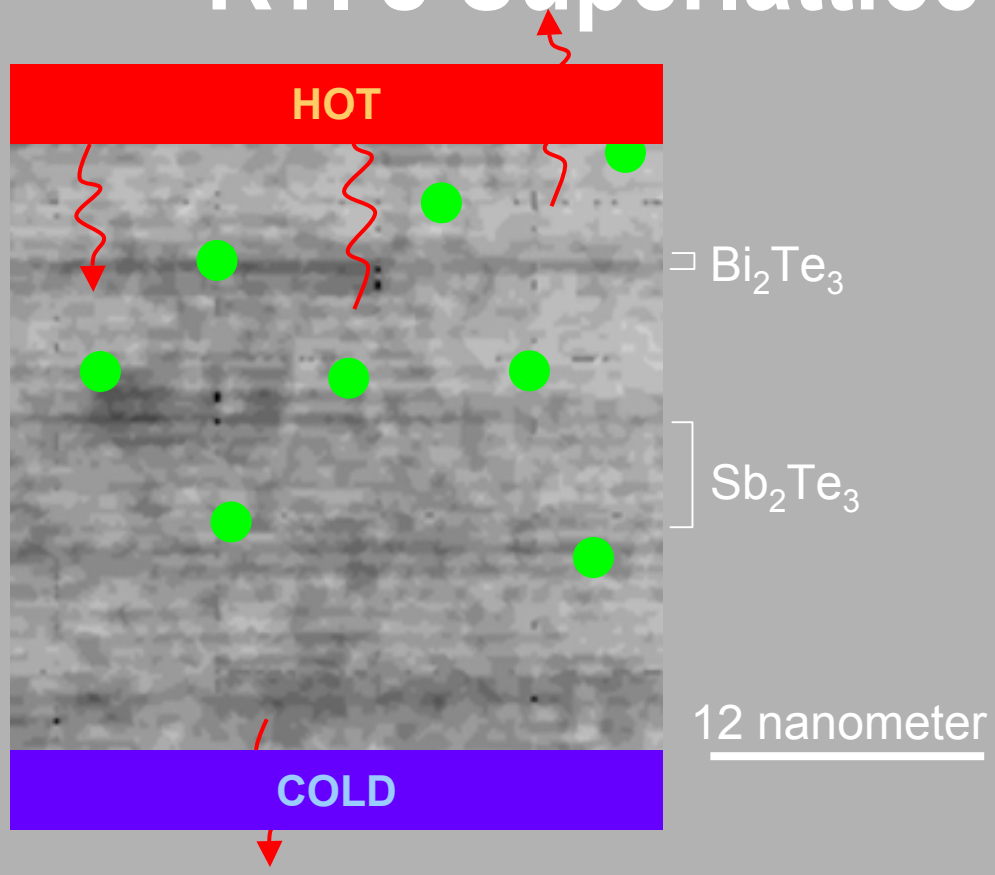

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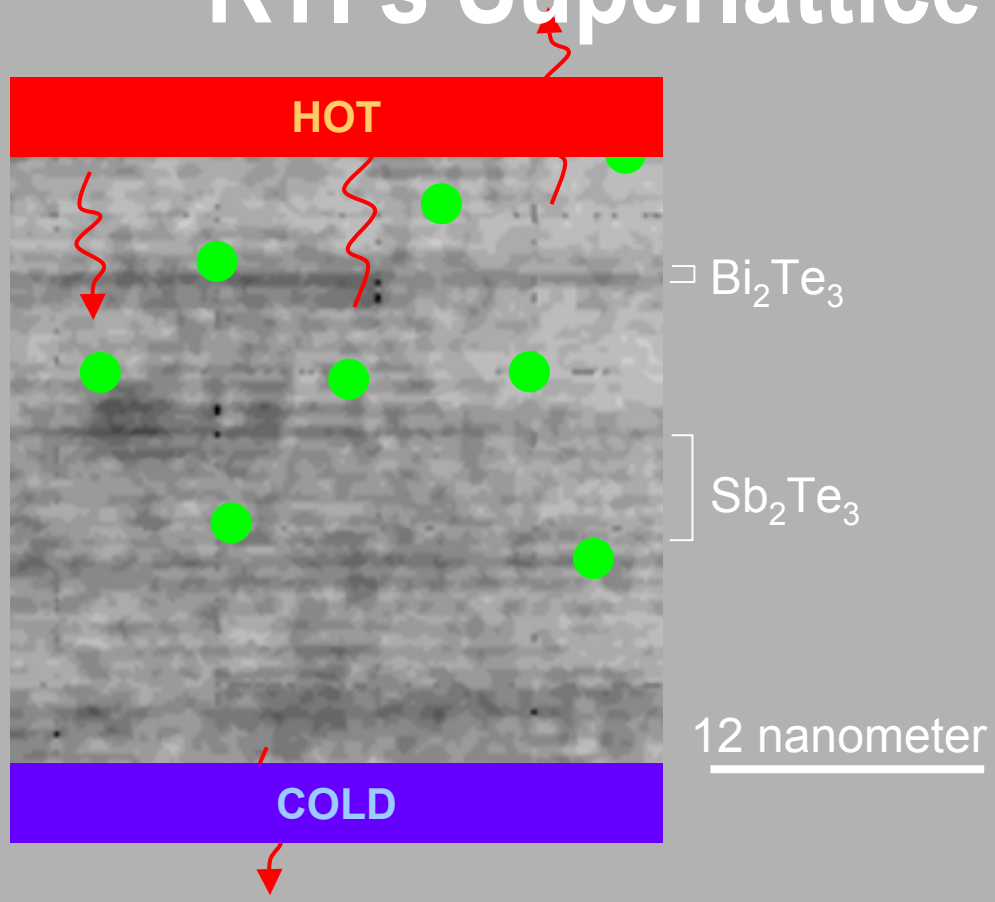

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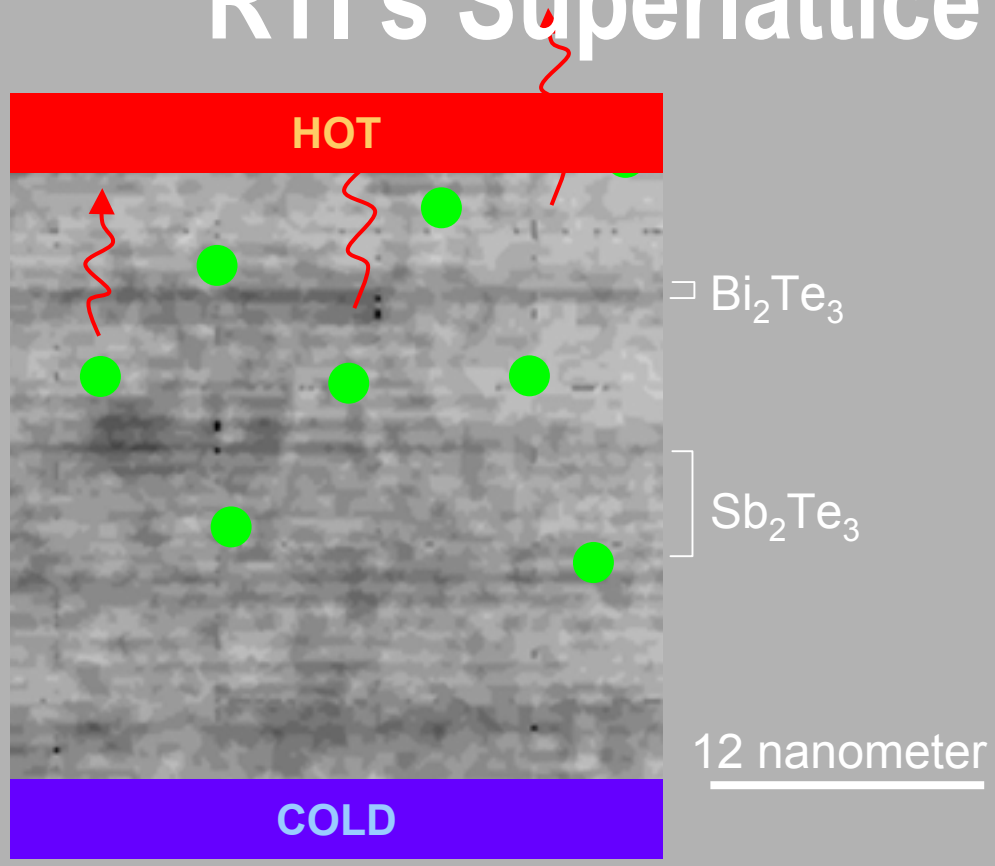

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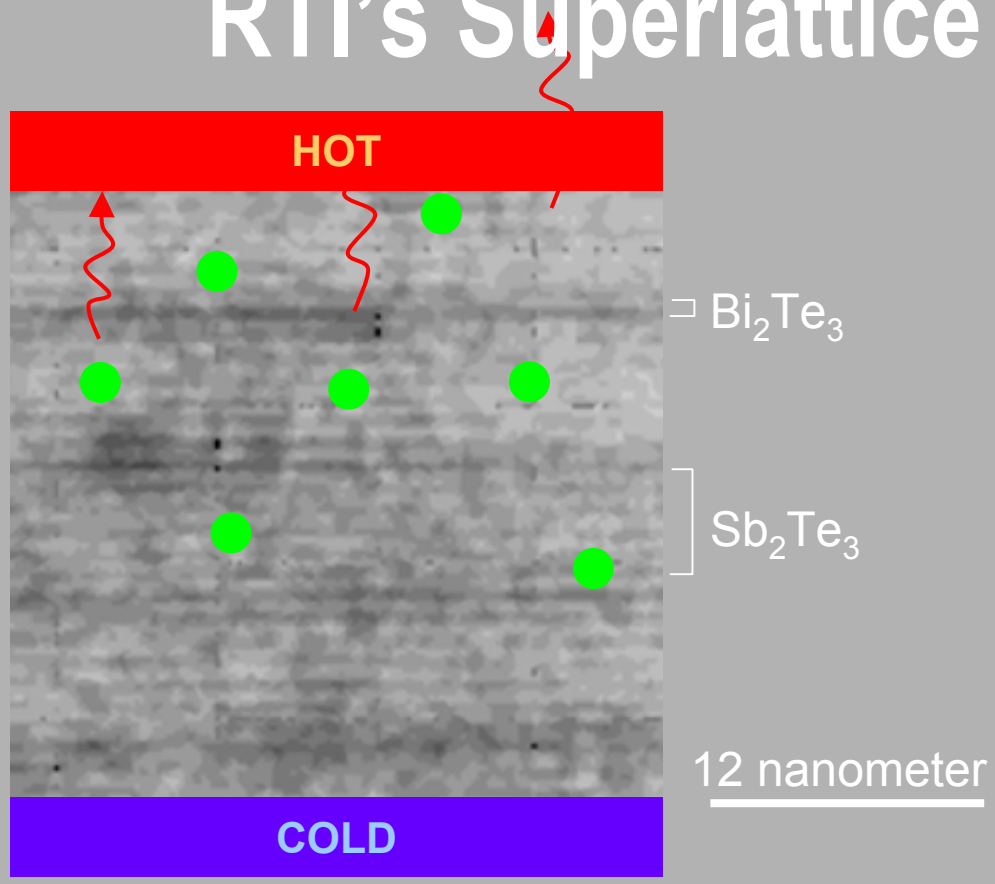

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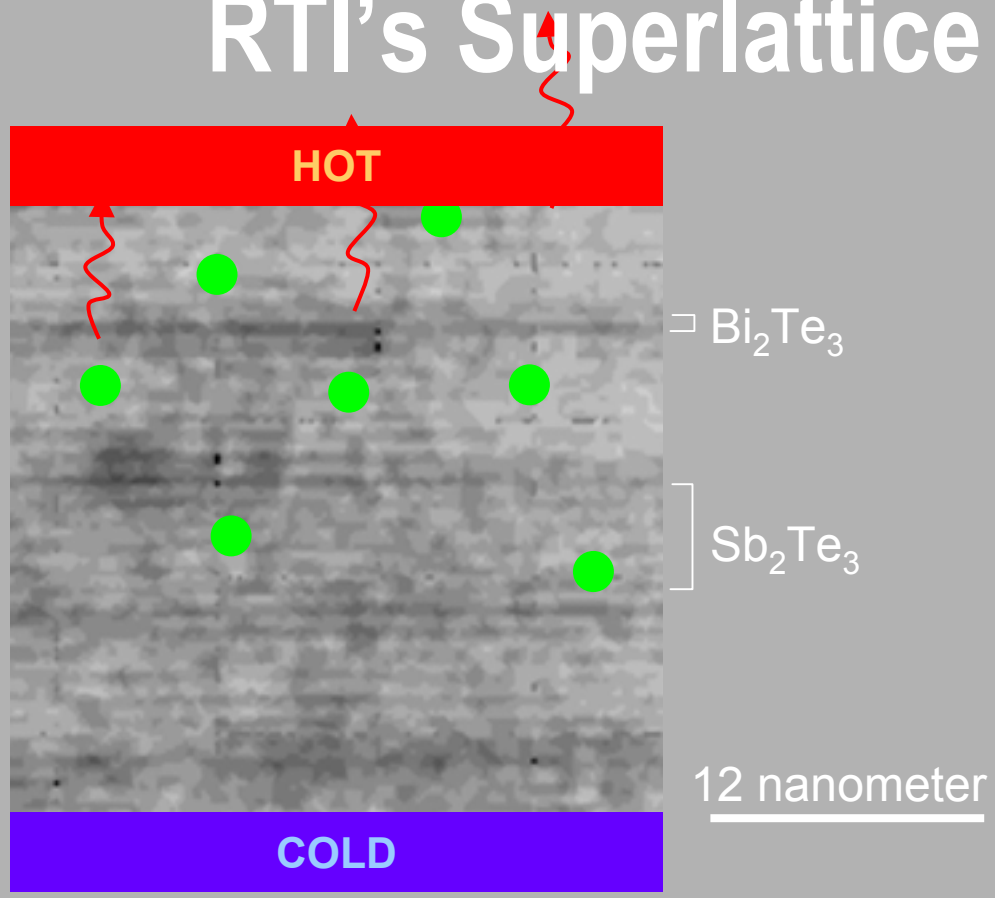
RTI's Superlattice Material



