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

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Applications and Implications
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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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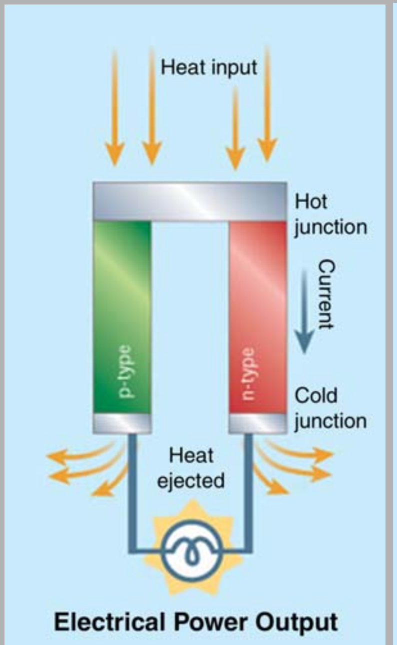
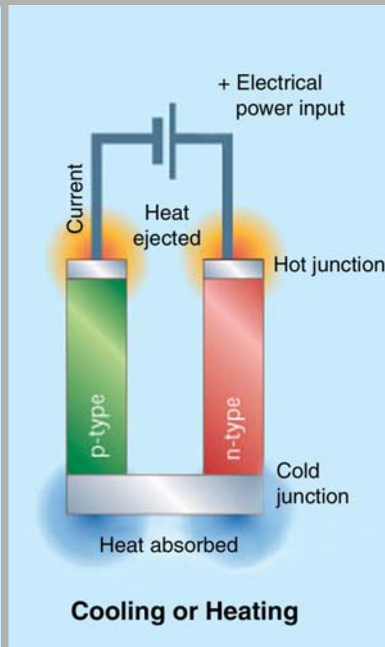
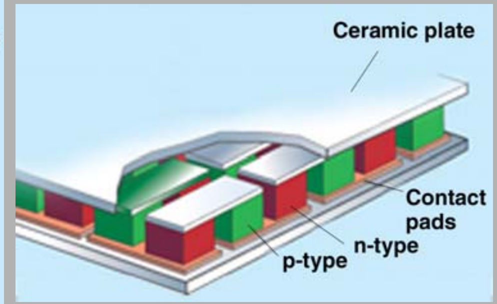
Thermoelectrics





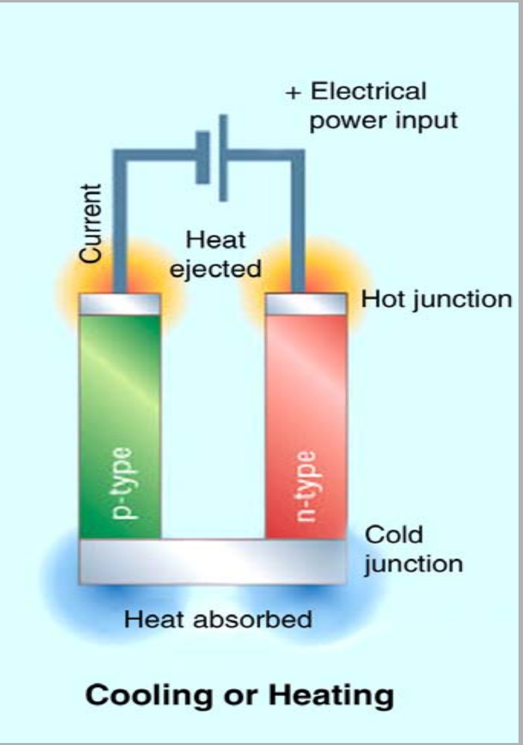


- Solid-State Technology
  - Solid-state Reliability
  - No Moving Parts
  - Vibration/Noise free
  - CFC-free
- Heat or Cool
  - Thermal Management
- Power Generation
- Thermal control functions
  - Chemistry, Biology, Physics

- **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?**

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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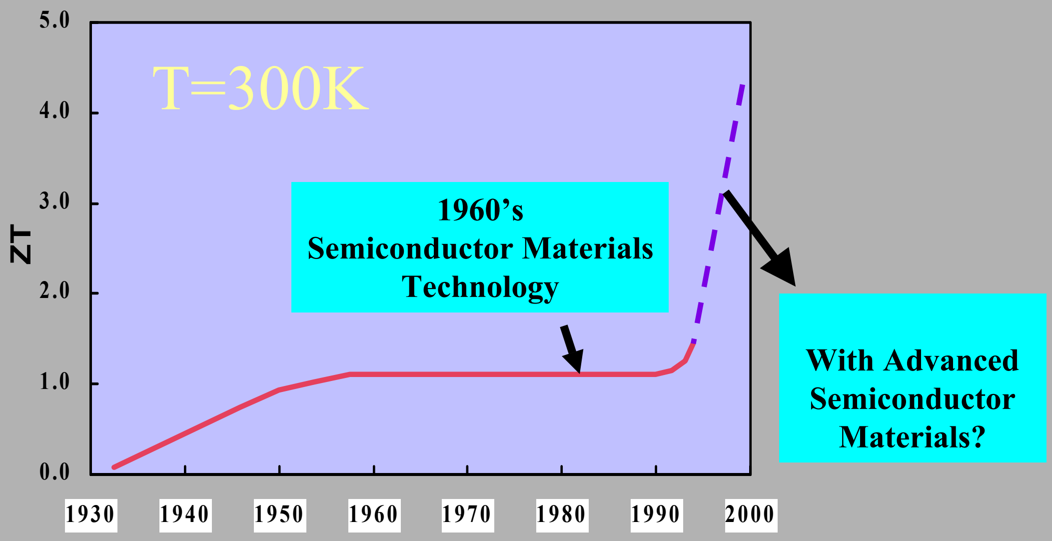
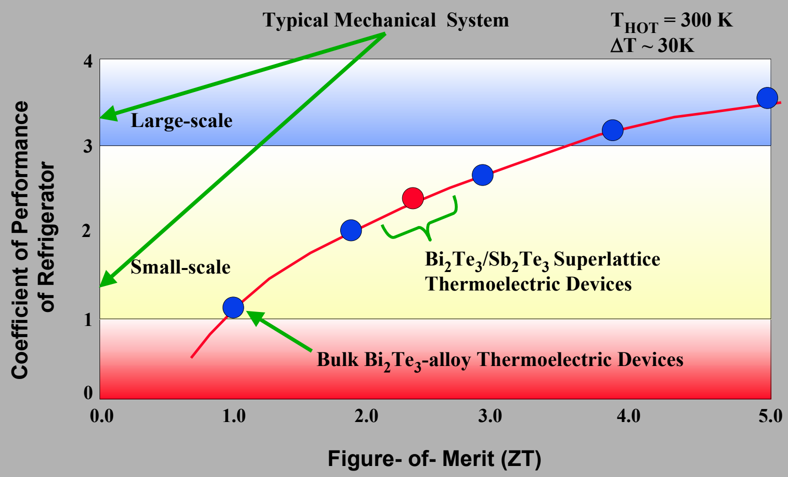
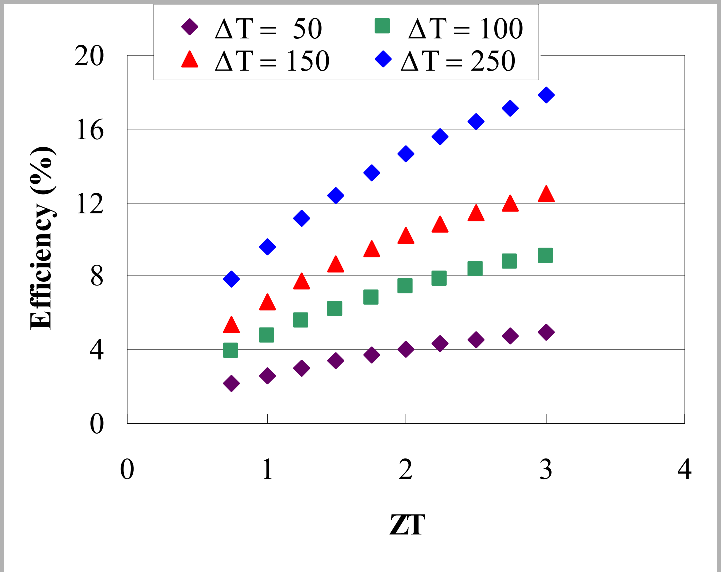
The Big Challenge





- 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



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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

Some Bulk Material and Nano-Material Progress

- Cs Bi_4Te_6 (Michigan State University)

  - Bulk Materials with a <u>ZT~ 0.8 at 225K but less than 0.8 at 300K</u> (*Science* **287**, 1024-1027, 2000)

- Filled Skuterrudites (JPL)

  - Bulk materials with a <u>ZT ~1.35 at 900K</u> (Proc. Of 15th International Conf. On Thermoelectrics, 1996)

- PbTe/PbTeSe Quantum-dots (Harman, MIT Lincoln Labs.)

  - <u>ZT~ 1.6 at 300K</u> based on cooling data (*Science* 297, Sep. 2002)

- Bi_2Te_3/Sb_2Te_3 Superlattices (RTI)

  - <u>ZT~2.4 at 300K</u> 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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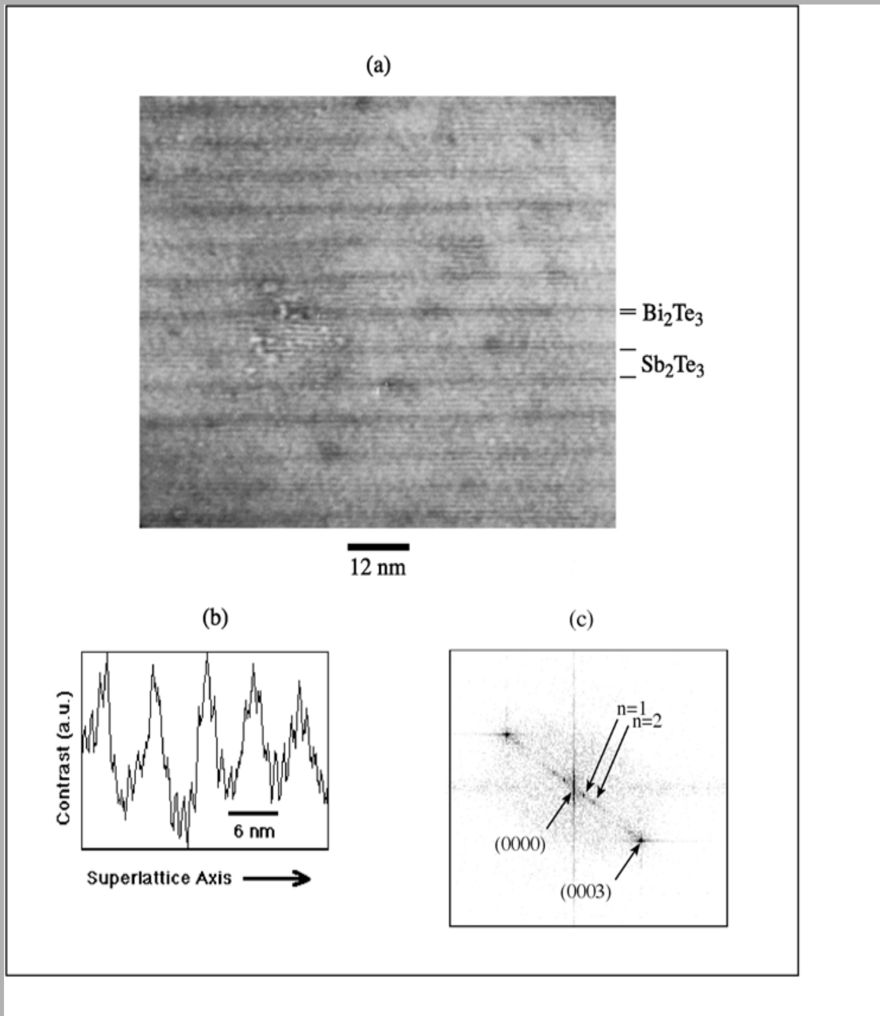
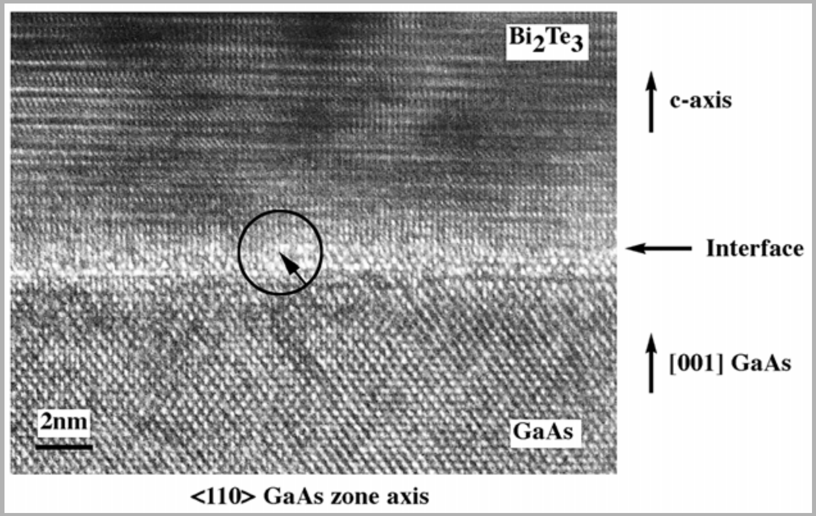
Nano-structured Superlattice Material



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



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- 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

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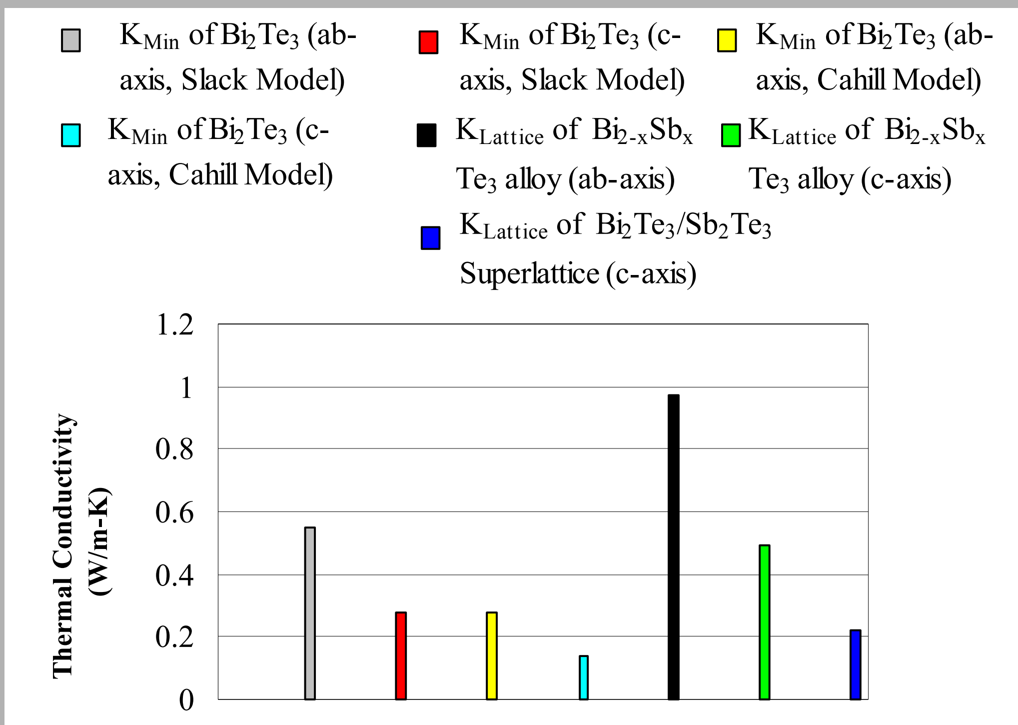
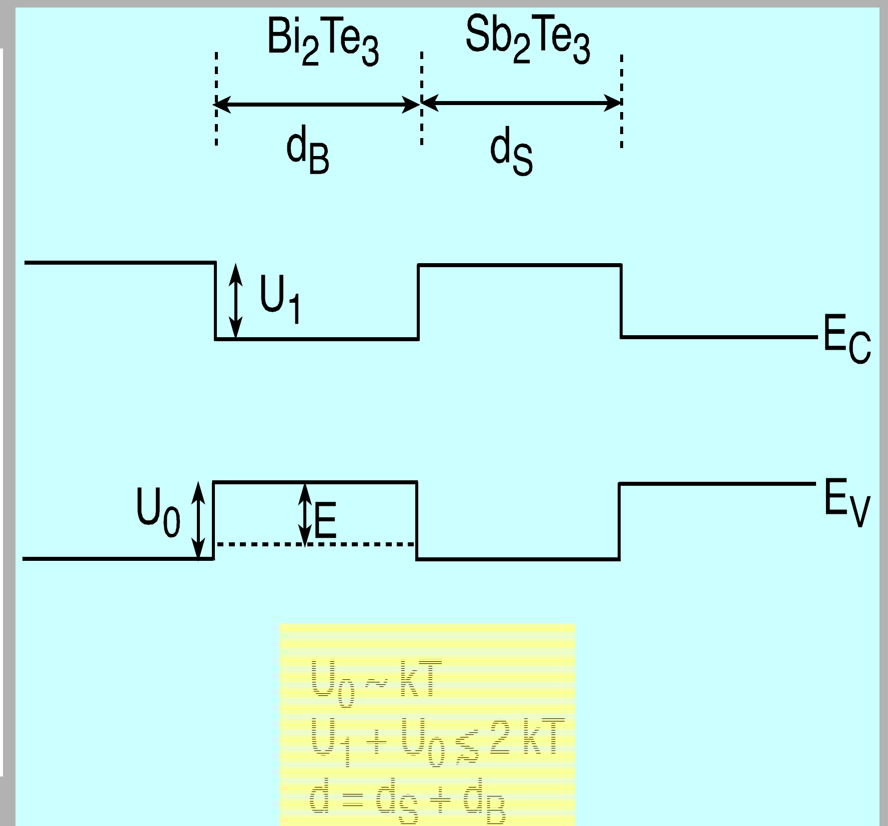
Physics Behind ZT Enhancement