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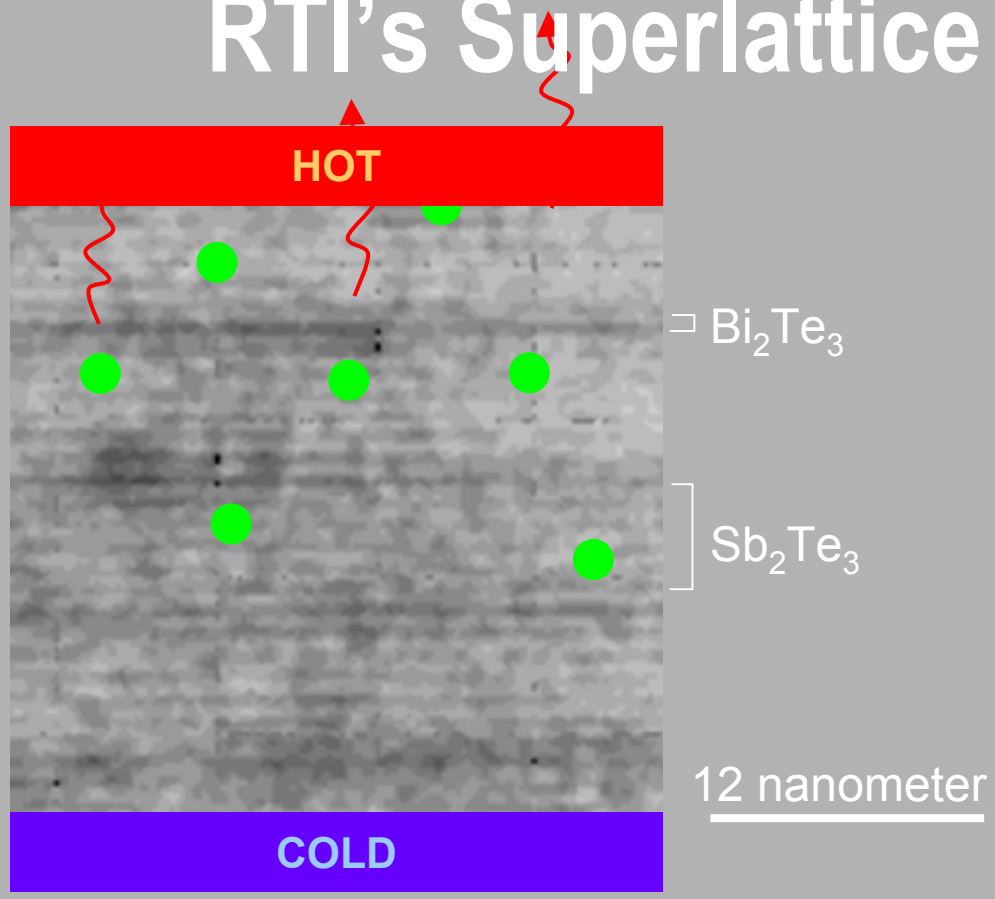

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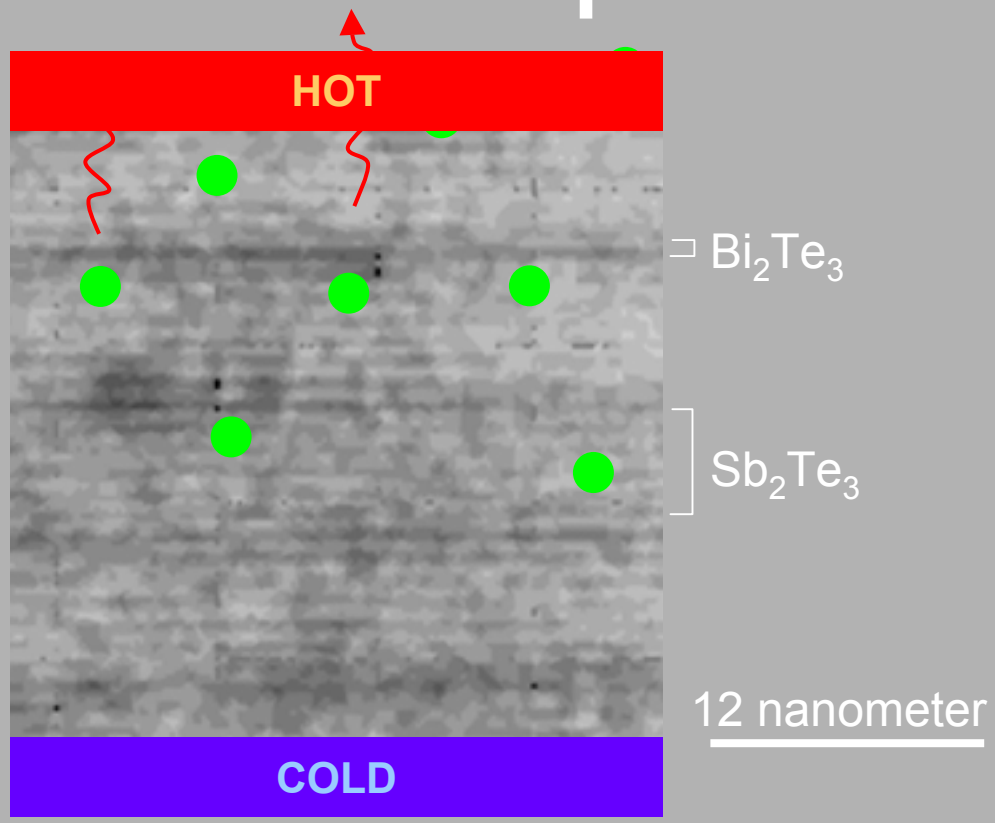

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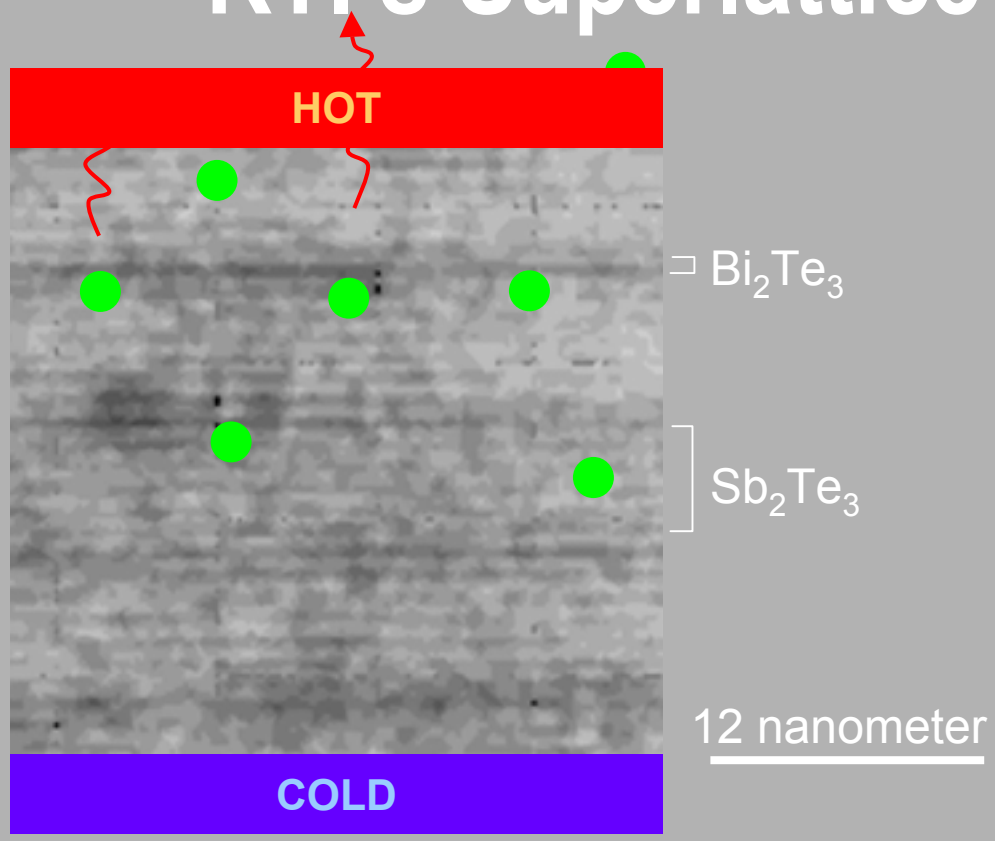

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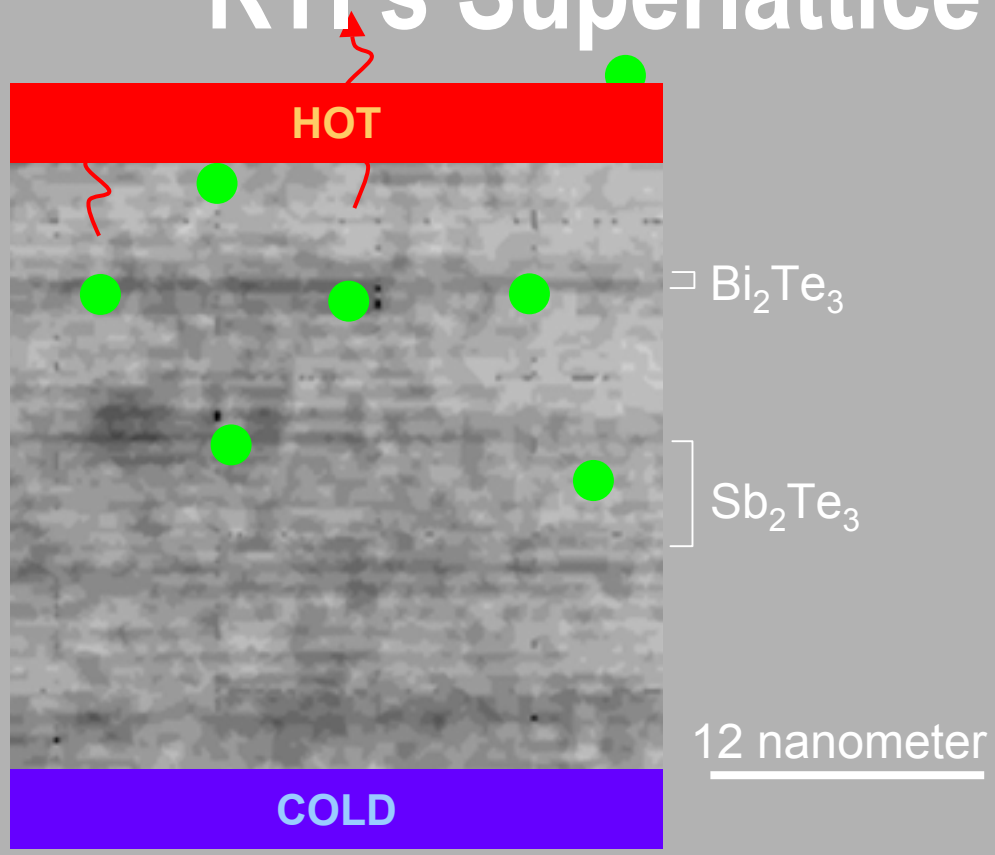

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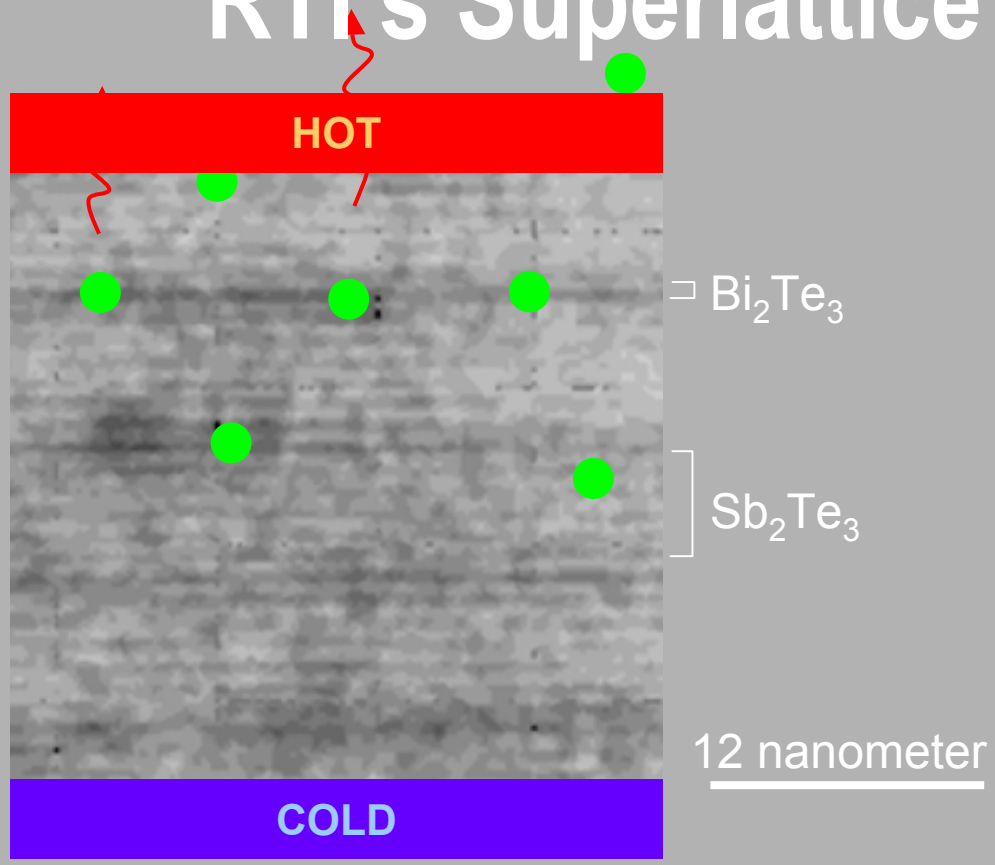

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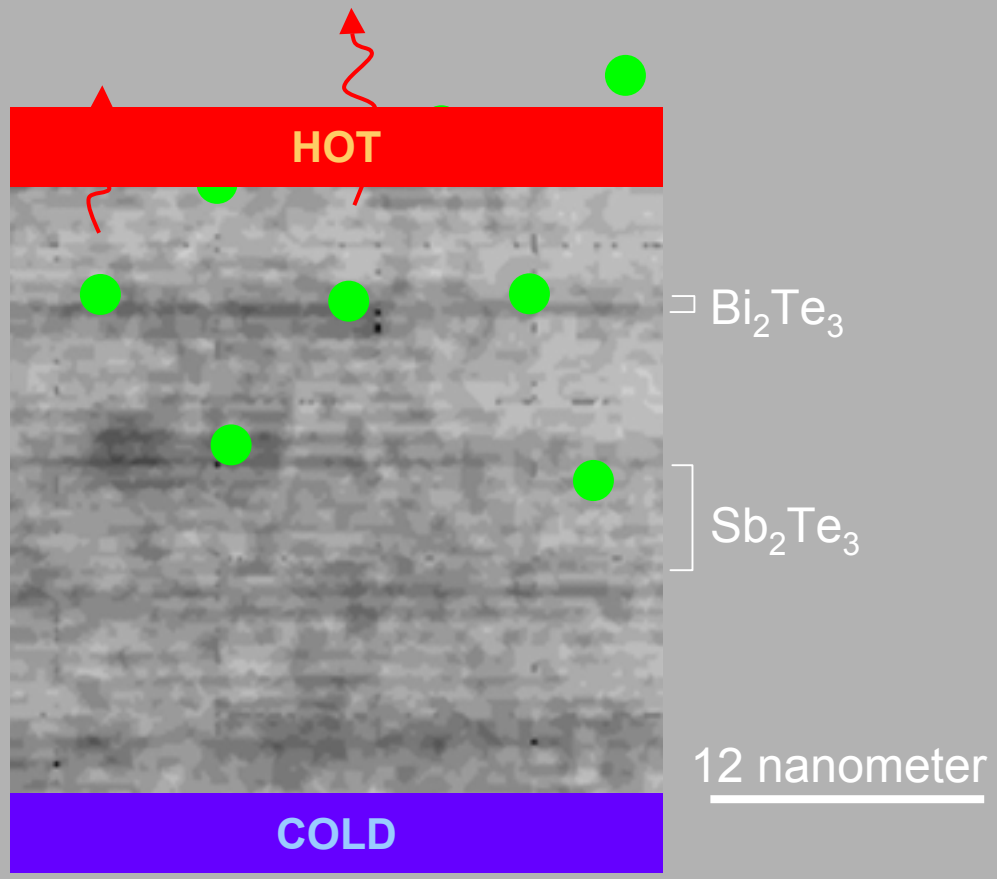

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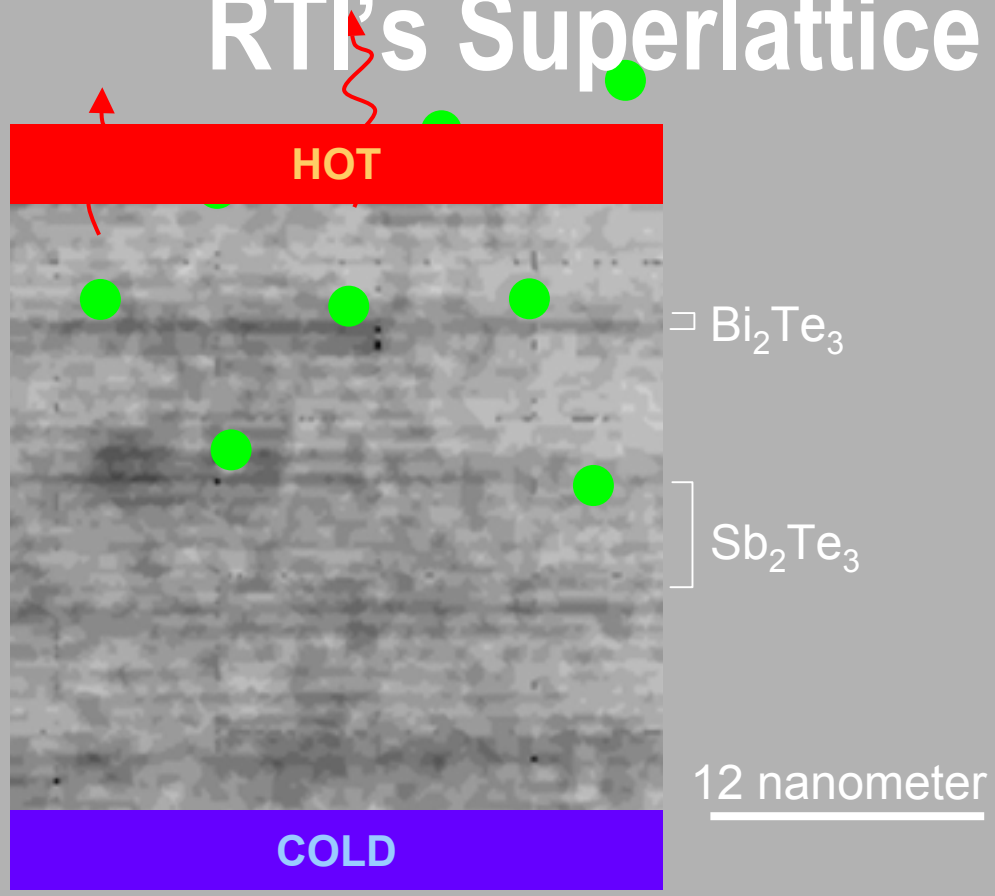

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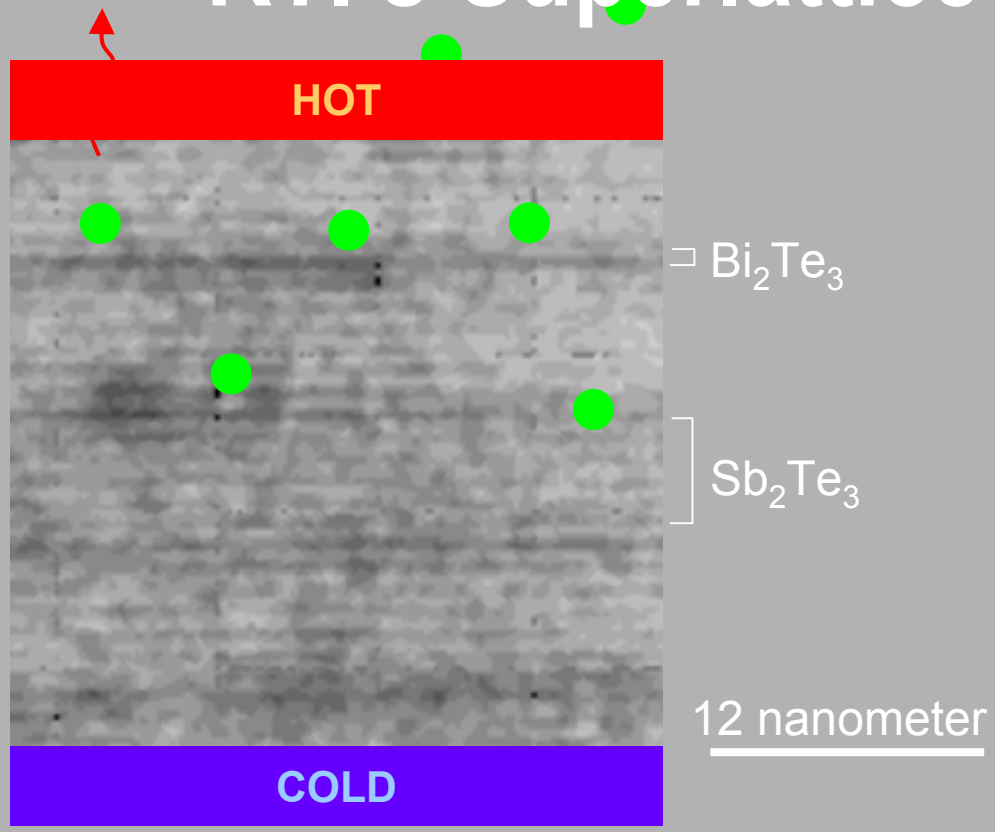