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

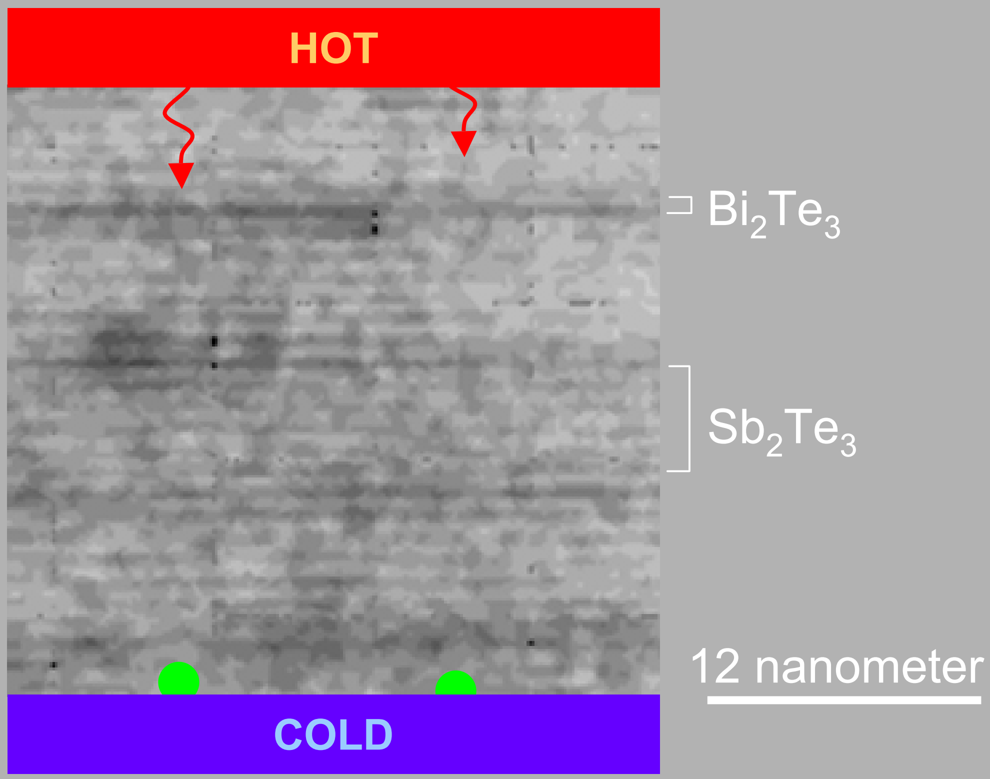


Efficient Cross-Plane Hole Mini-band Transport in Bi_2Te_3/Sb_2Te_3 Superlattices



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

RTI's Superlattice Material



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

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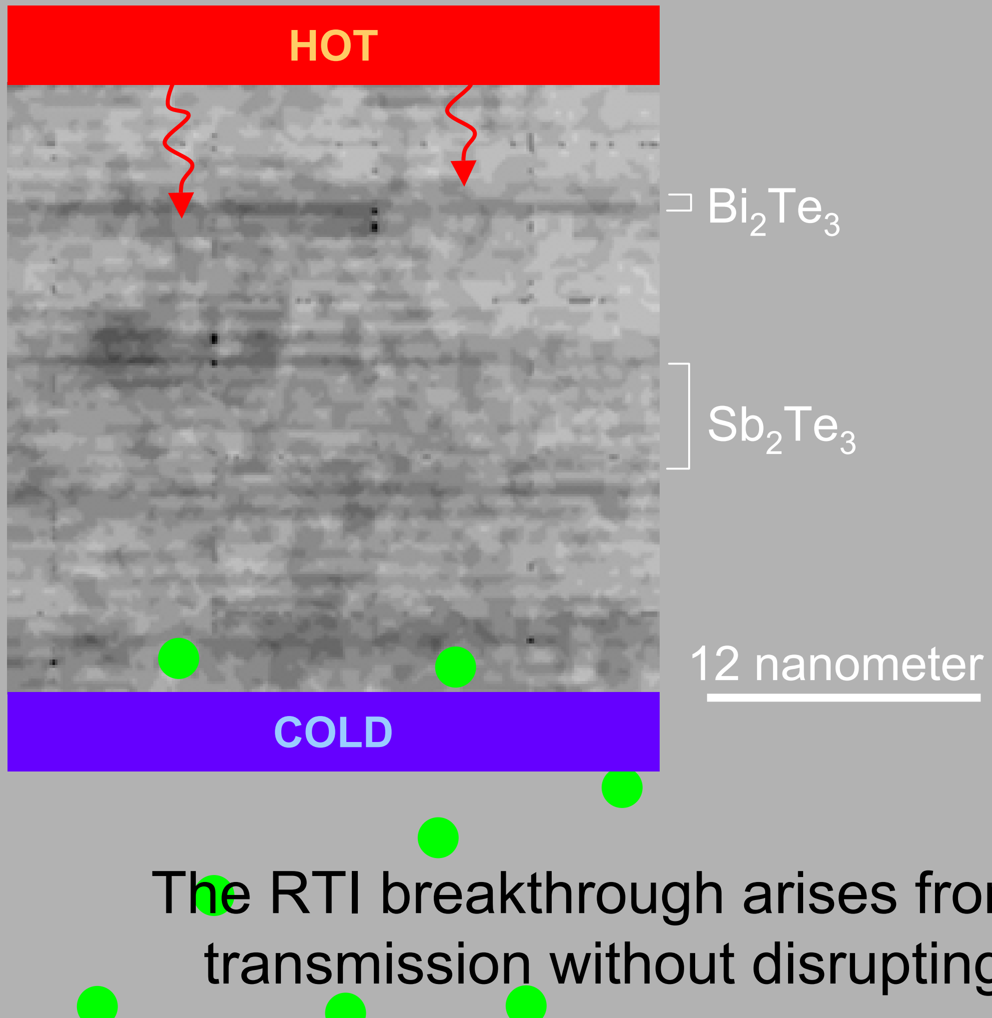

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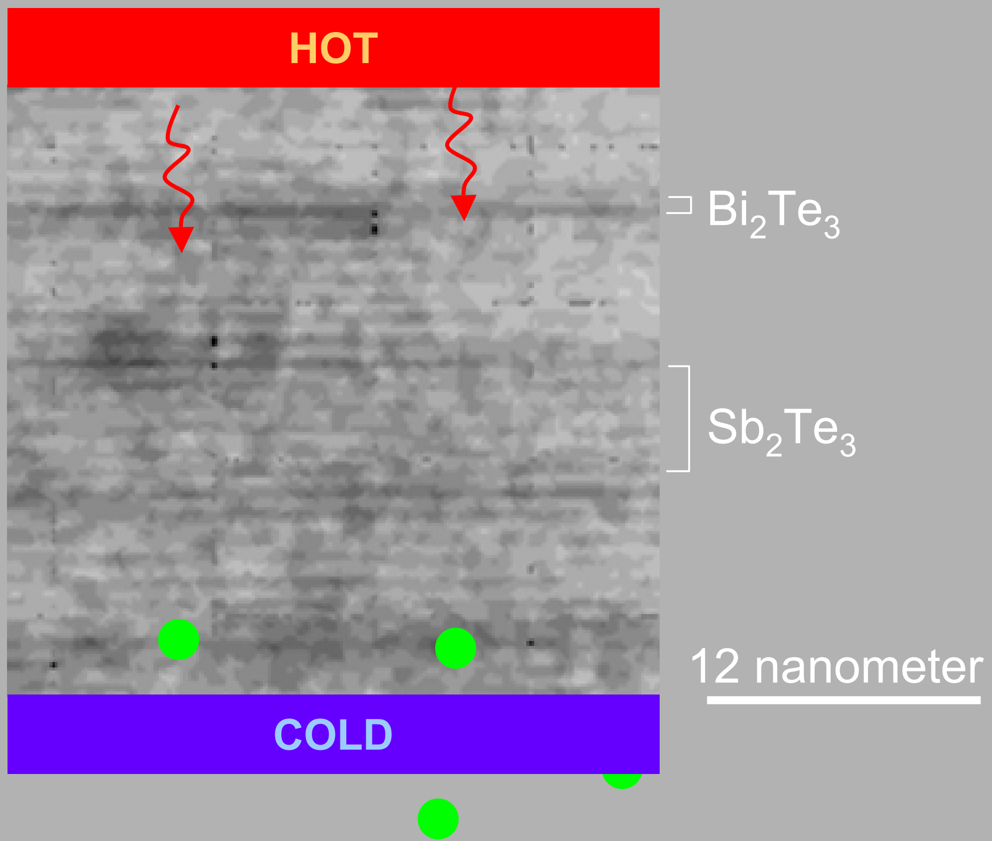

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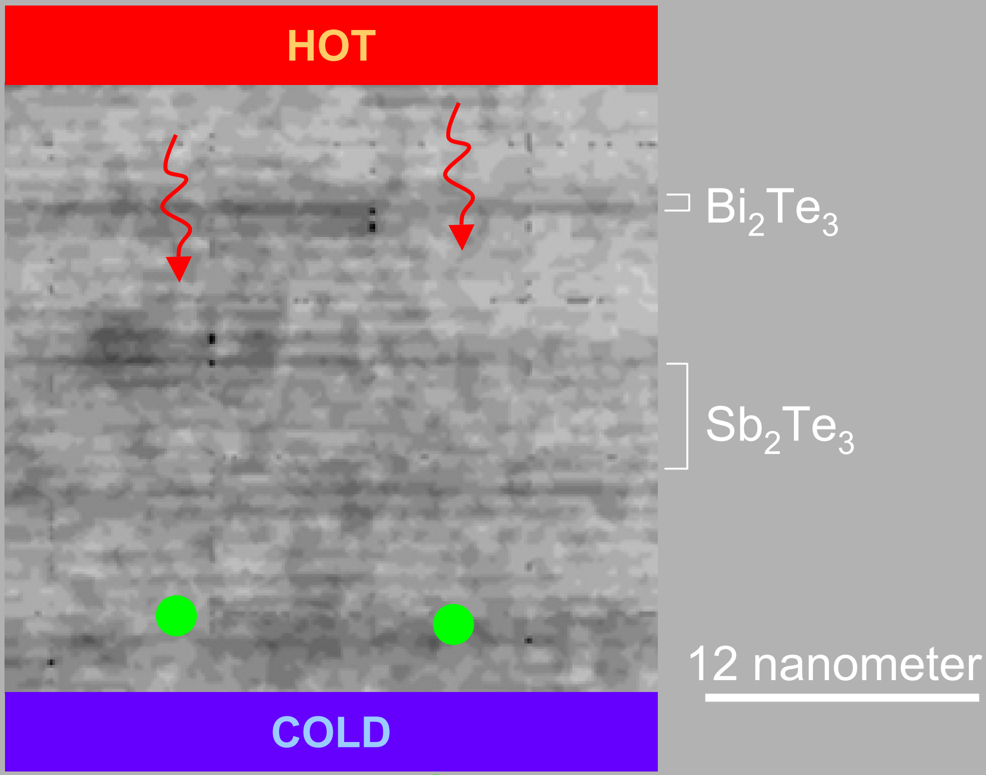

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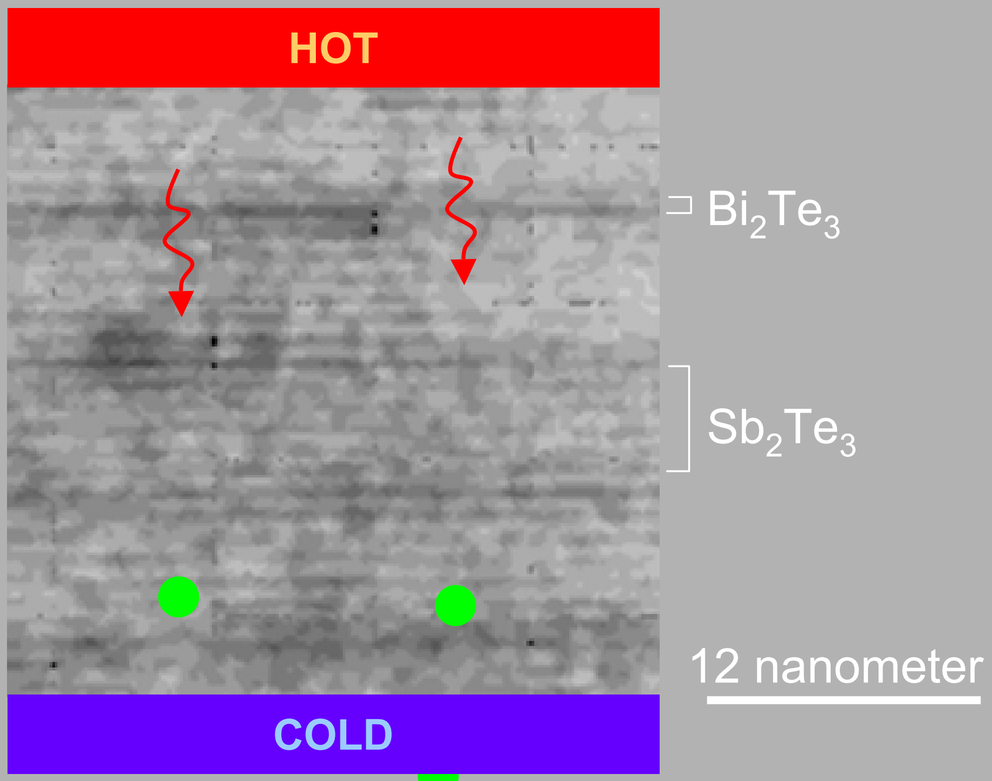

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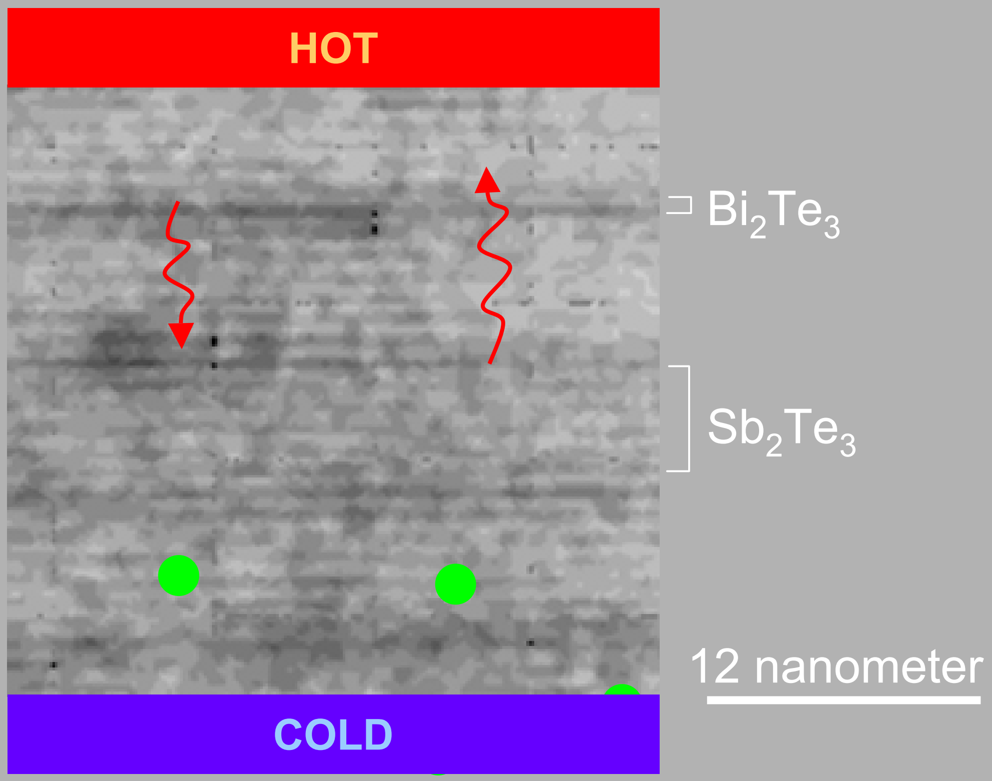

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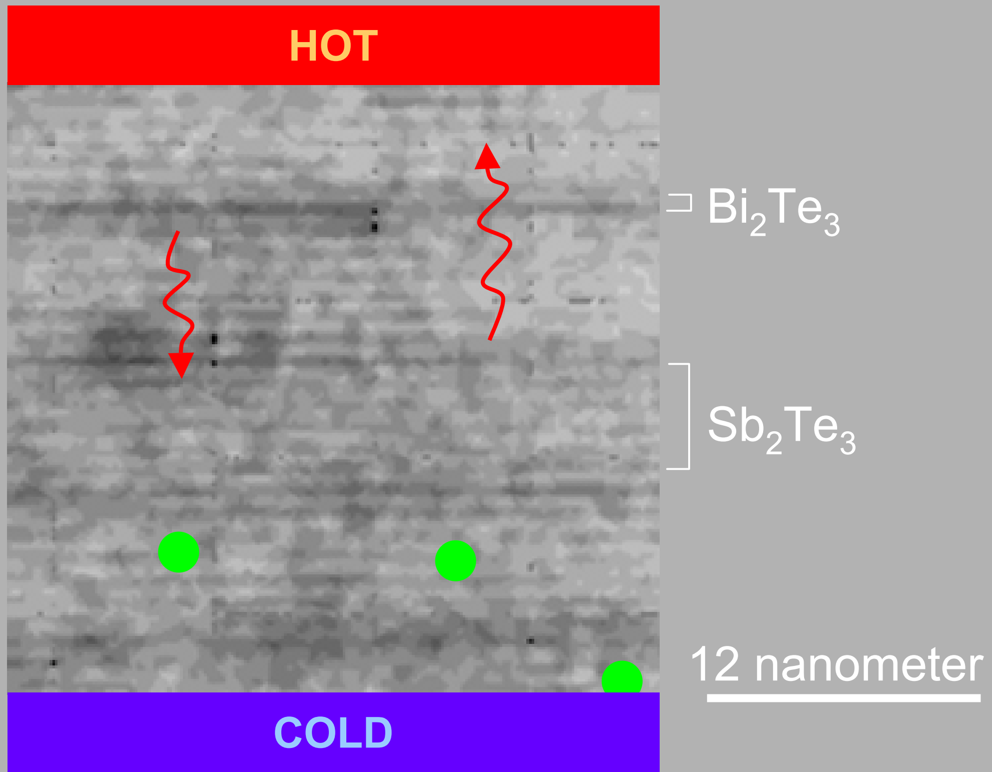