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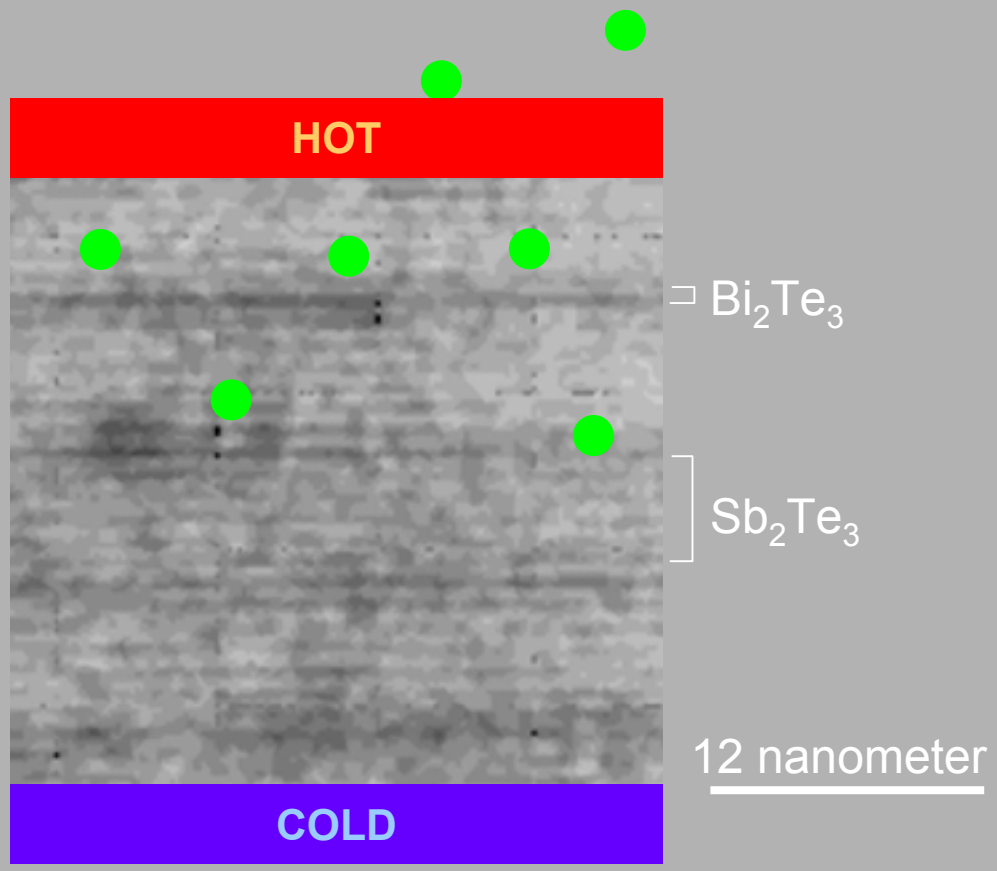
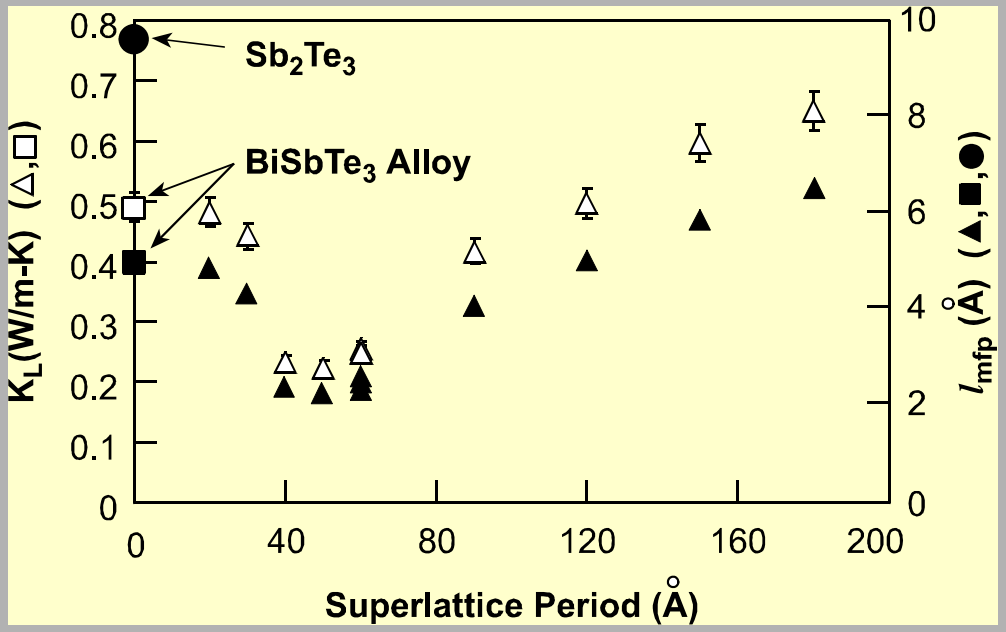
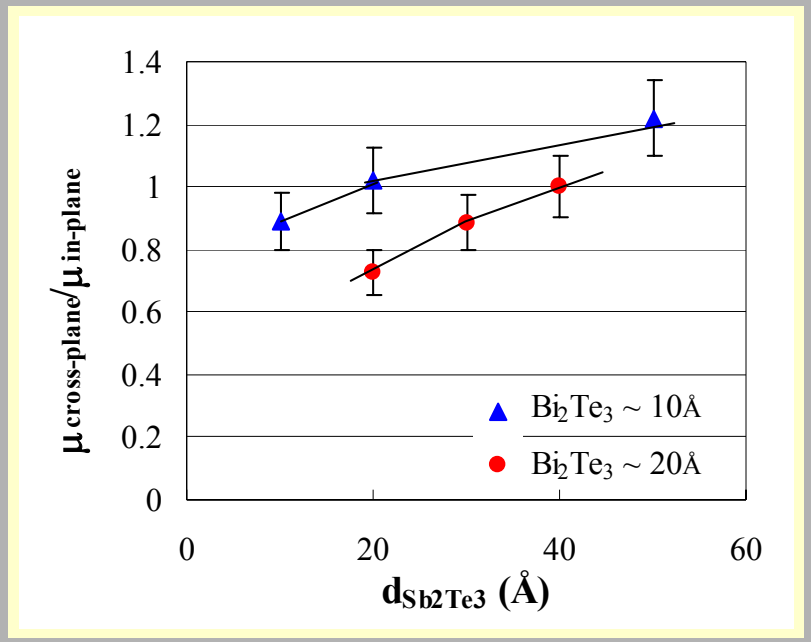


The RTI breakthrough arises from reducing heat transmission without disrupting electron flow

Finer Control of Structure/Period in Optimizing Both Phonon Blocking, Electron-Transmitting Structures



Physical Review B, 61, 3091 (2000)



Nature, 413, 597-602 (2001)

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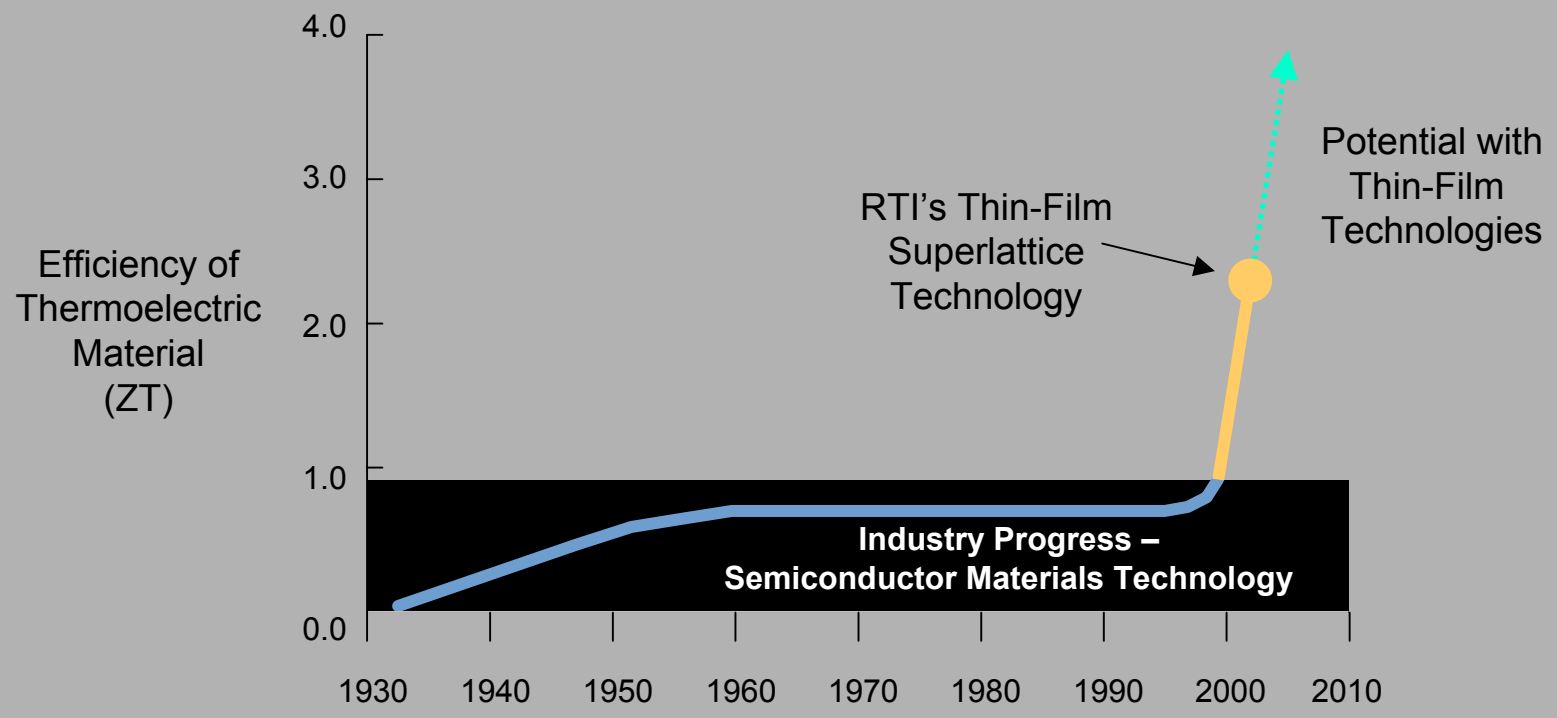
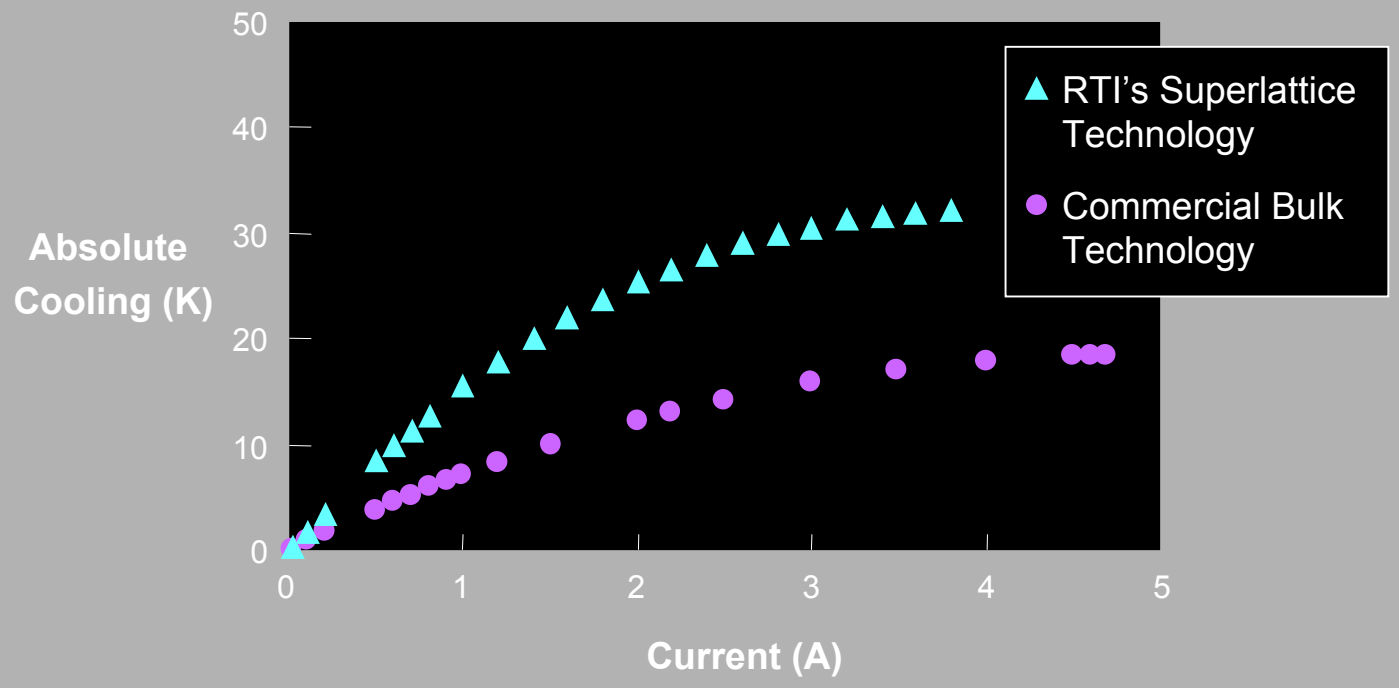
Big Jump in ZT with the Phonon-Blocking, Electron-Transmitting Structures



Venkatasubramanian, Siivola, Colpitts, O'Quinn, Nature, 413, 597 (2001)

Advantages of Superlattice Thermoelectric Technology

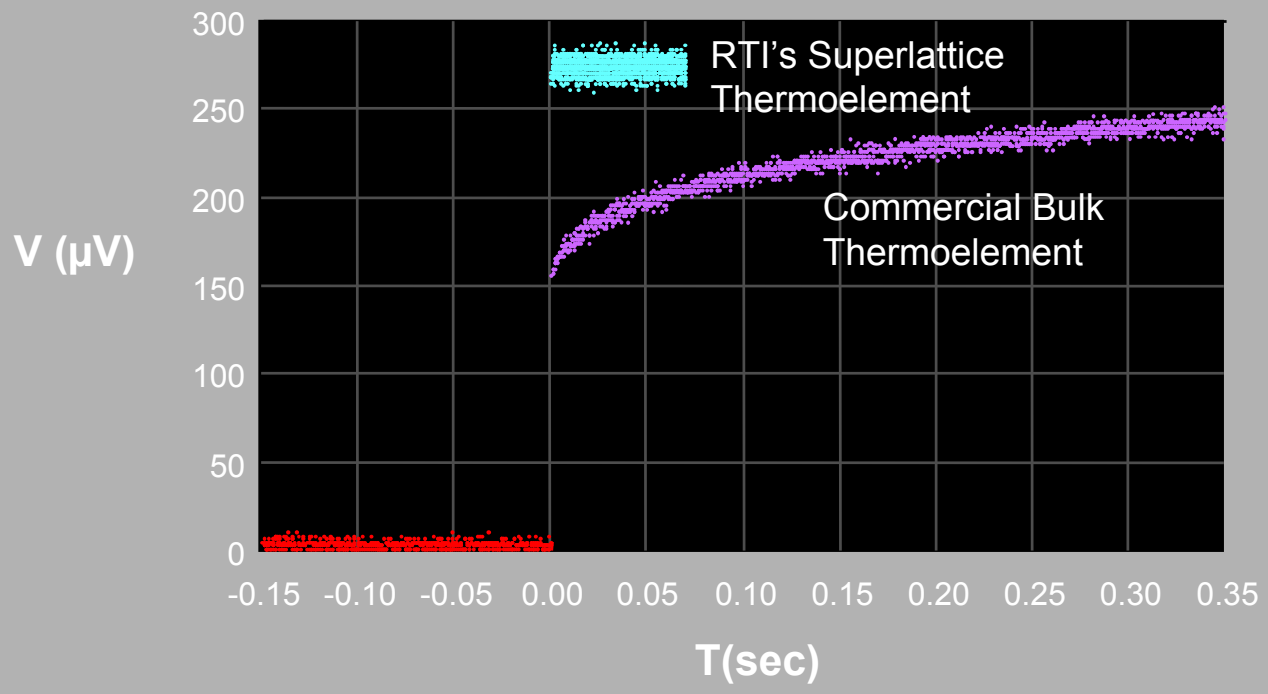
- Enhanced efficiency compared to bulk TE element under similar test conditions