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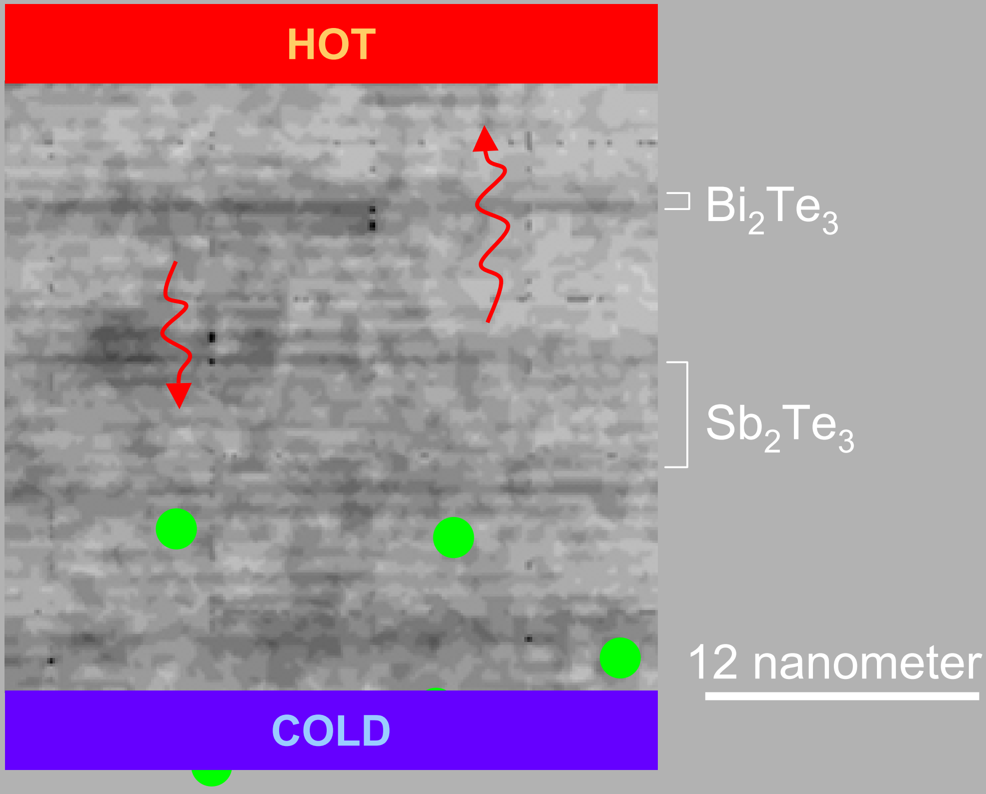

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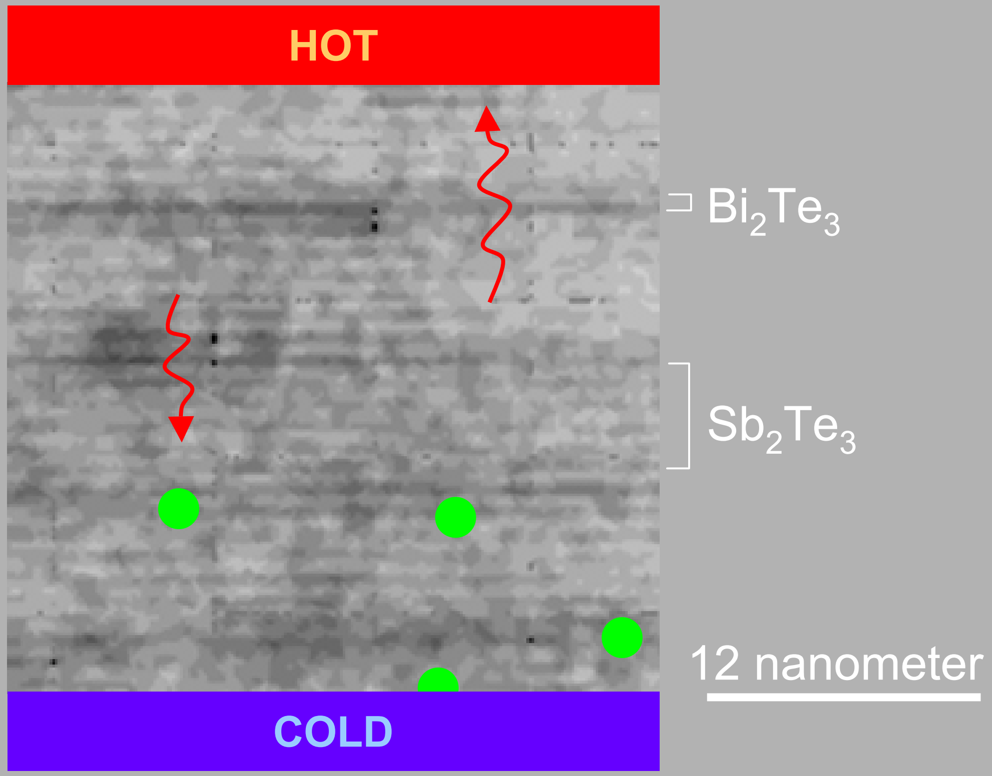

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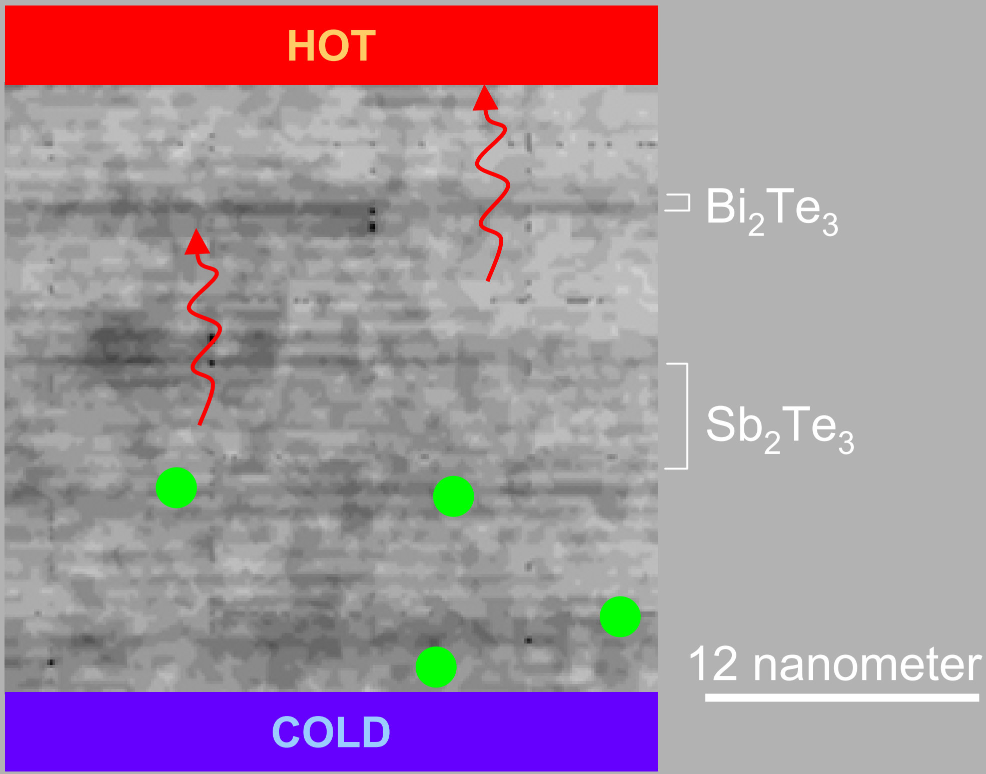

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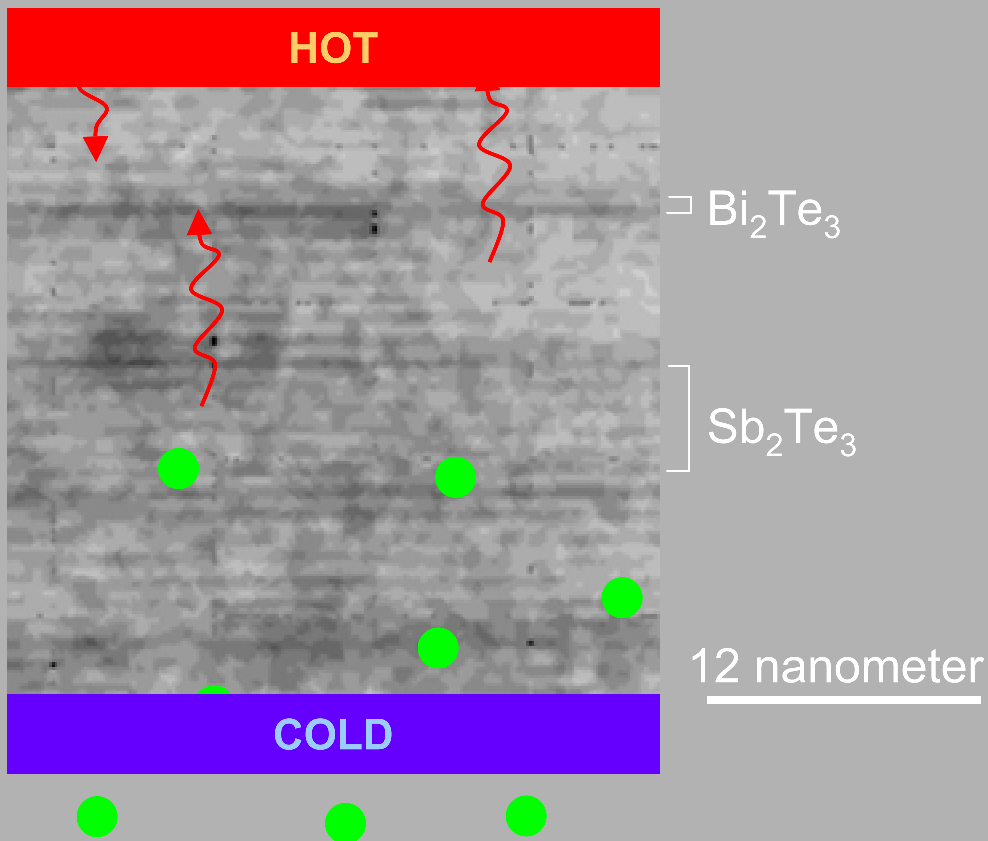

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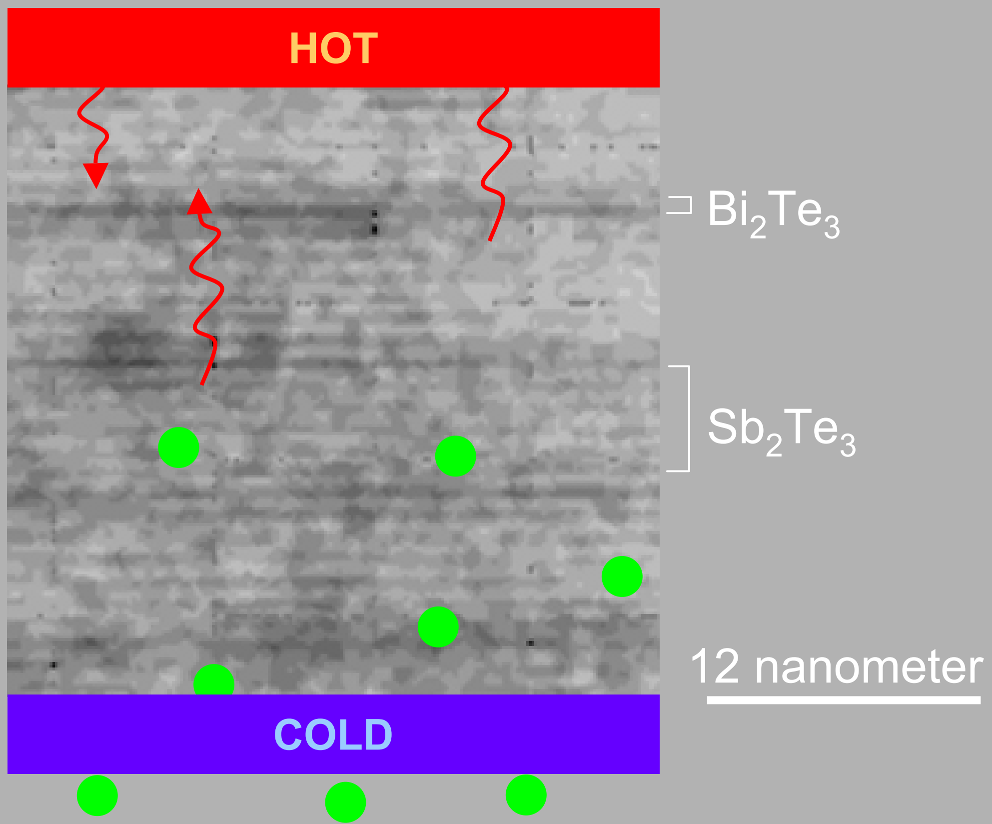

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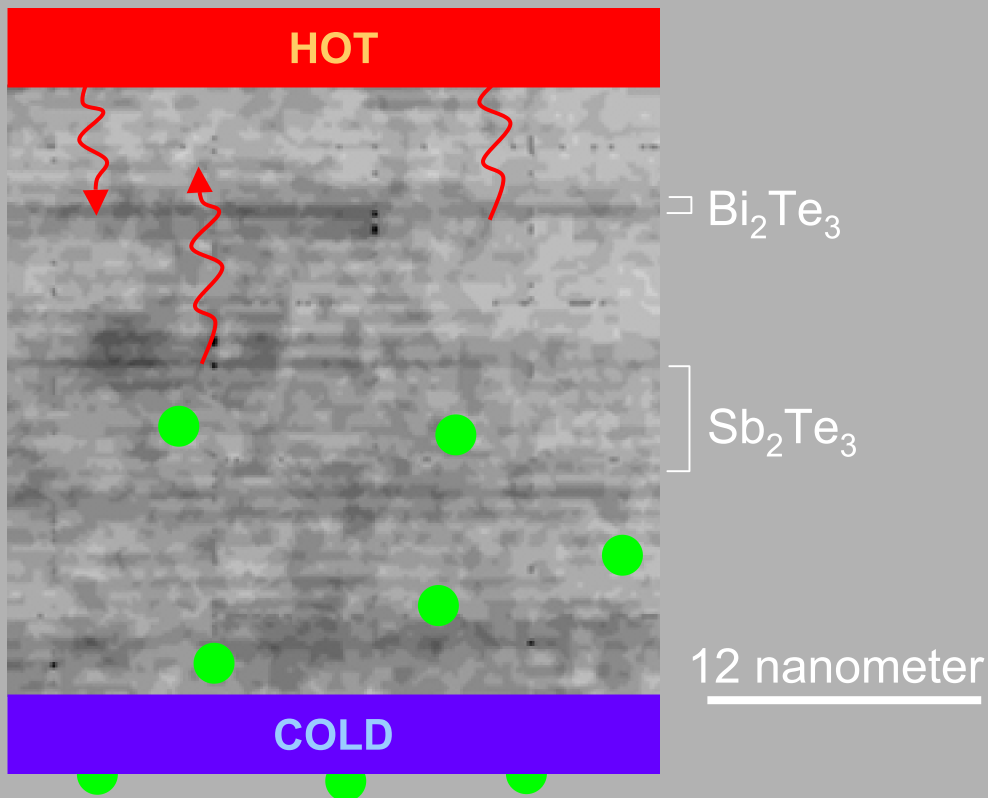

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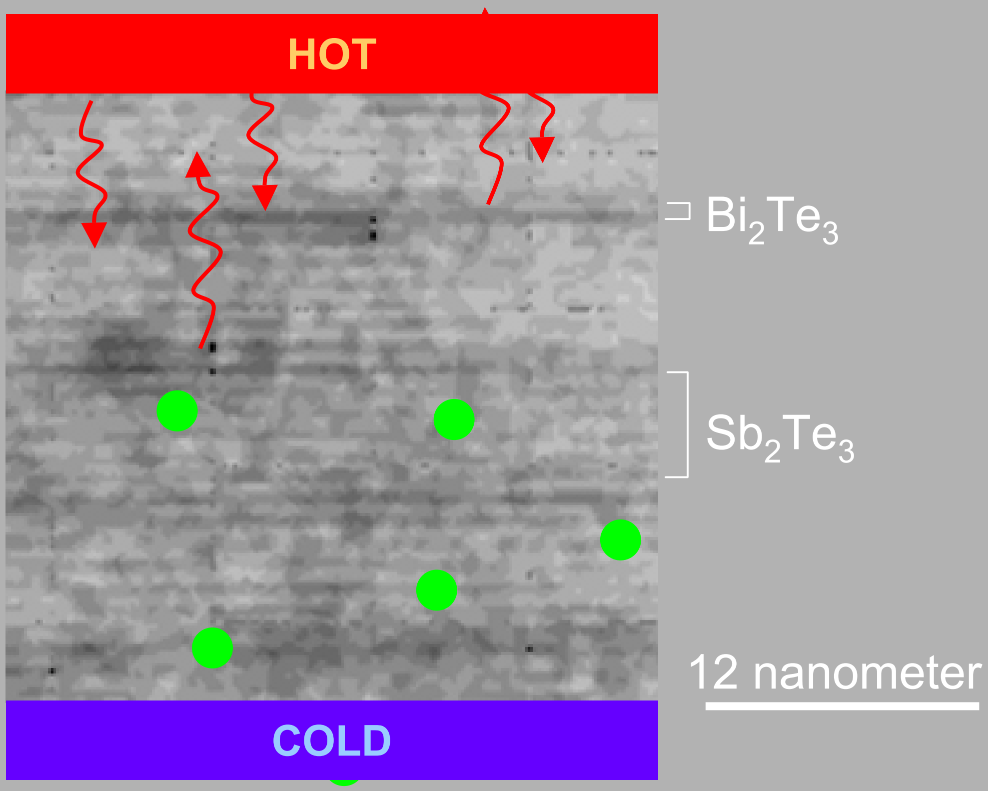

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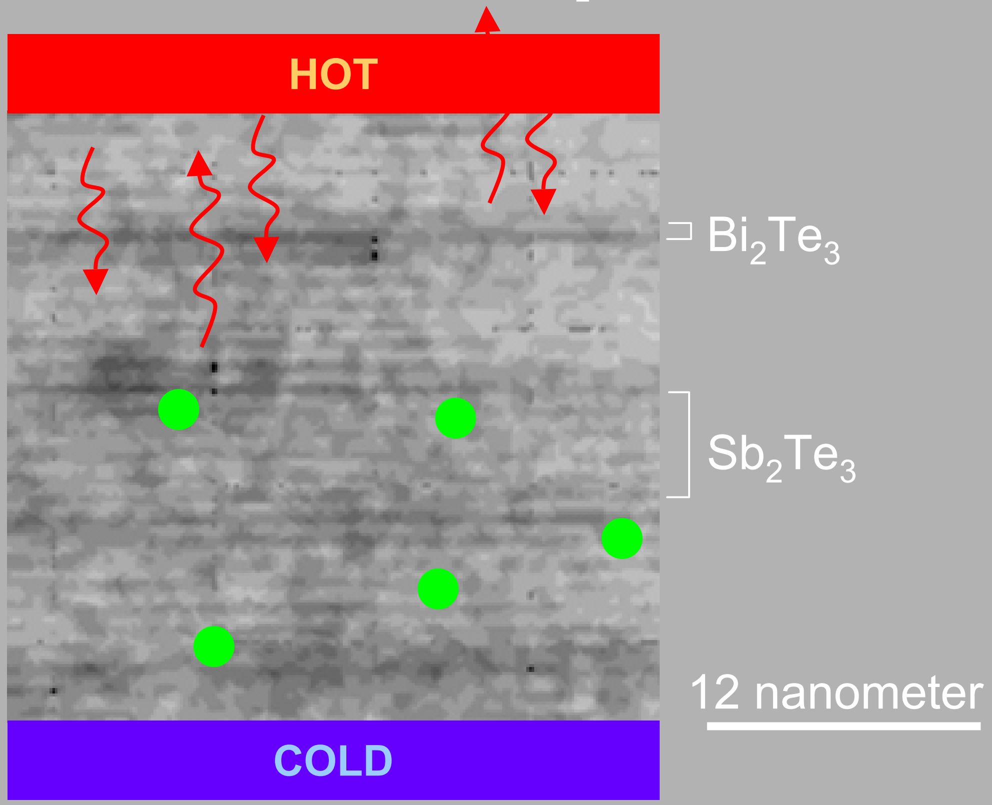

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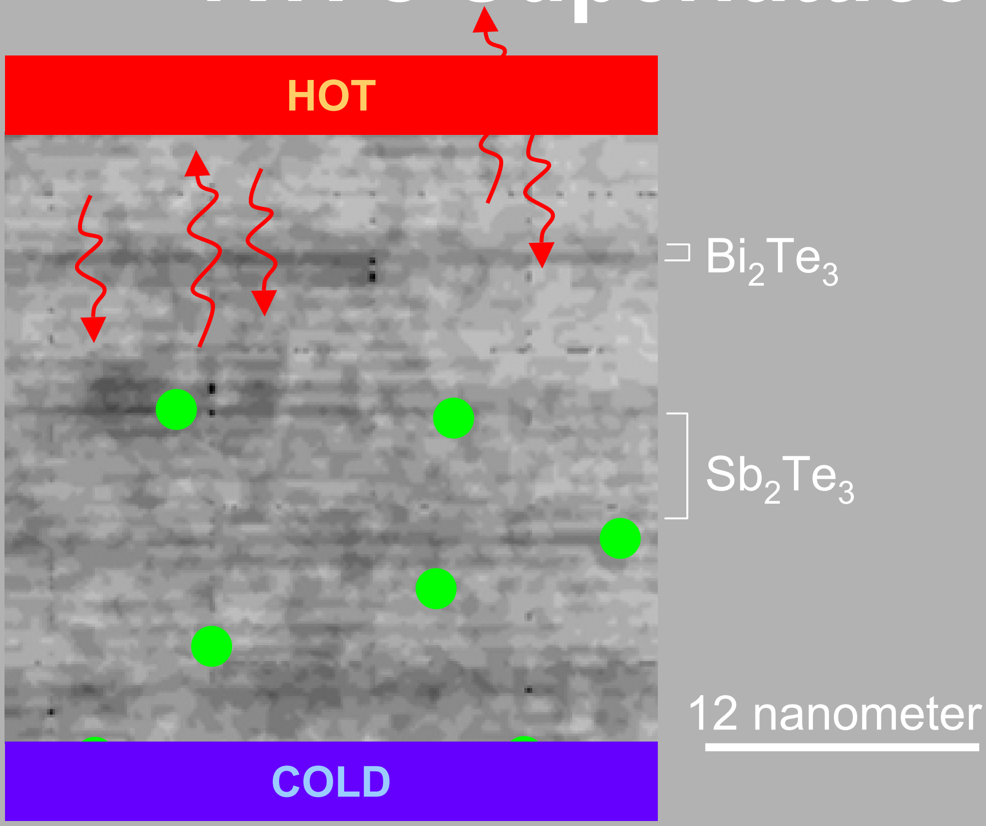

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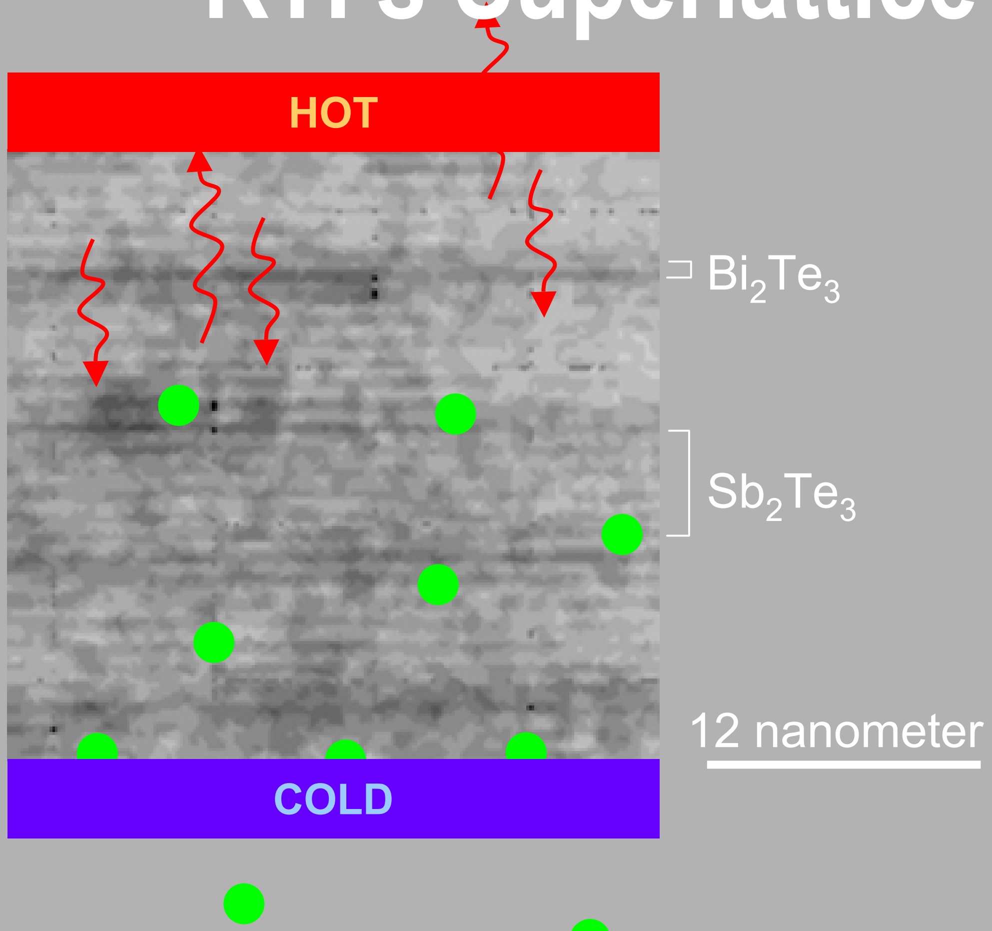

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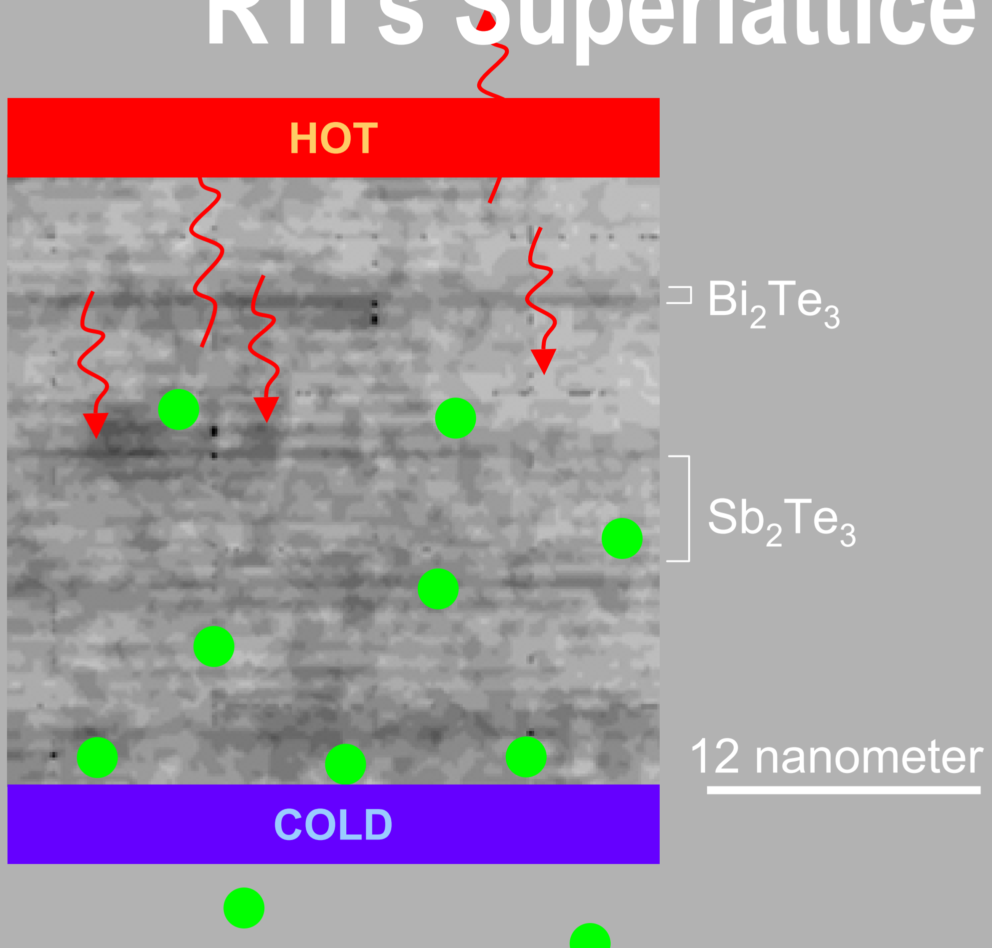

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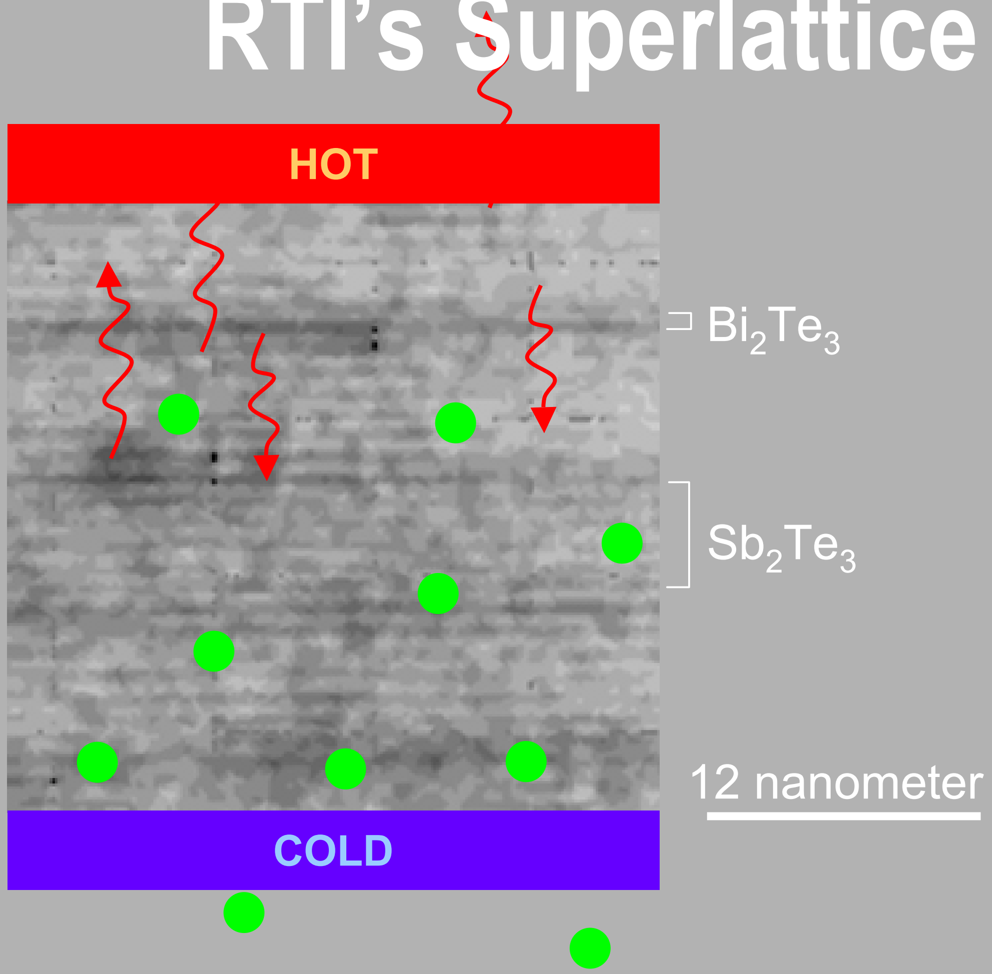

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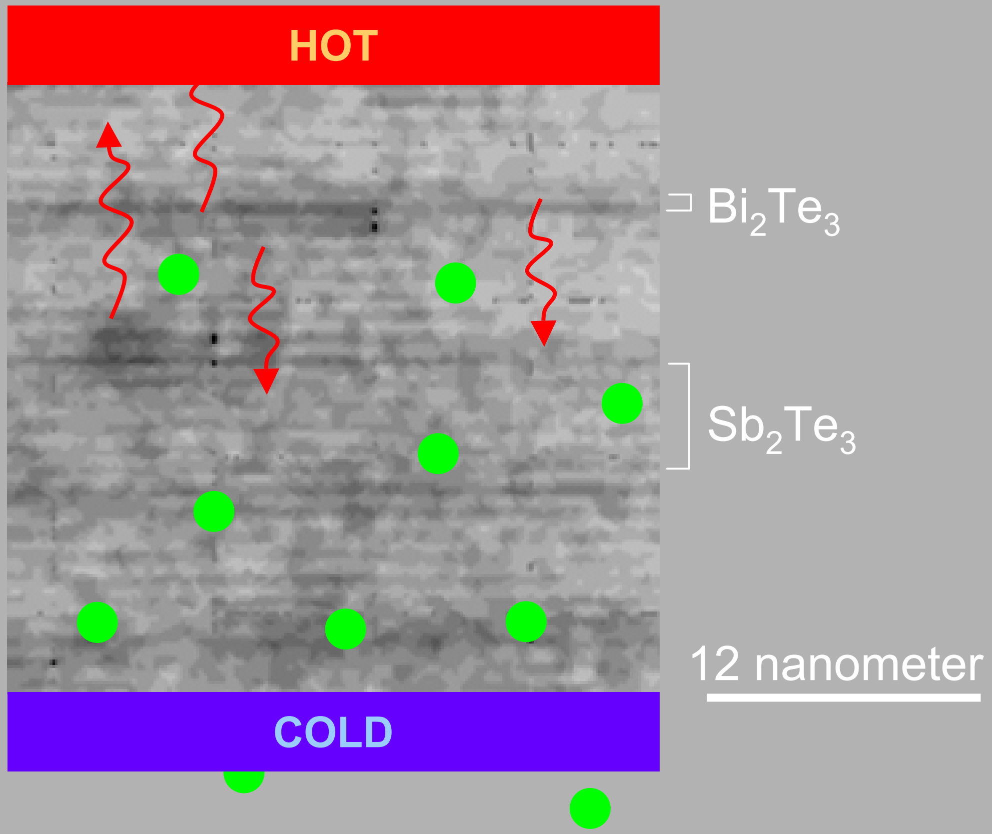