Nature, 413, 597 (2001)

Advantages of Superlattice Thermoelectric Technology

- Enhanced efficiency
- Super-fast cooling and heating



***Nature*, 413, 597 (2001)**

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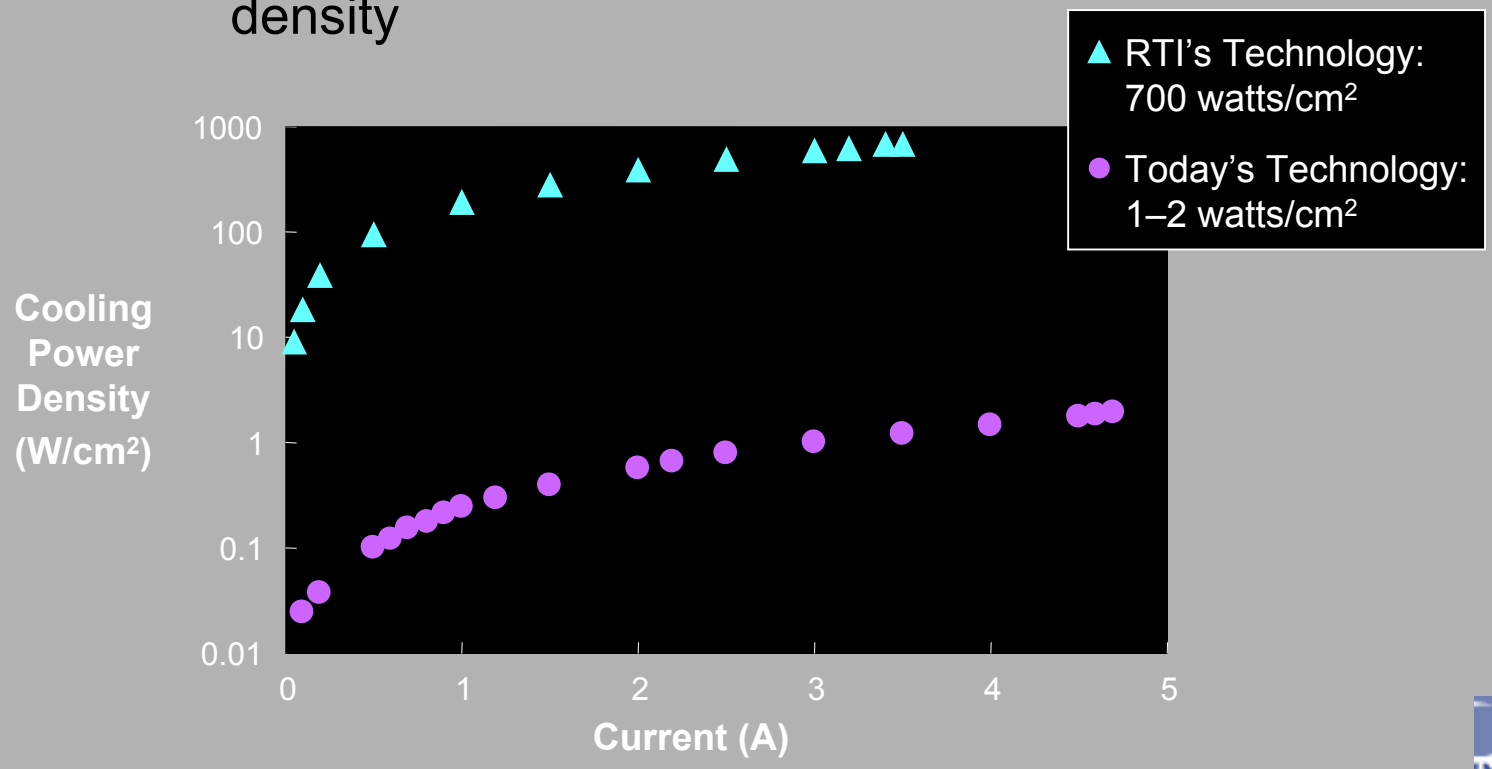
Advantages of Superlattice Thermoelectric Technology

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



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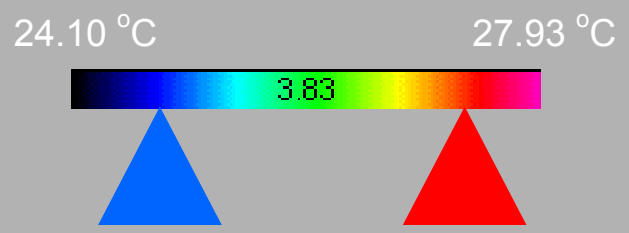
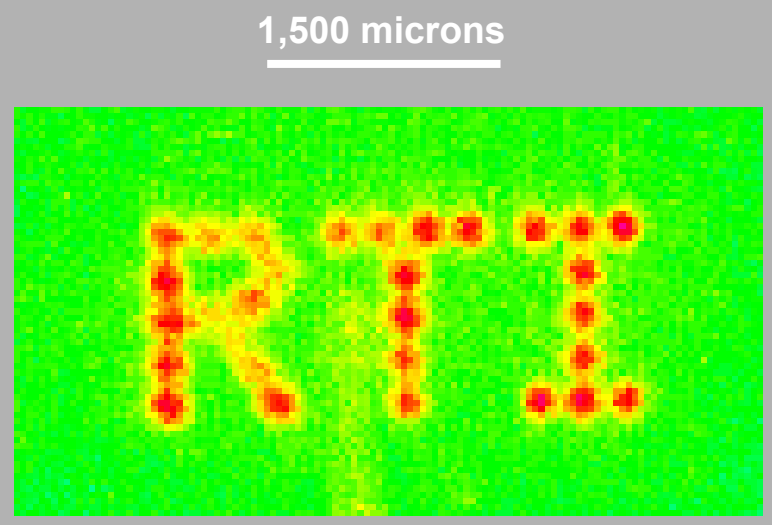
Advantages of Superlattice Thermoelectric Technology

- Enhanced efficiency
- Super-fast cooling and heating
- Enhanced cooling power density
- Localized cooling/ heating technology

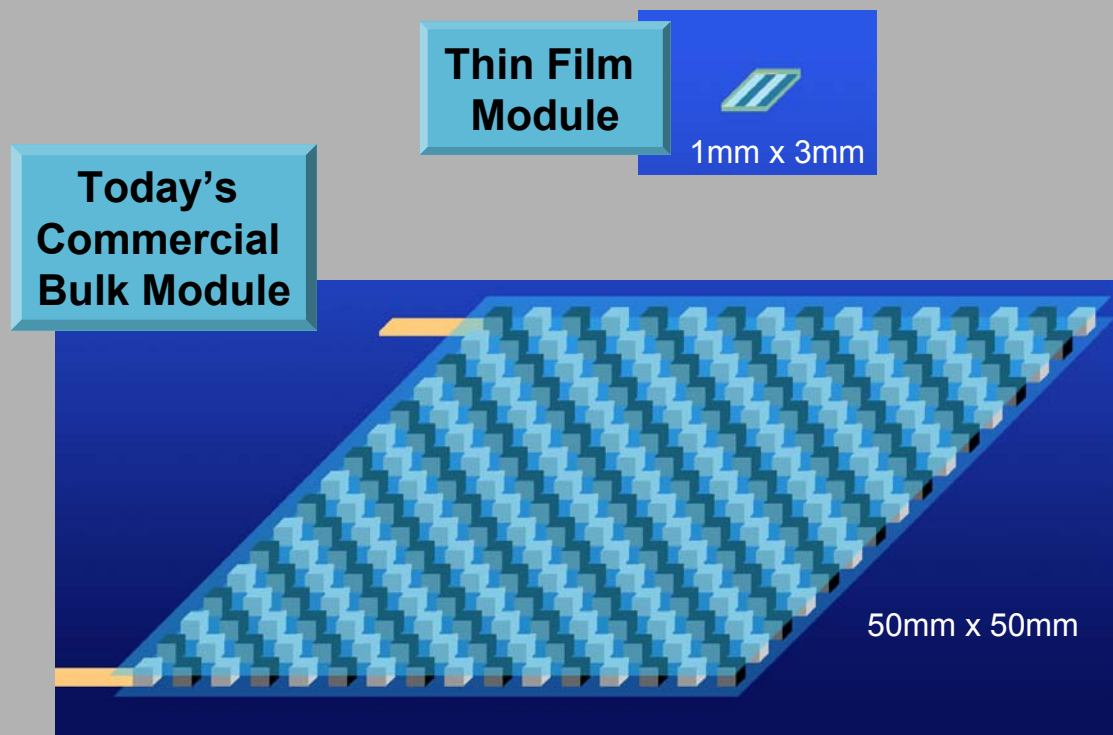




Nature, 413, 597 (2001)

Advantages of RTI's Superlattice Thermoelectric Technology

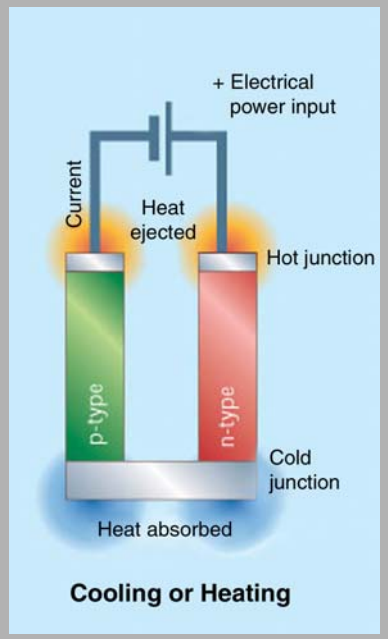
- Enhanced efficiency
- Super-fast cooling and heating
- Enhanced power density
- Localized cooling/ heating technology
- 1/40,000th the actual TE material requirement of bulk technology for same functionality – low recycle costs – Eco-friendly technology

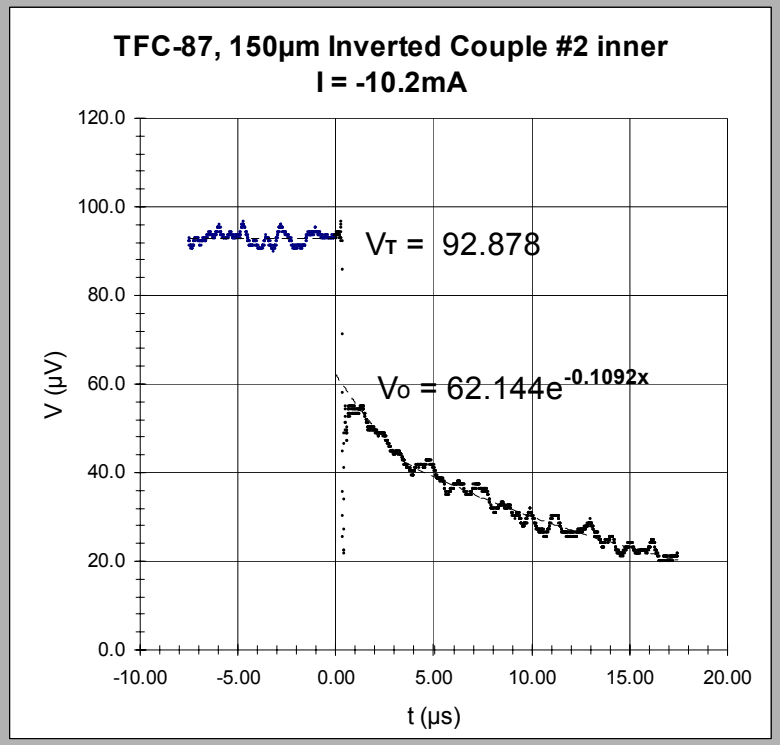


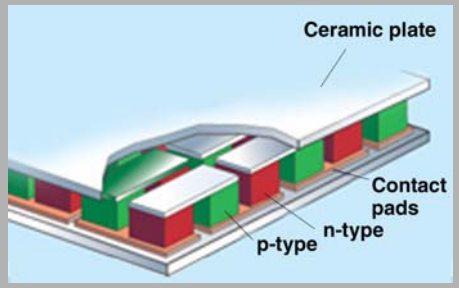
Technology Overview

Recent Results in Transitioning the Materials Advancement

Progress in Thin-film P-N Couples – the fundamental cooling or power conversion unit for transitioning to modules