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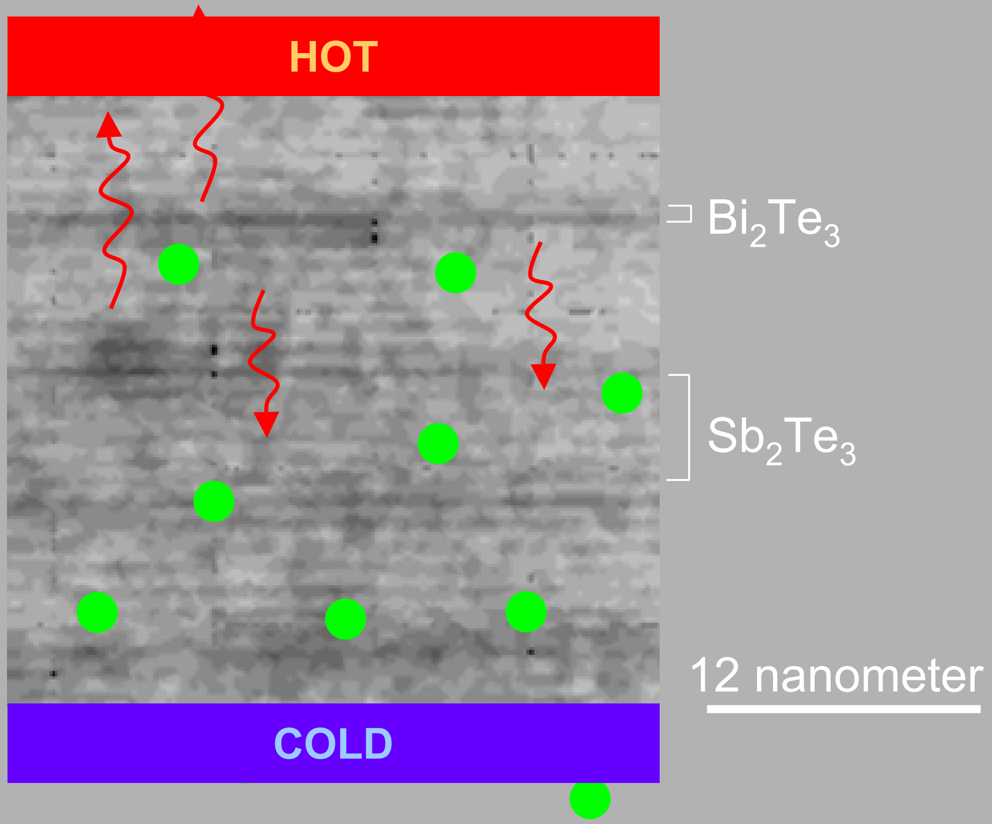

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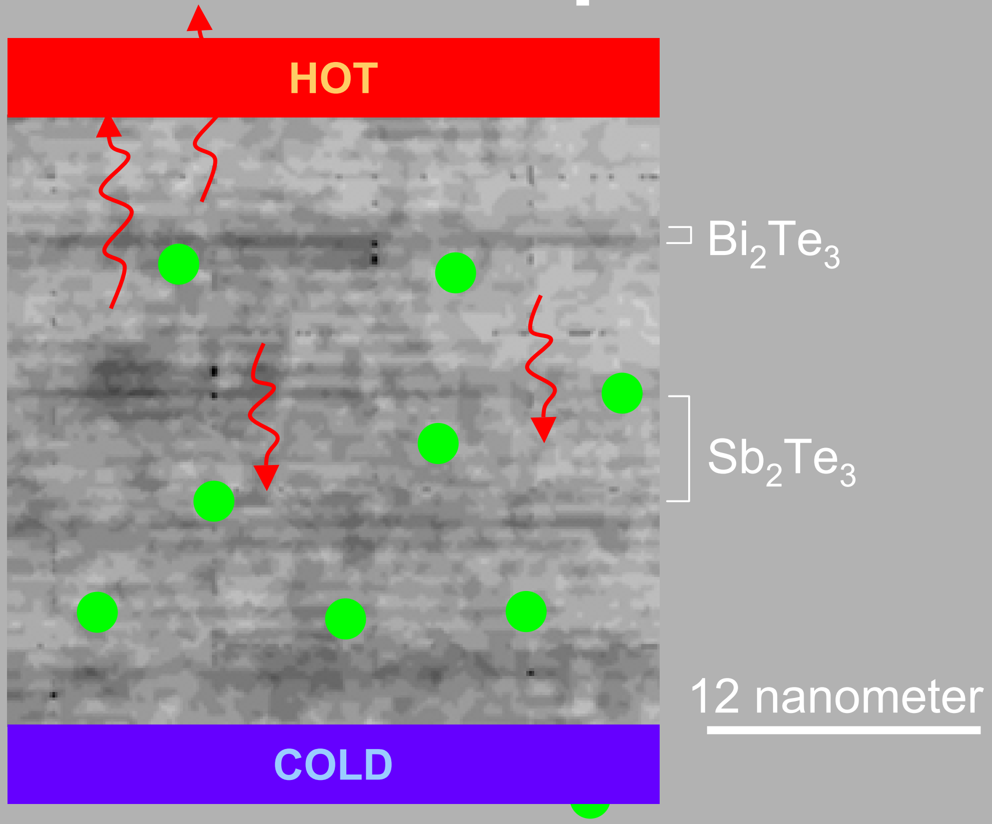

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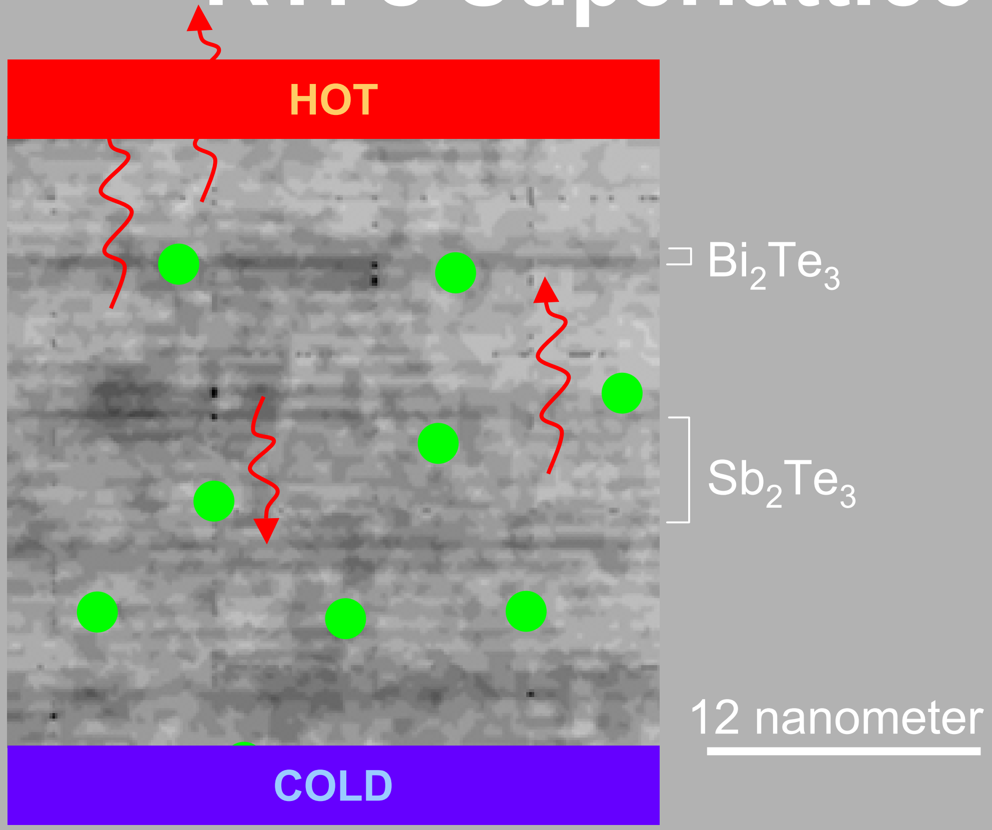

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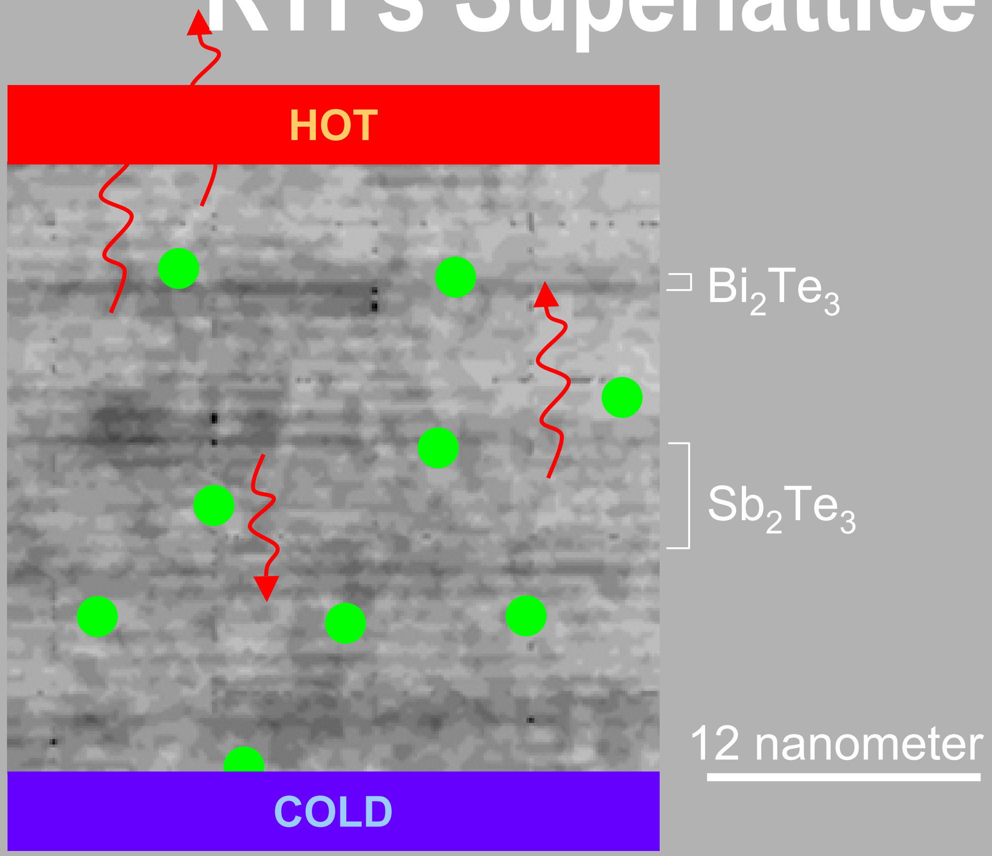

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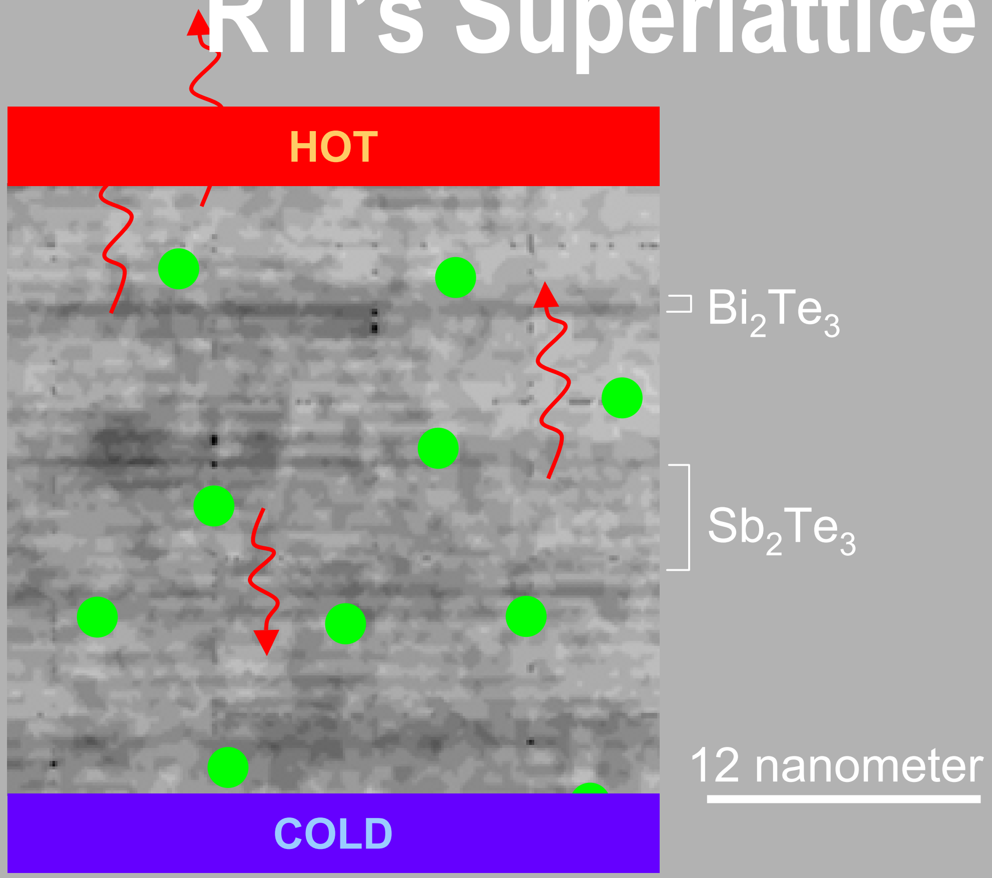

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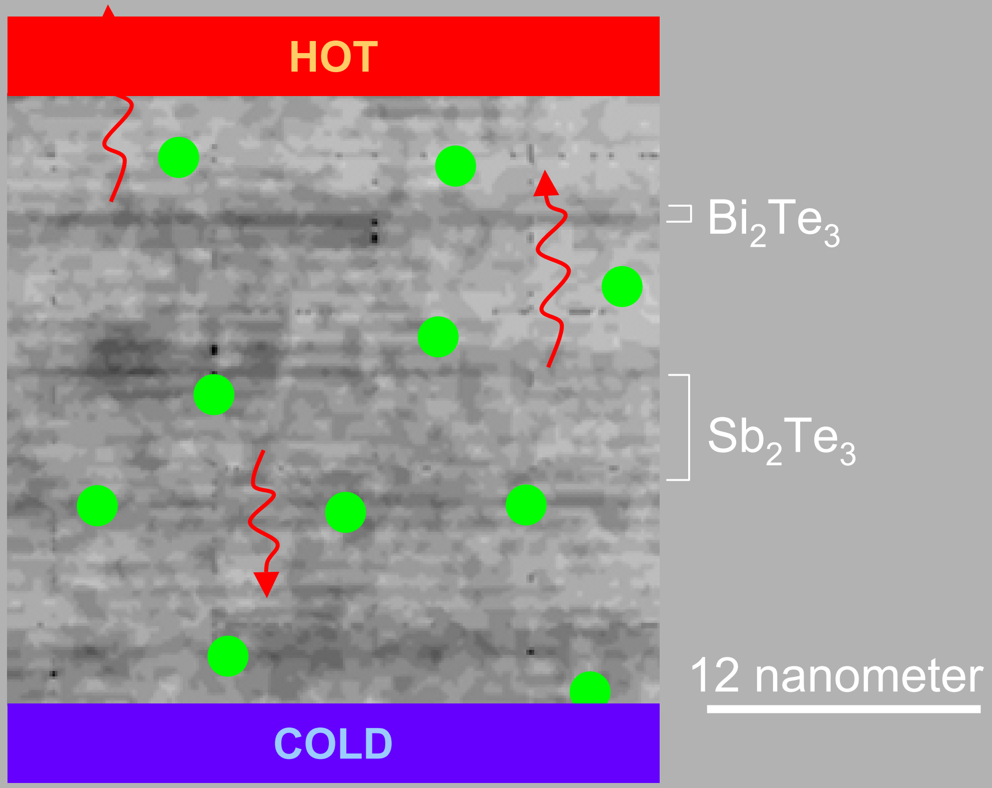

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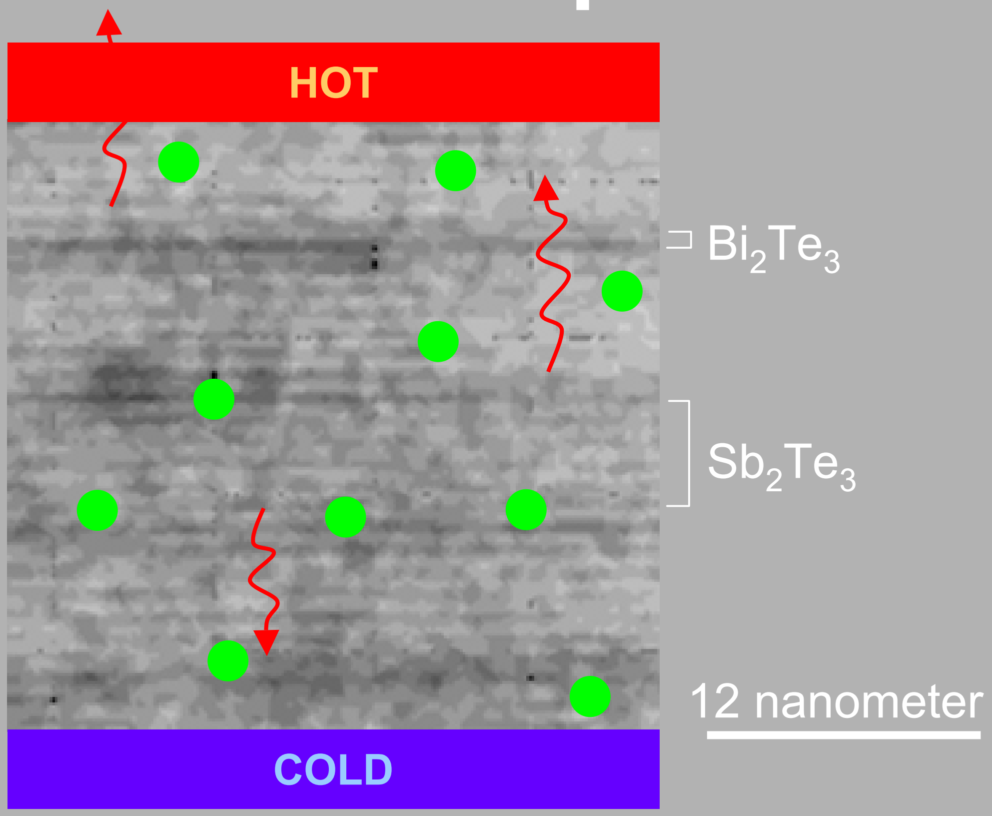