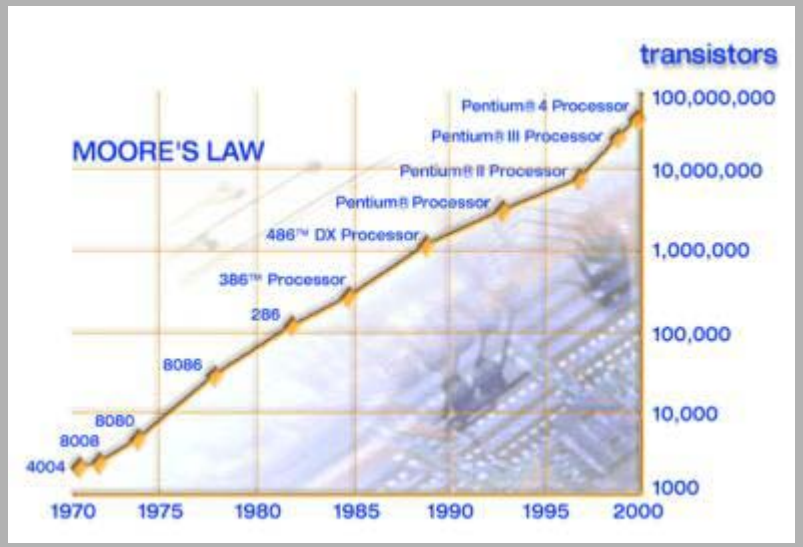


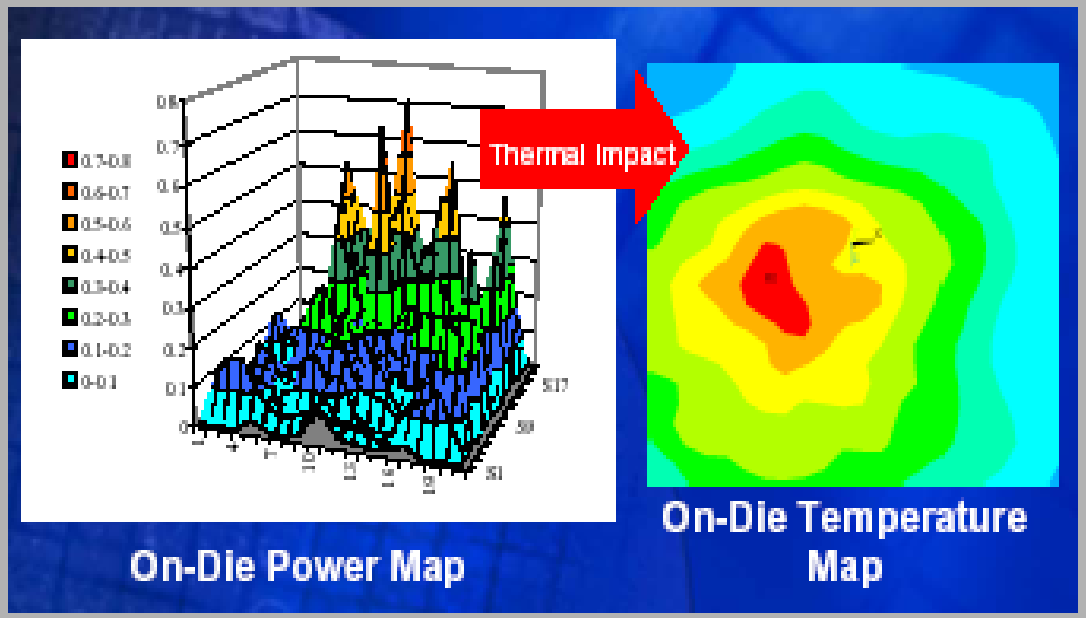


- ZT ~ 2 at 300K
- The individual ZT of p- and n- SL materials has been transitioned to the ZT of couple

Thermal Management for Electronics

Superlattice Thermoelectrics: Also Useful for cooling hot-spots in microprocessors - Match foot-print of Heat-load with that of Micro-Thermoelectric Devices





"If nothing changes, these chips will produce as much heat, for their proportional size, as a nuclear reactor. We have a huge problem to cool these devices."

— Pat Gelsinger, Intel CTO

February 5, 2001

Ref: www.intel.com

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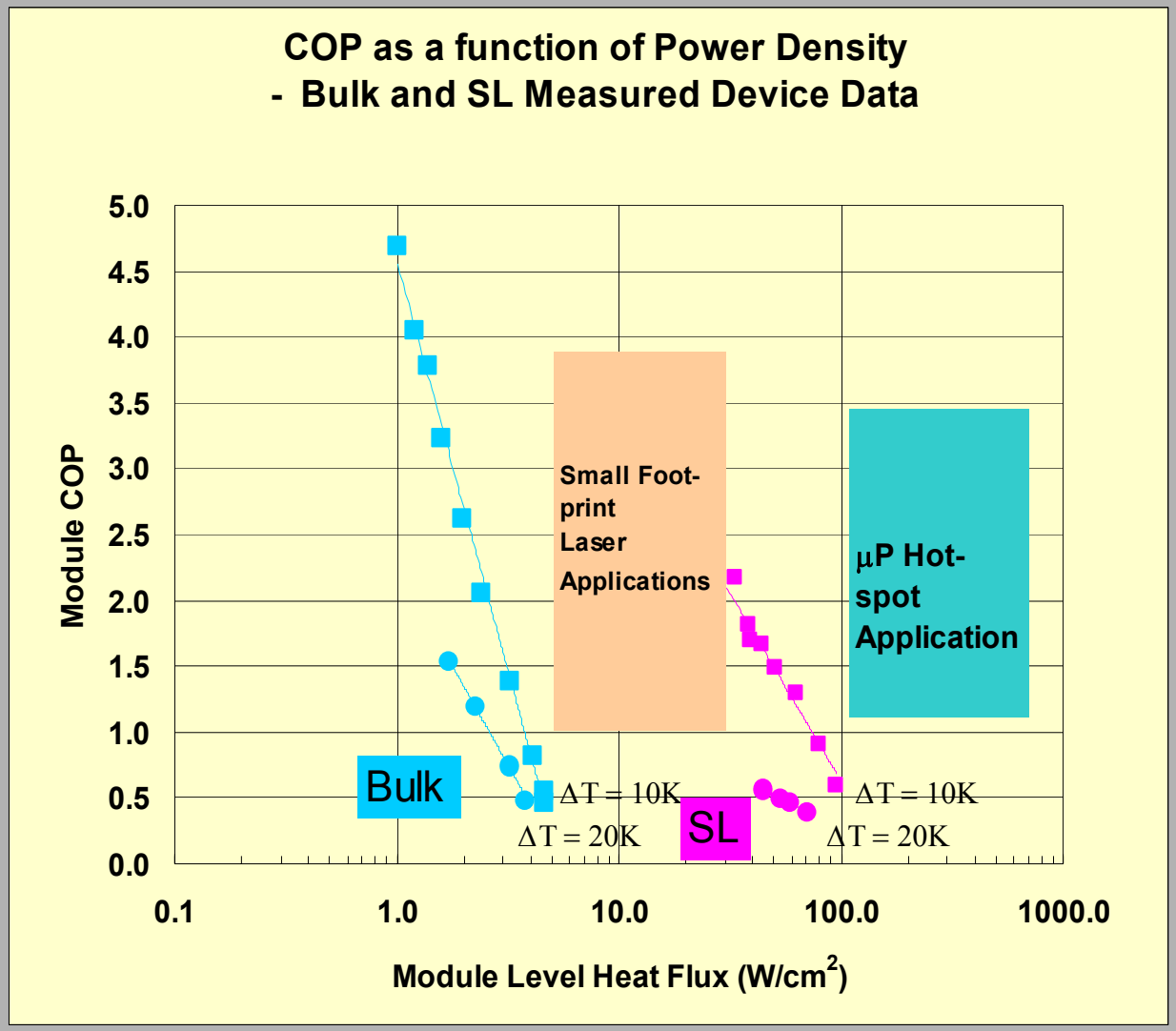
Thermal Management of High Heat Fluxes – Better Efficiencies at High Heat Fluxes with State-of-the-art Superlattice Devices



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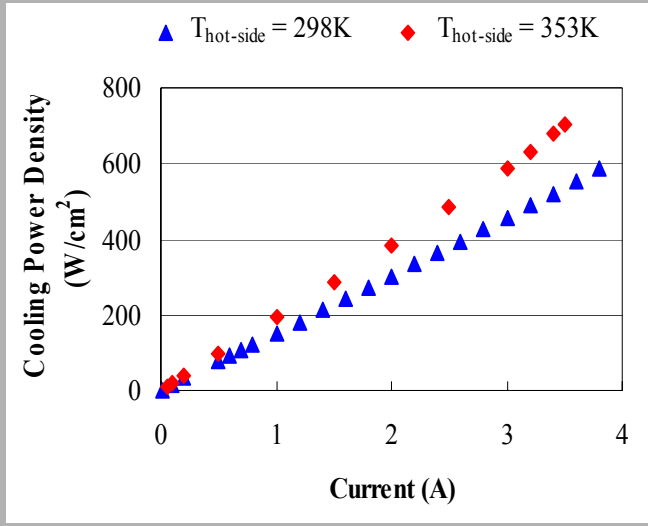
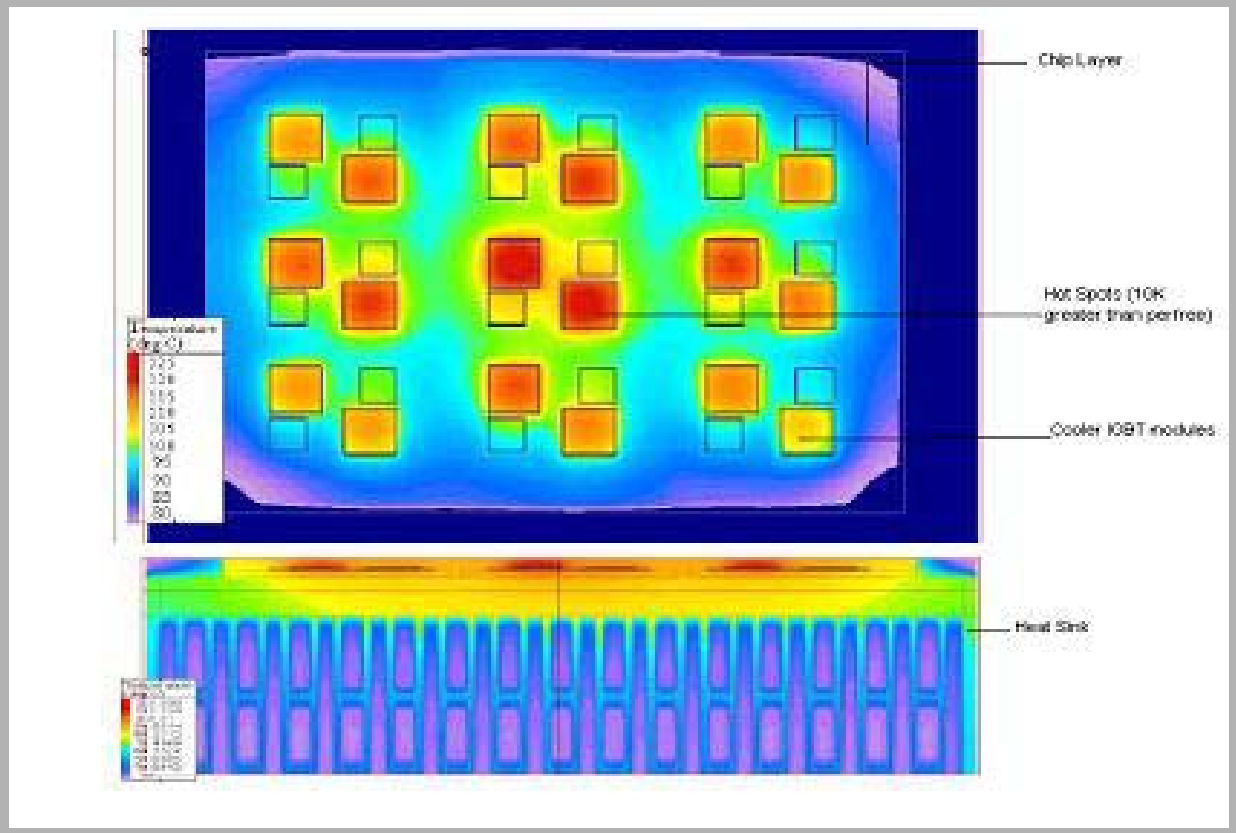
Better System Efficiencies Possible in the Thermal Management of Power Electronics That Switch Large Powers





- Potential Application of High Cooling Power Density to IGBT Chip Cooling – Automotive Power Electronics
  - Most thermal management decided by hot-spots
- Cool the Hot-spots so that system-level cooling are lower

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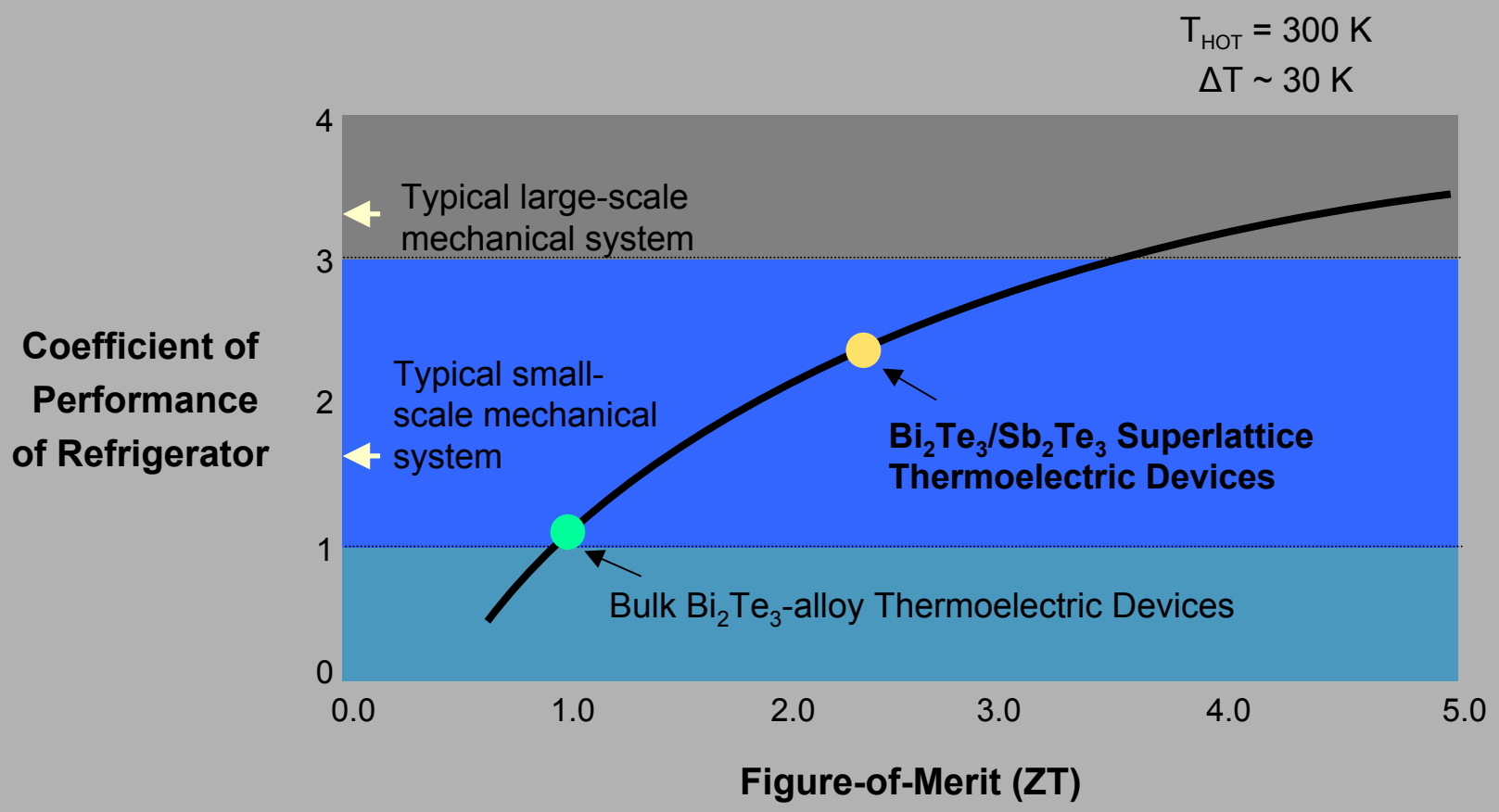
Advanced System-Level Concepts to further leverage nano-materials advancements

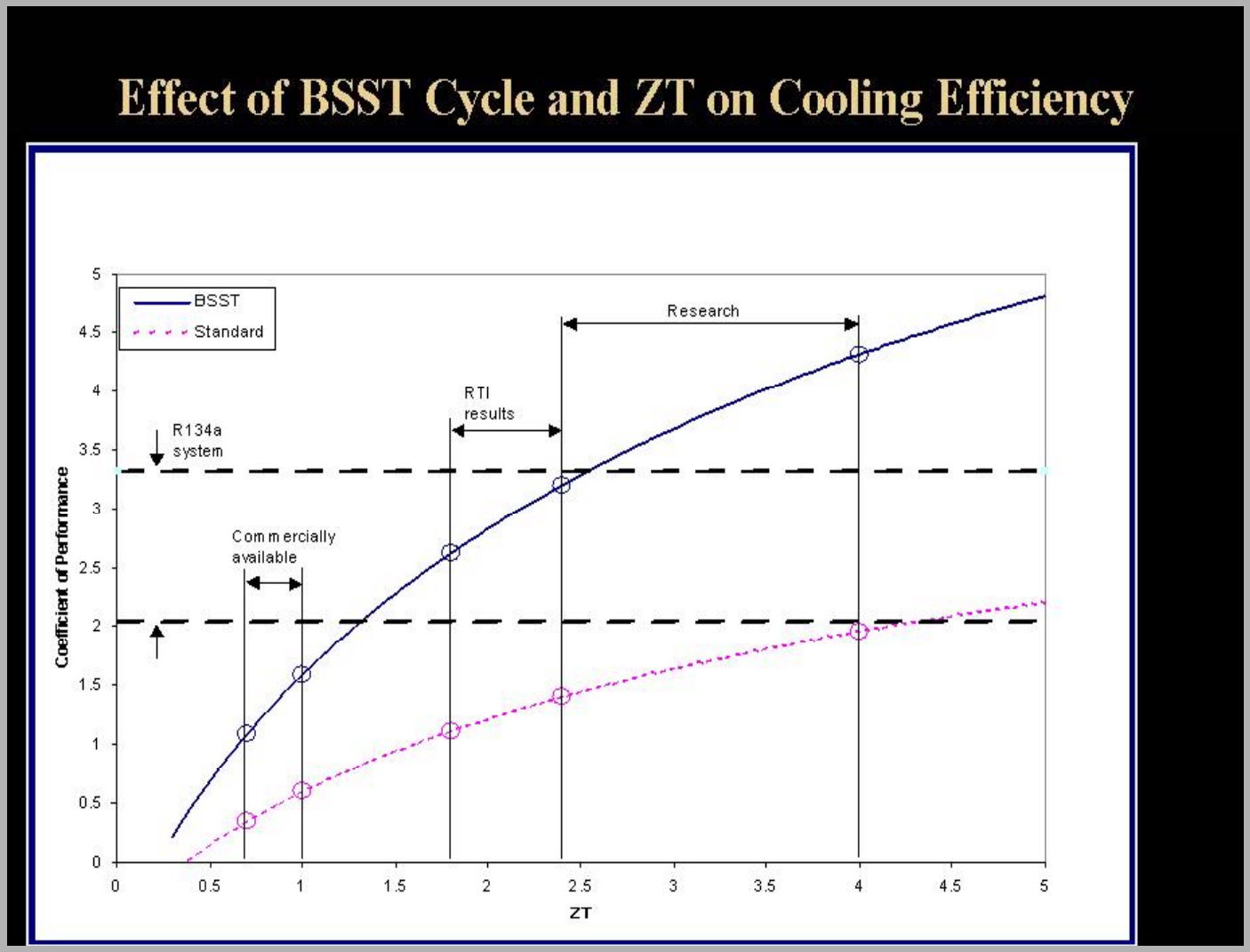
RTI's Superlattice Device on Cooling Efficiency



Nature, 413, 597 (2001)

- **Higher ZT – Incentives for New Approaches to Implement Higher COP Concepts like Novel Thermodynamic Cycles and Novel Heat-Transfer Approaches**

Impact of New Heat Removal Schemes Combined with High ZT



Ref: Lon Bell (BSST, Division of Amerigon Inc.) - Pioneering Car-seat cooling and other auto climate control systems

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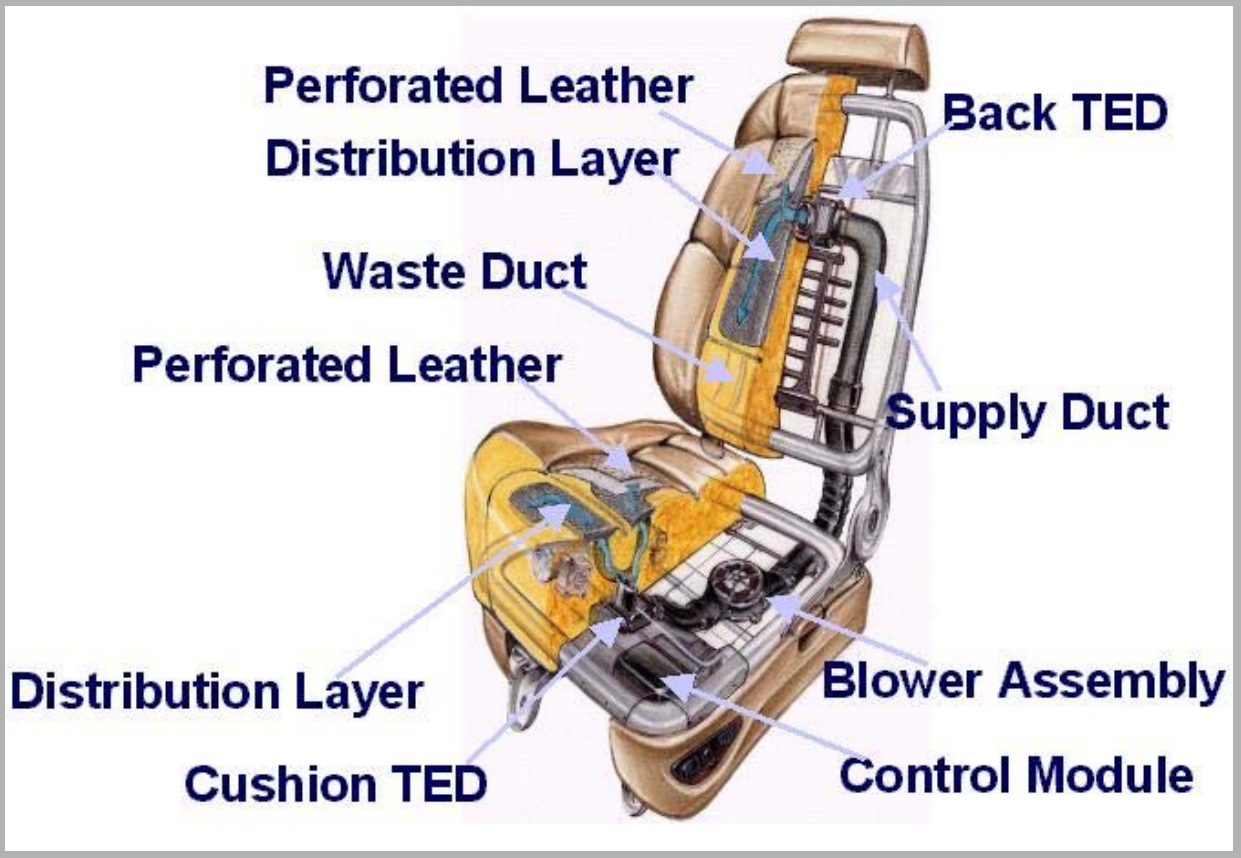
TE Climate Control Technologies Available Today - Automotive Seat to Personal Space



Courtesy of BSST, Division of Amerigon Inc.

- Cool/Heat Where You want - Higher System Efficiencies
  - Major Economic and Environmental Implications
    - Will Benefit from Higher ZT TE Materials

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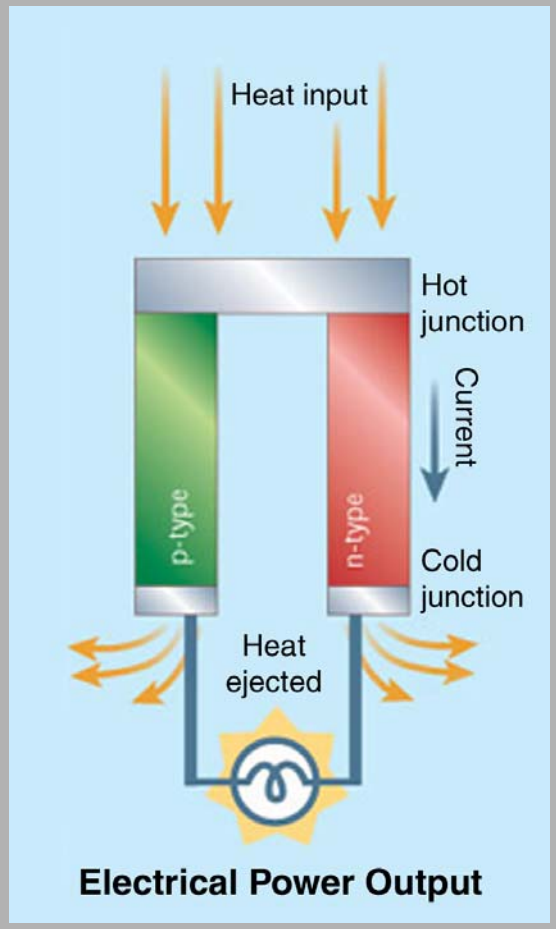
Direct Thermal-to-Electric Energy Conversion

- Compact Power Sources
- High Specific Power (Potentially 500 W/gm)
- High Power Density (Potentially 5 W/cm^2)