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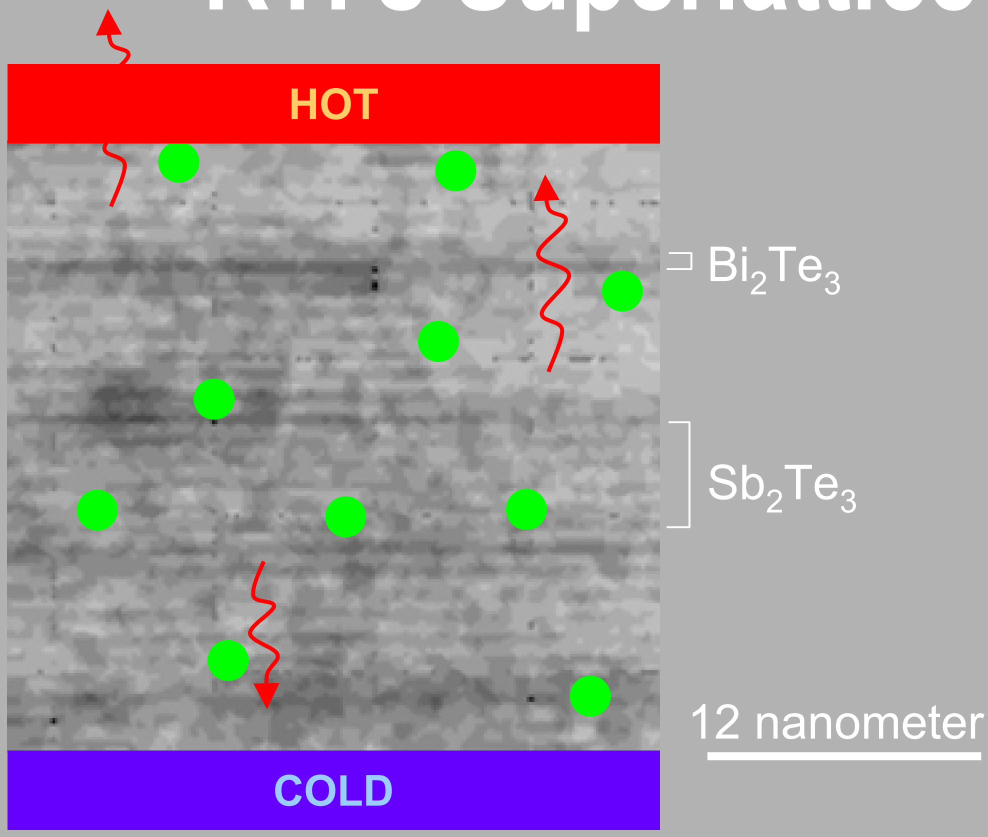

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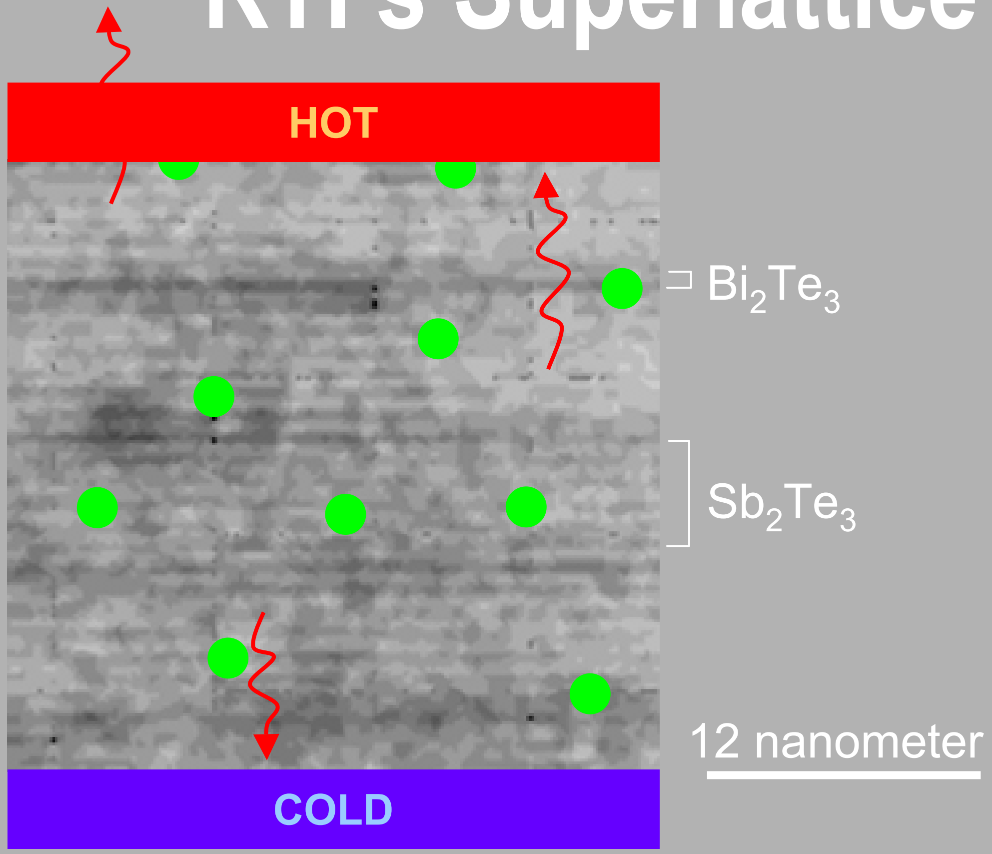

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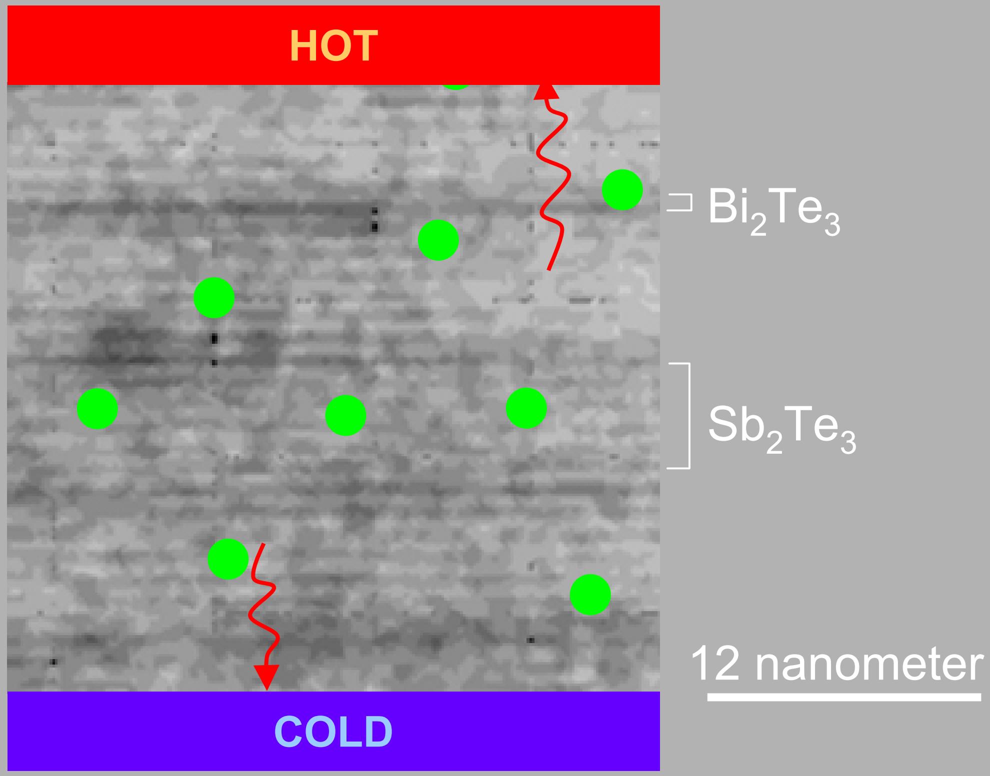

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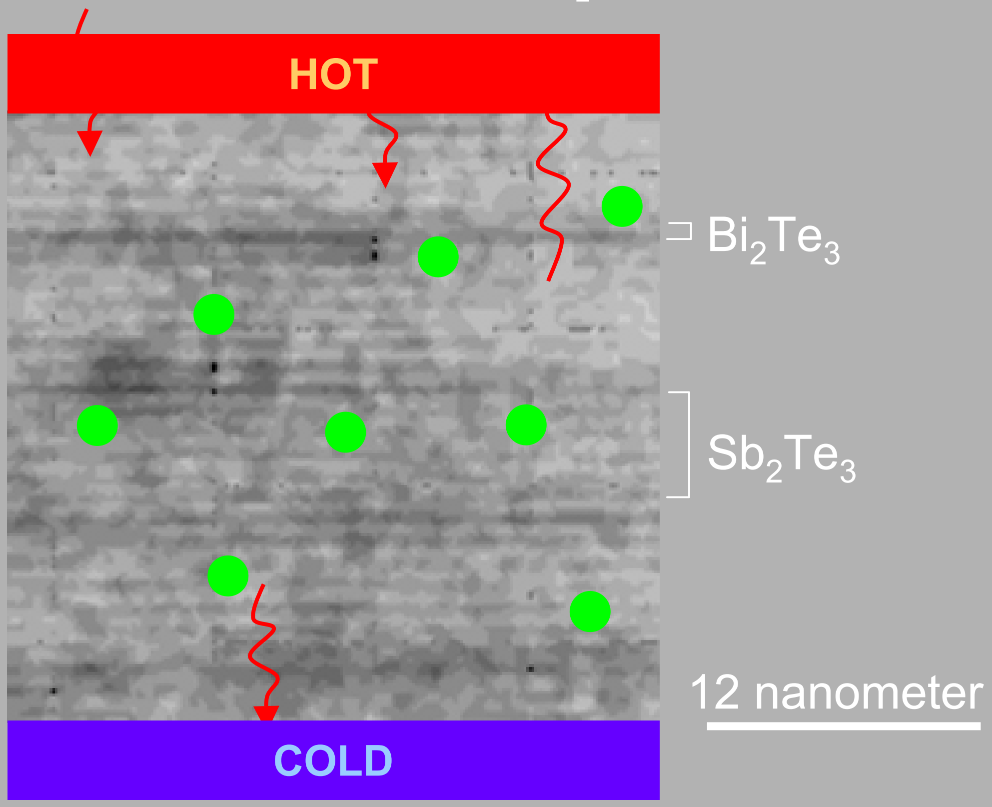

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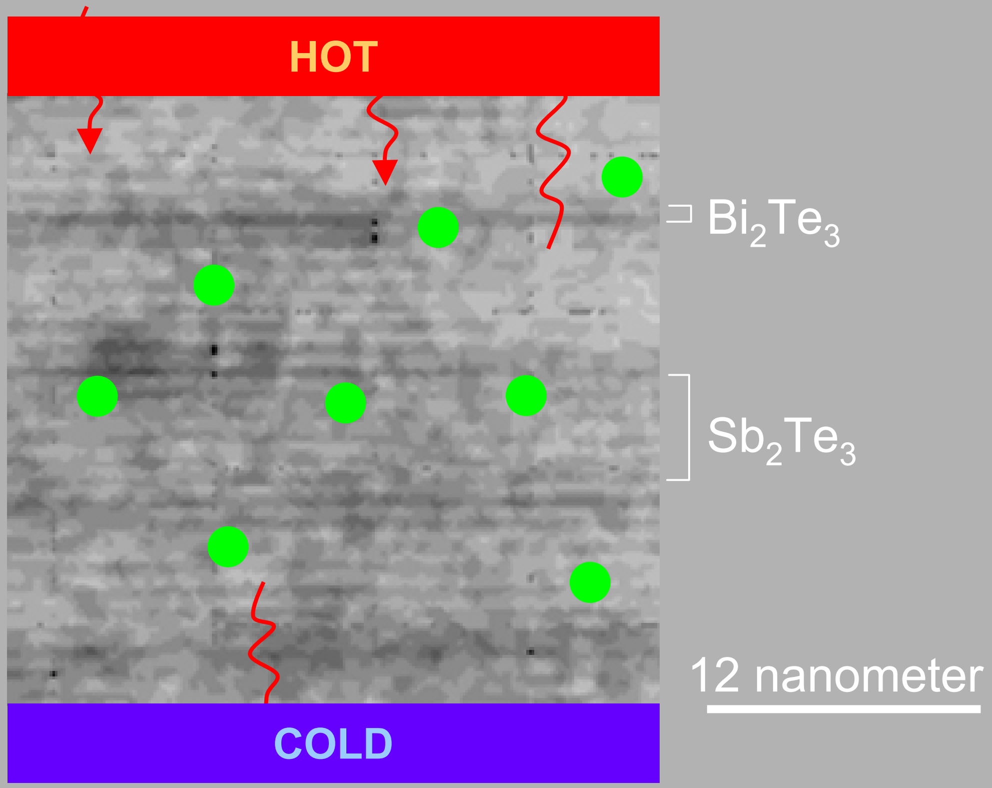

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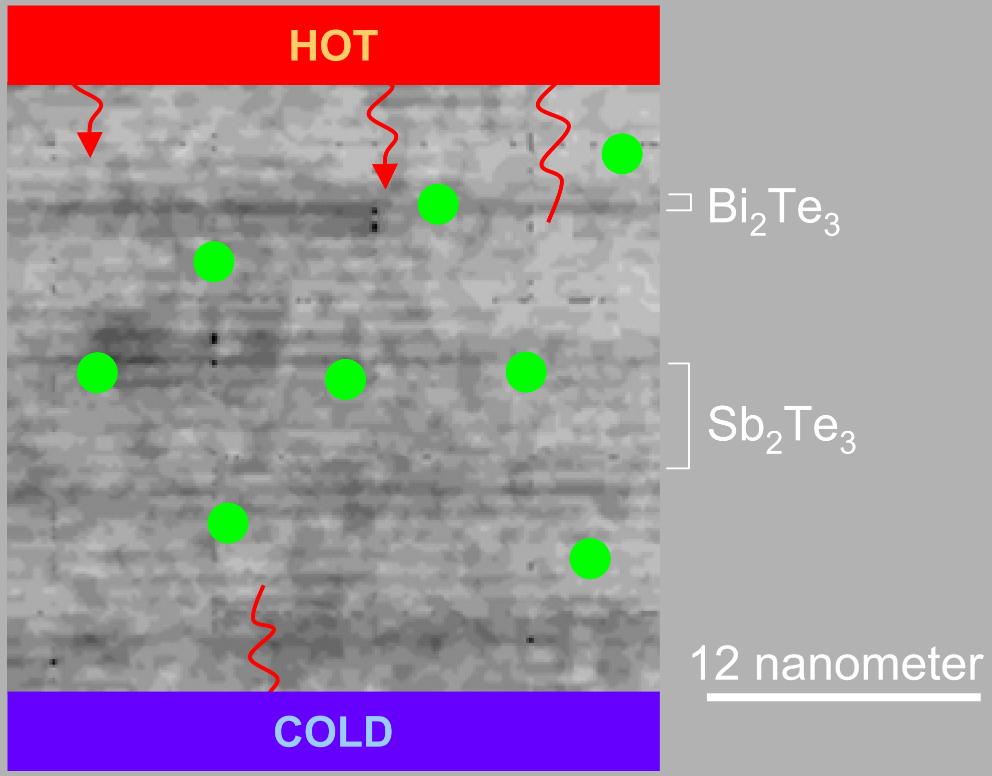

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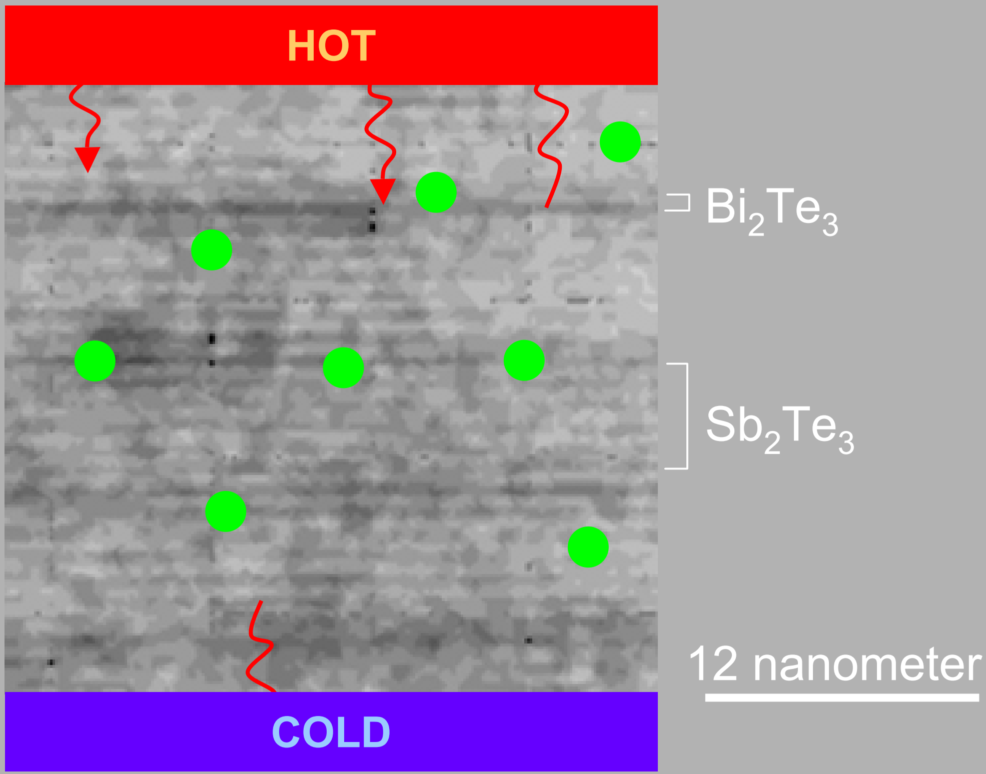