Thermoelectric Power Conversion

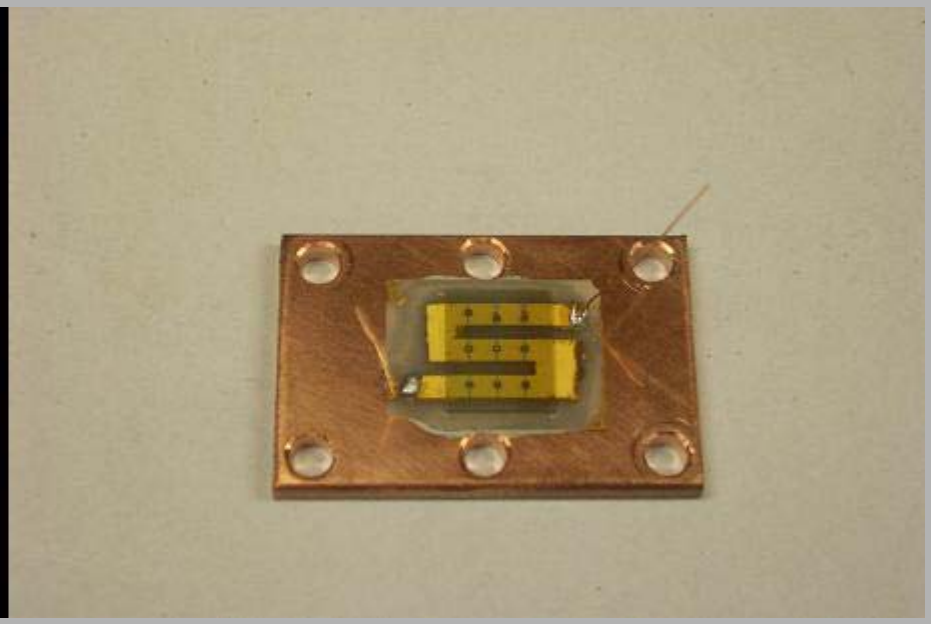


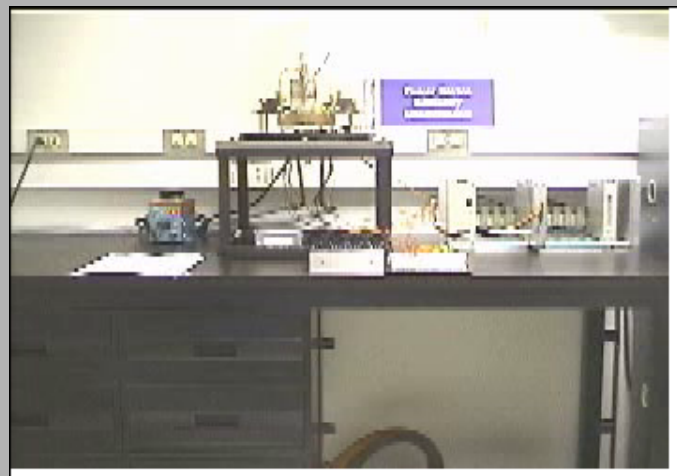
$$\psi = \frac{(T_h - T_c)}{T_h} \frac{\{(1+ZT)^{1/2} - 1\}}{\{(1+ZT)^{1/2} - 1\} + T_c/T_h}$$

- Power Conversion Efficiency critically dependent on the material Figure of Merit (ZT)

- Maximize ΔT
  - Thermal management (getting the heat out from the heat-sink) is important to generating the maximum ΔT

Power Conversion with Modules





PowerMod_fans.mpg

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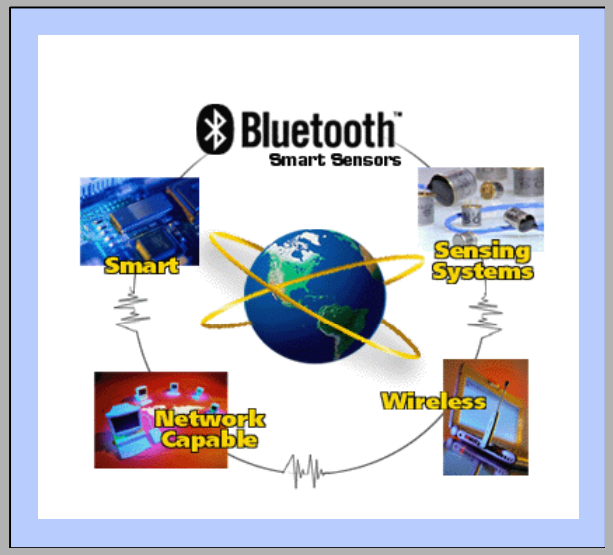
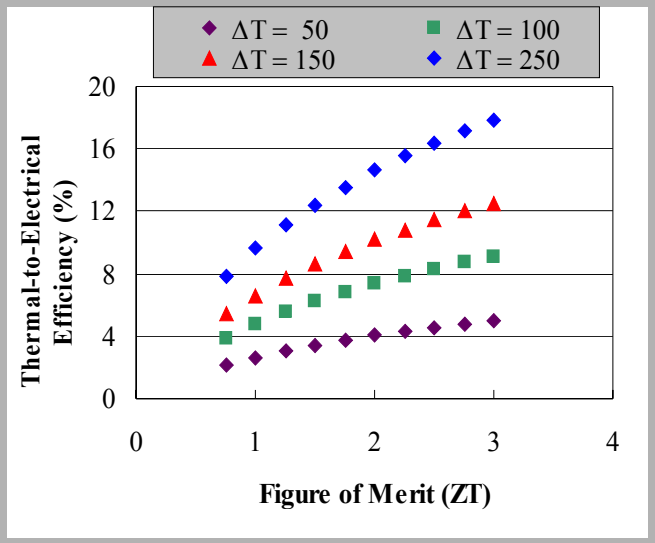
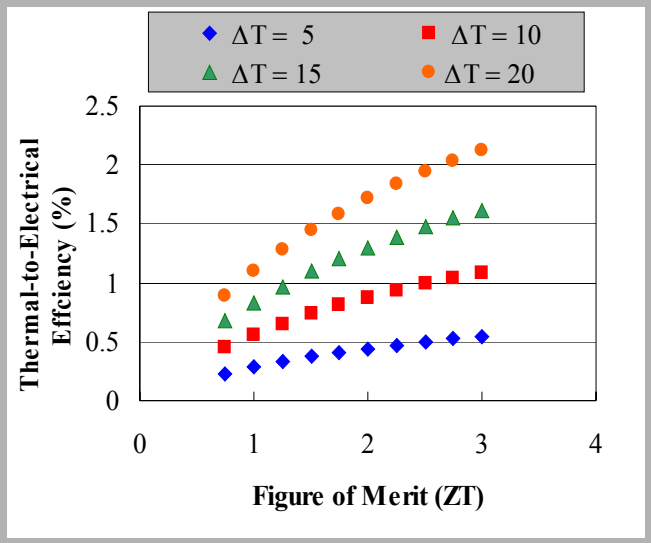
Implications for Power

- Replace Batteries using Chemical-to-Thermal-to-Electrical Conversion
- Power Sensors for Equipment Monitoring Using Naturally-Occurring **Small ΔT**







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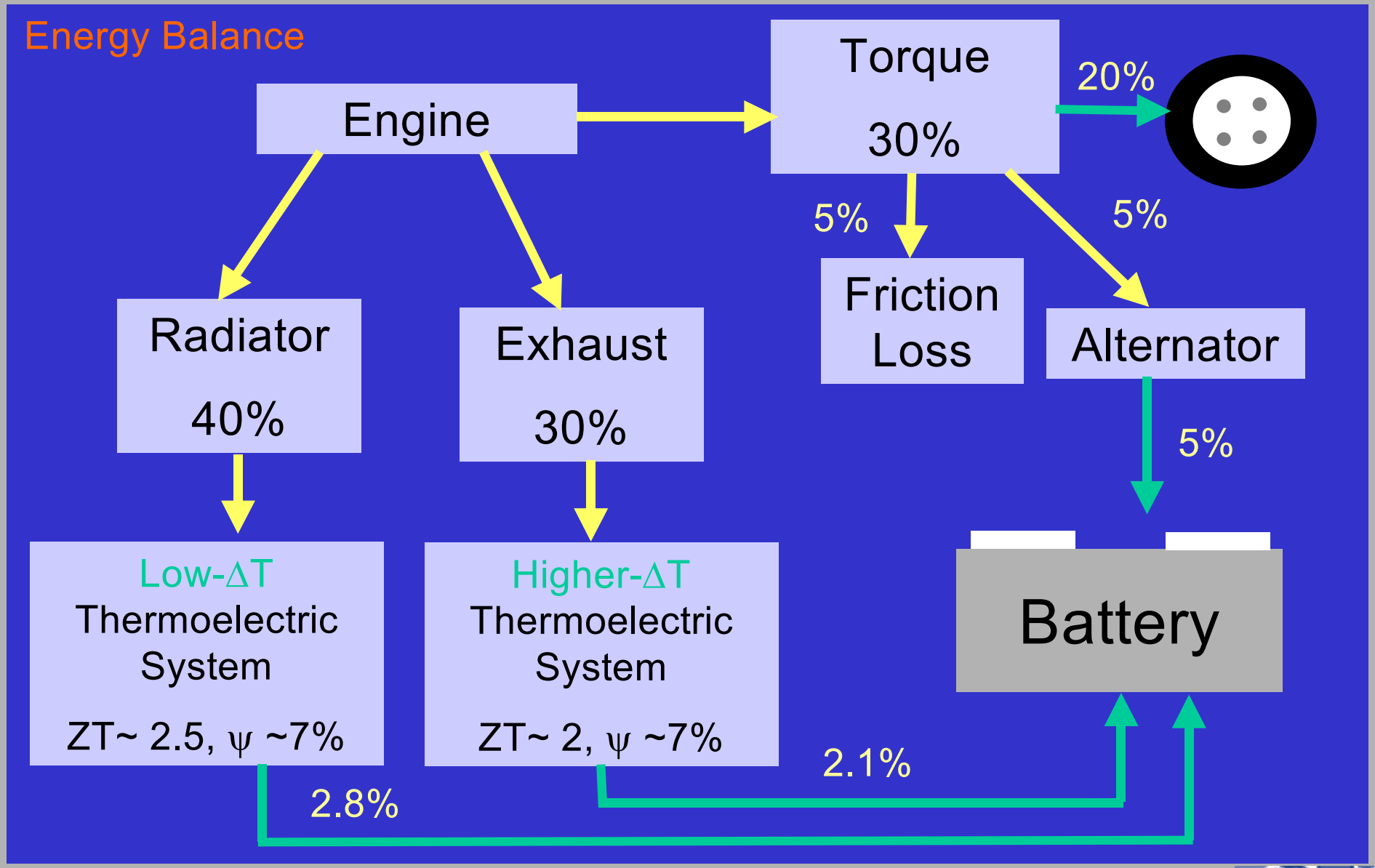
Impact of Light-weight, High-Efficiency Thermoelectric Technology with Waste-Heat Recovery

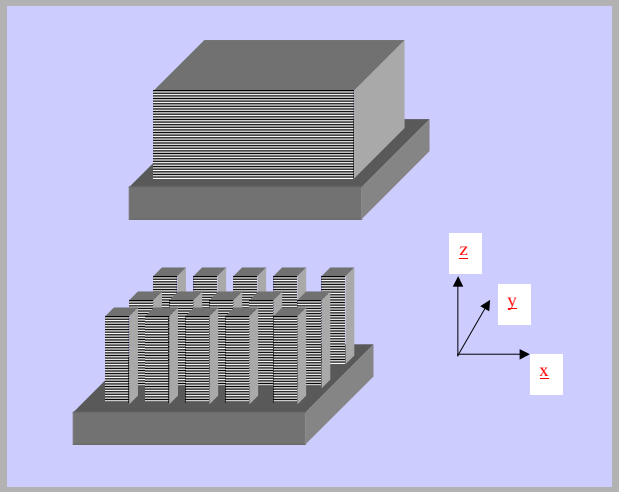


Further Possibilities with Nano-scale Thermoelectrics

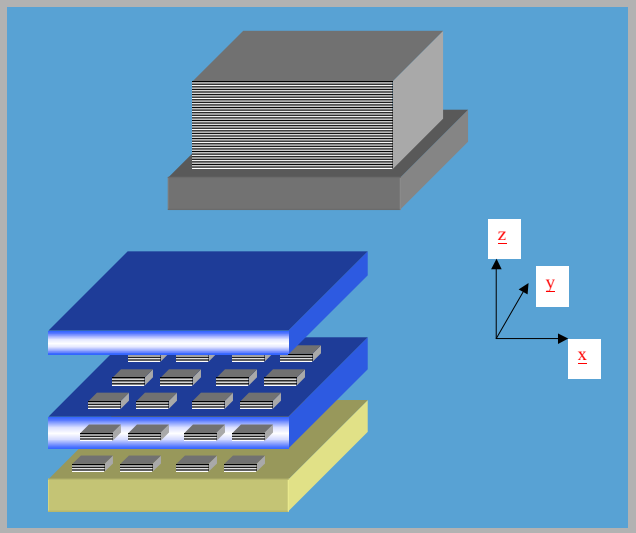
RTI INTERNATIONAL

Transitioning from Two-dimensional Superlattices to One-dimensional wires and Quantum-Boxes for Nano-scale Thermoelectrics

- Combine Phonon-Blocking, Electron-Transmitting Structures Along Heat Flow with Orthogonal Quantum-Confinement for ZT in the range of 4 to 5?



Layered SL Patterned to form 1-di Quantum-Wires – **Orthogonal Quantum Confinement**



Layered SL Patterned to form Quantum-Boxes – **Orthogonal Quantum Confinement**

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