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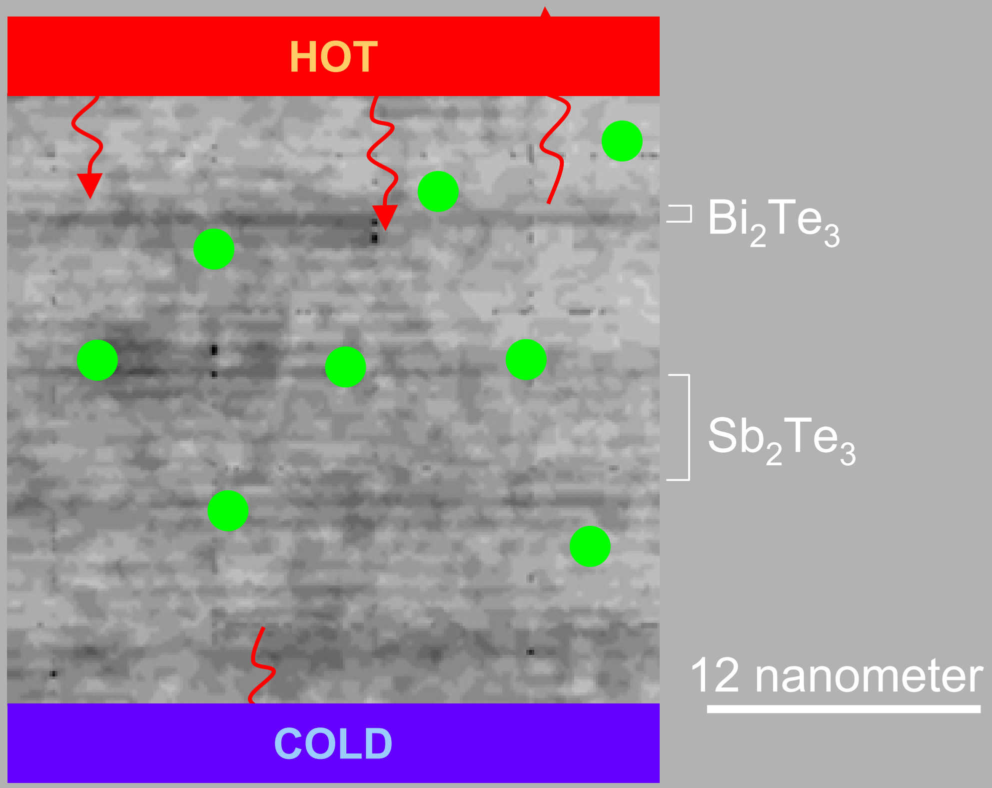

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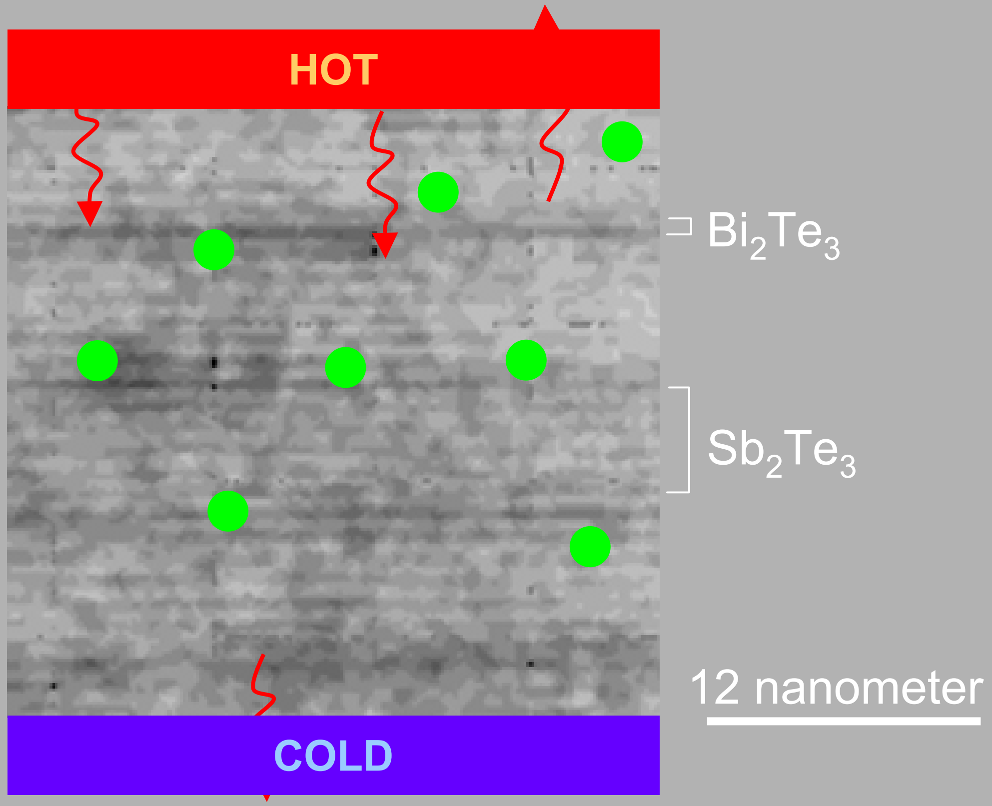

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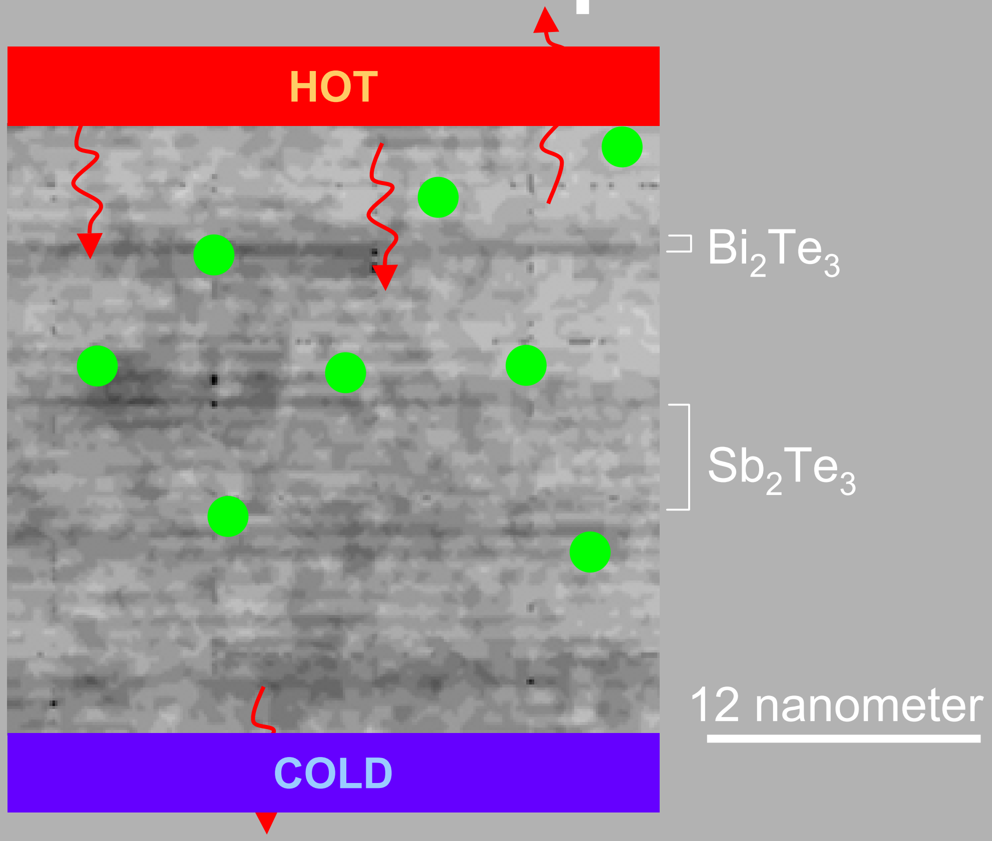

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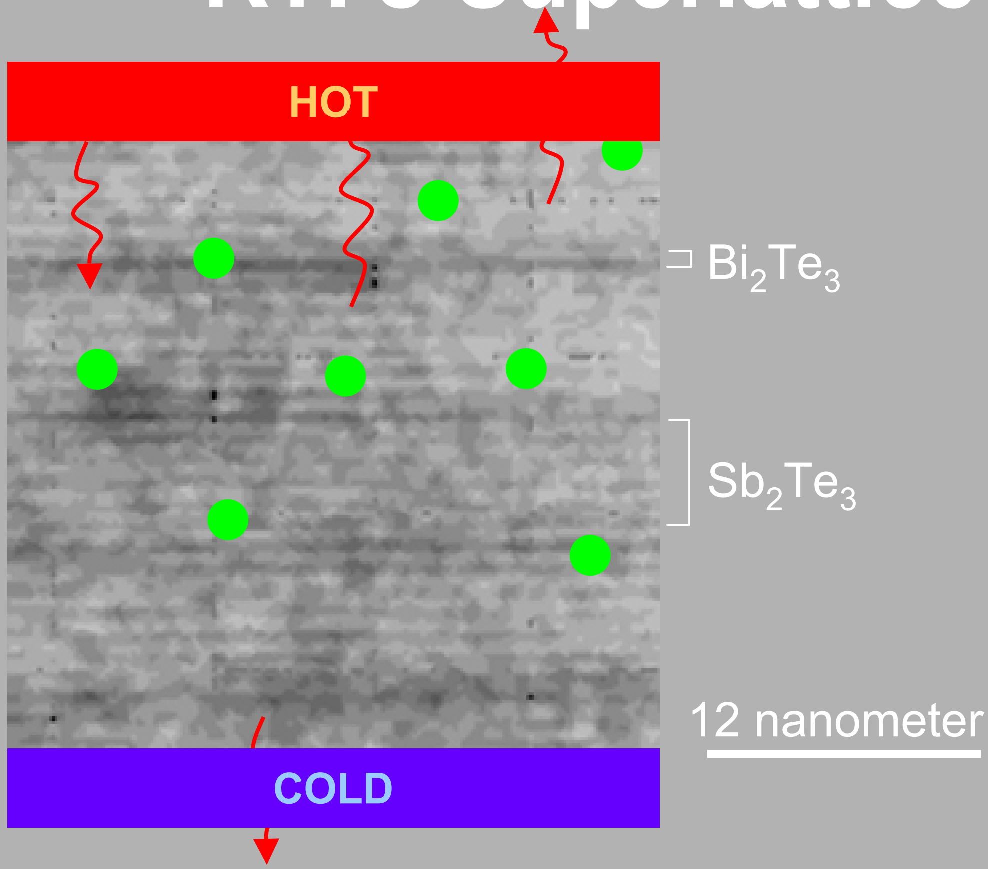

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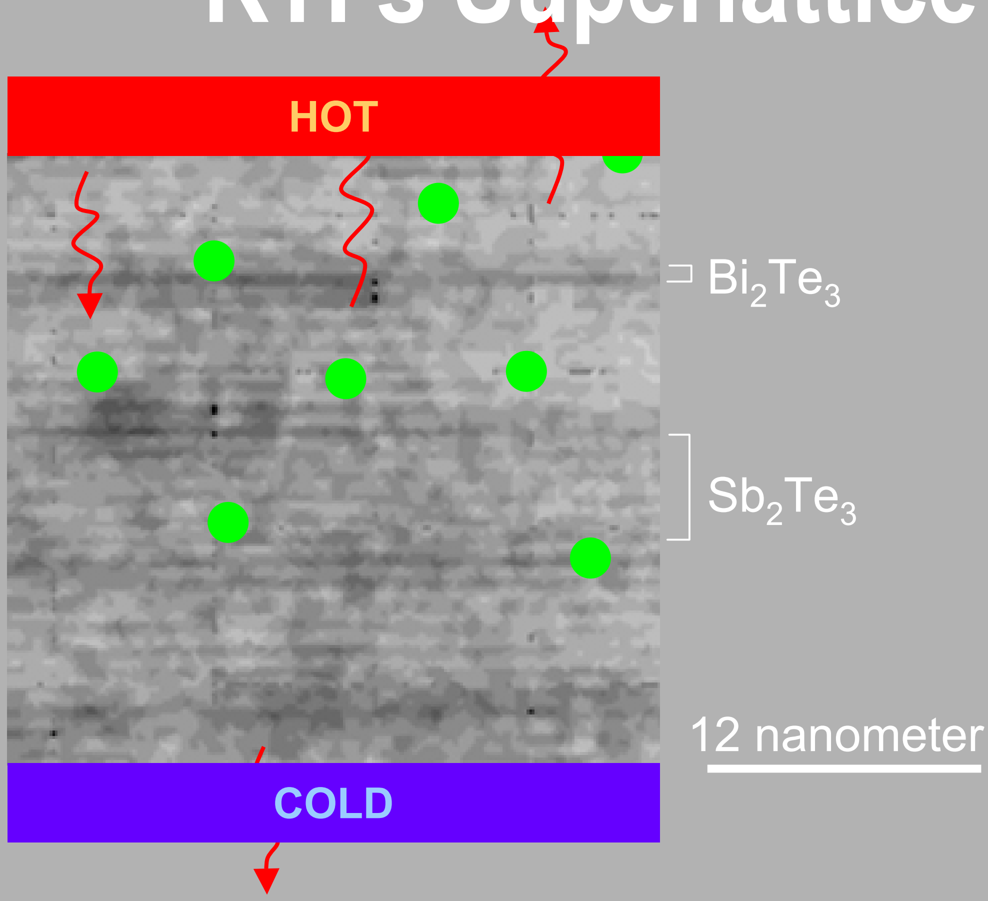

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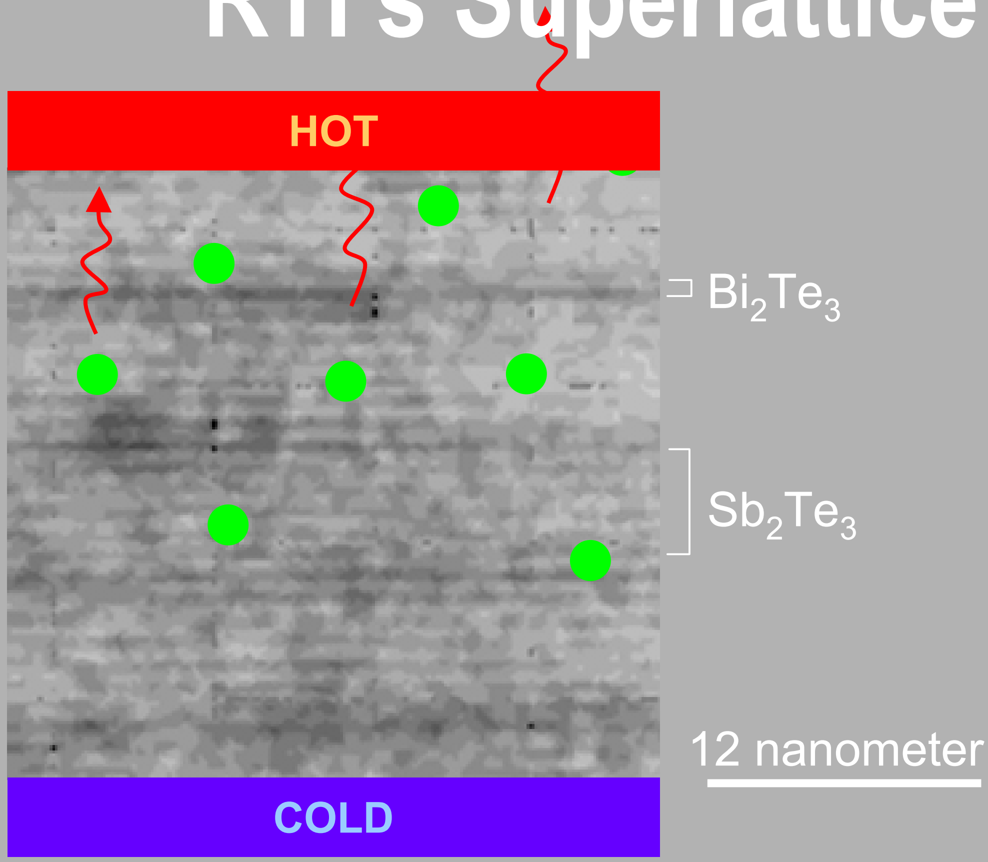

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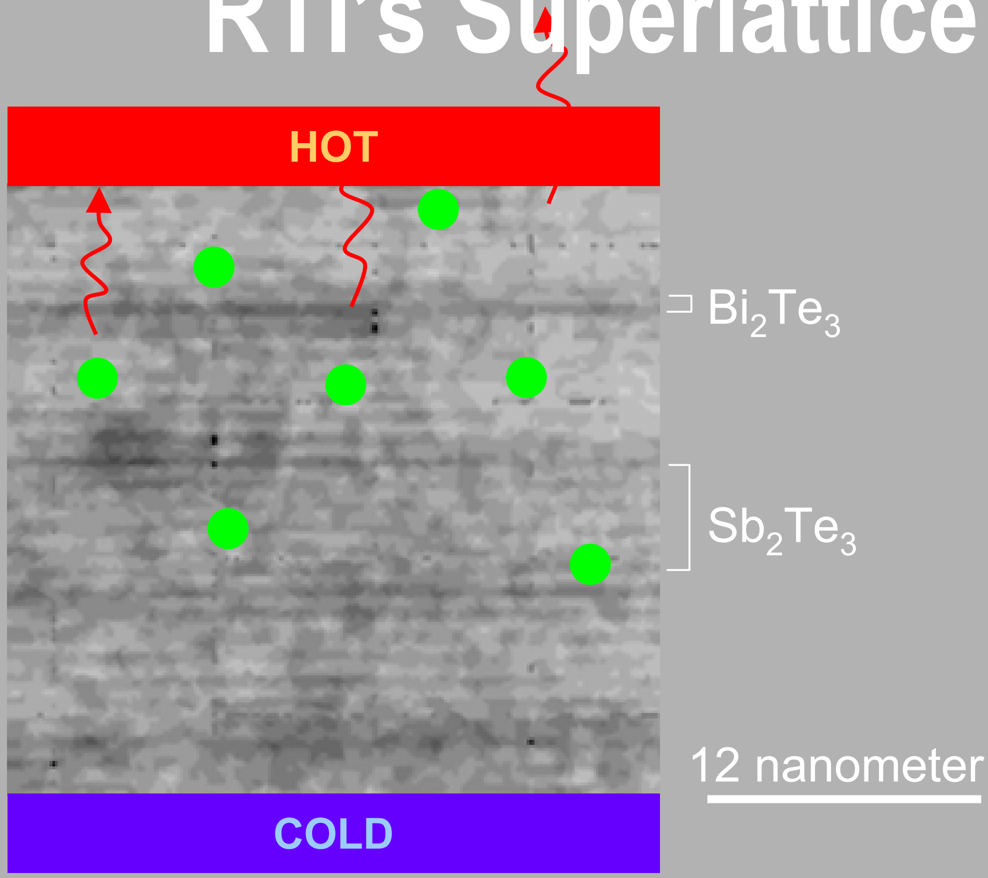

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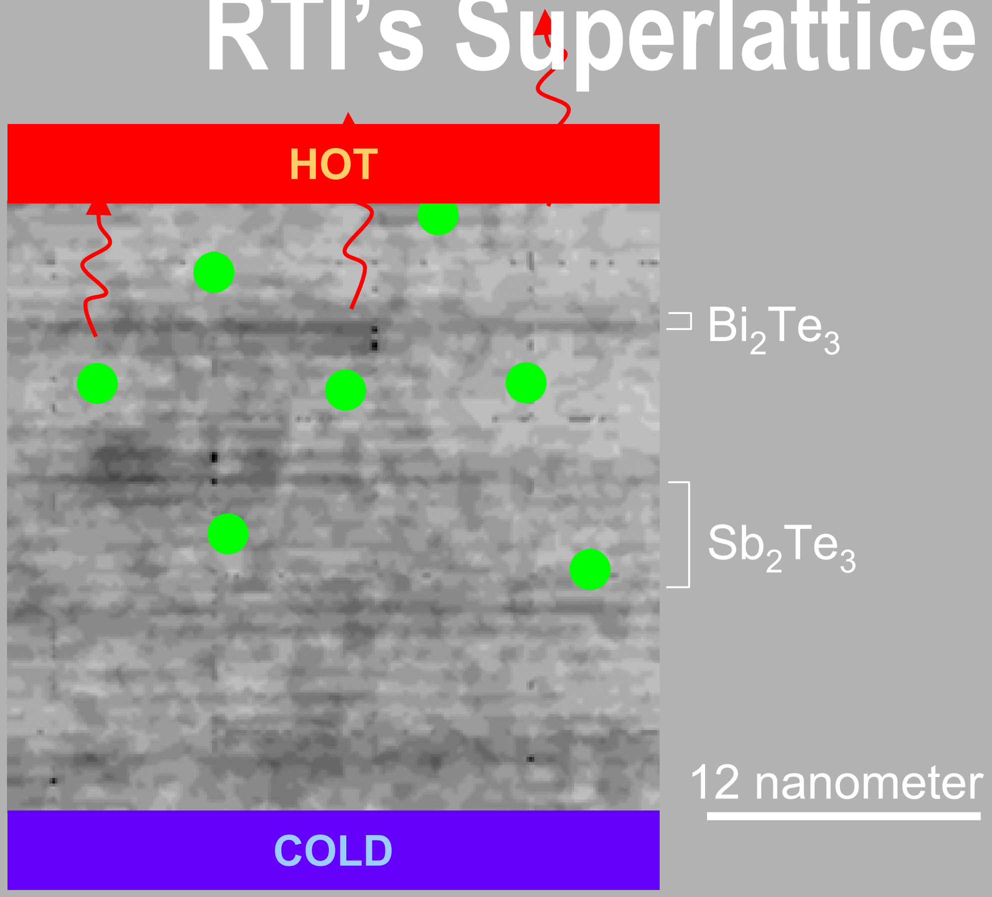

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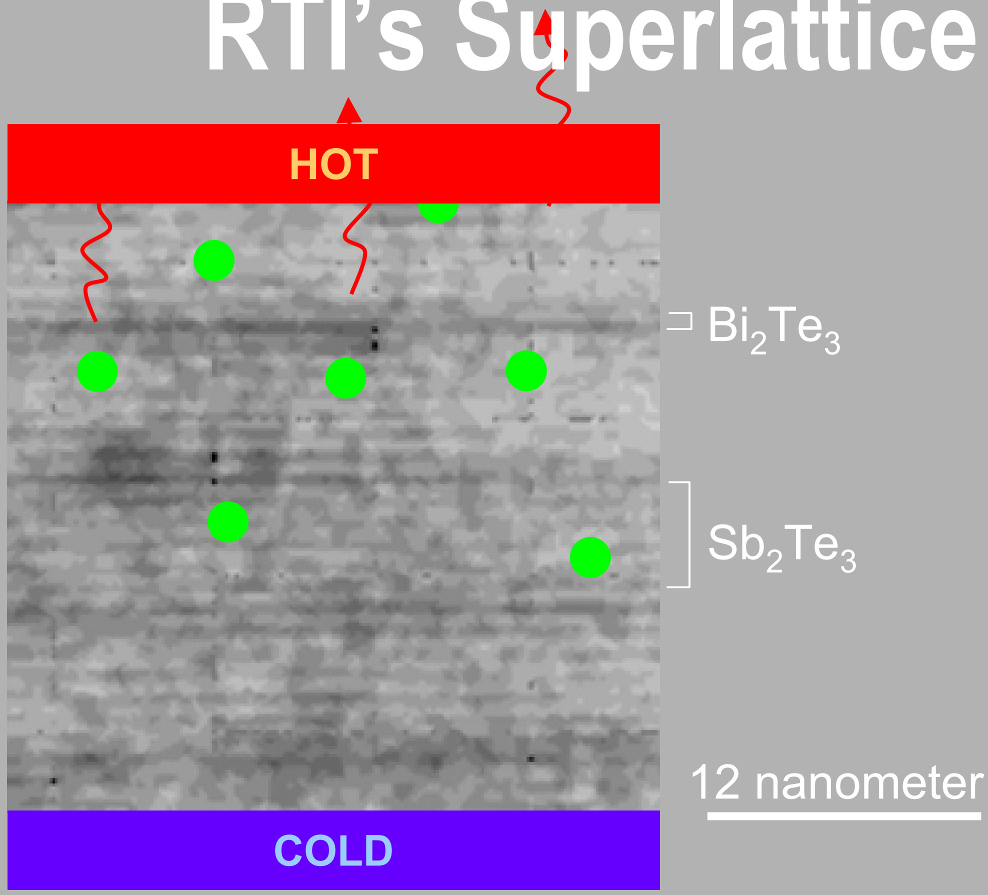

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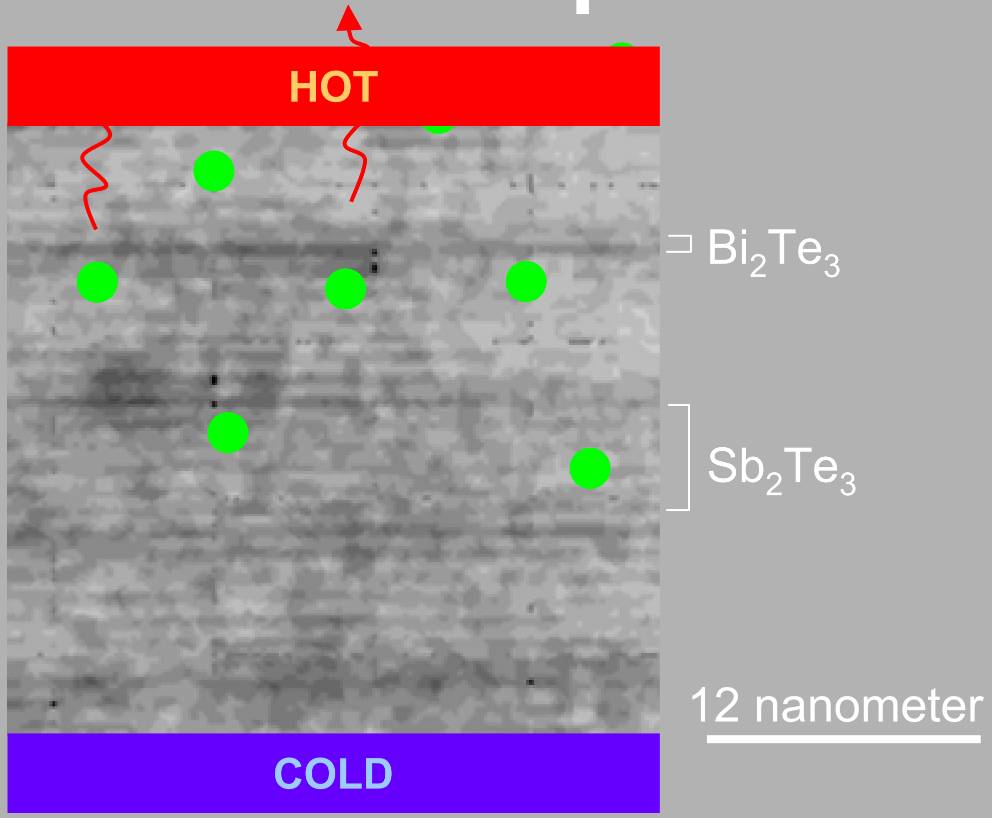
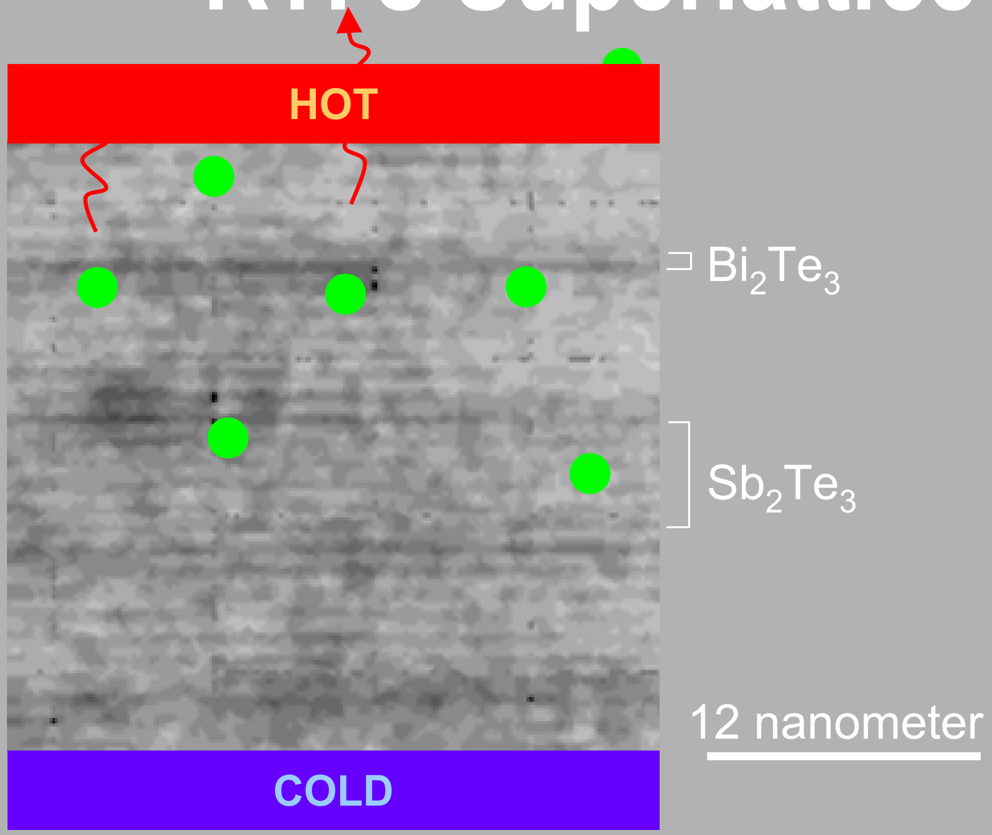


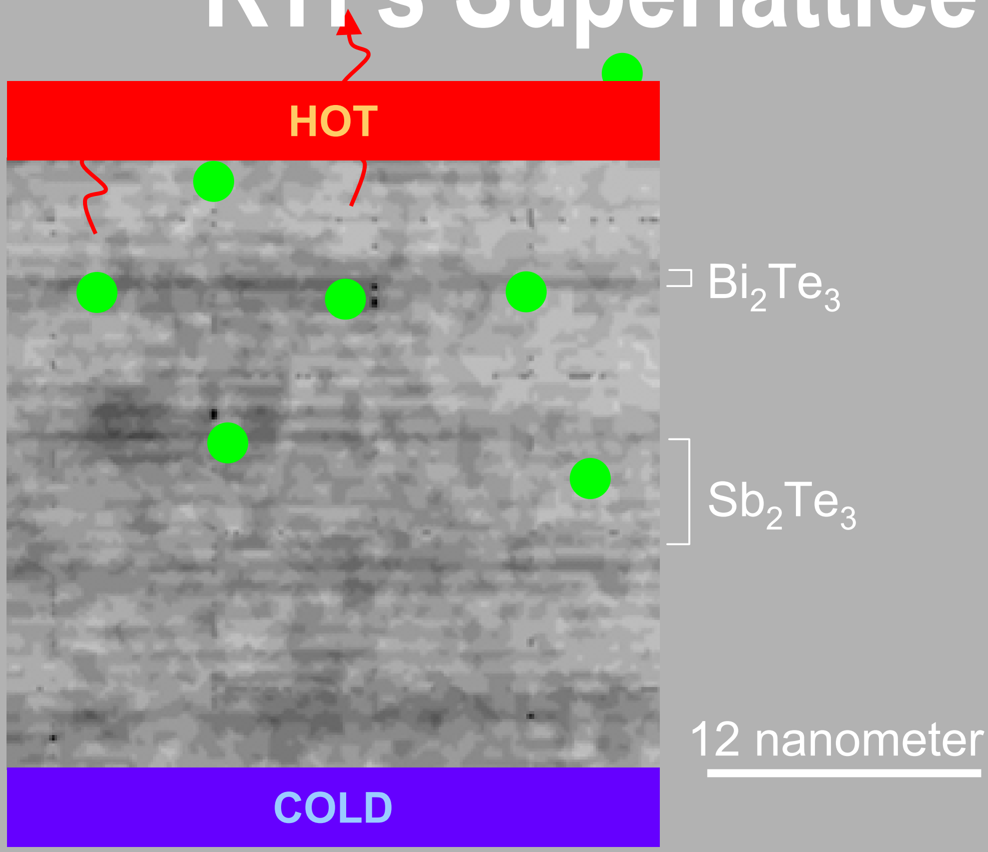
The RTI breakthrough arises from reducing heat transmission without disrupting electron flow

RTI's Superlattice Material



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

RTI's Superlattice Material



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

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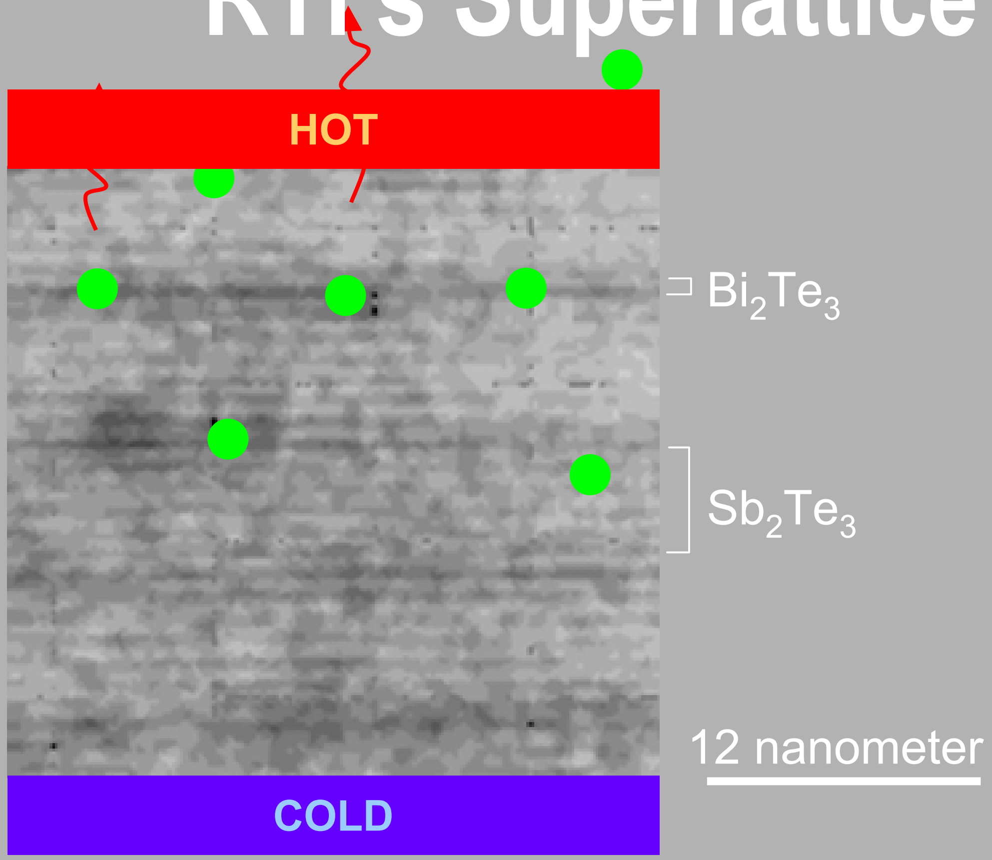
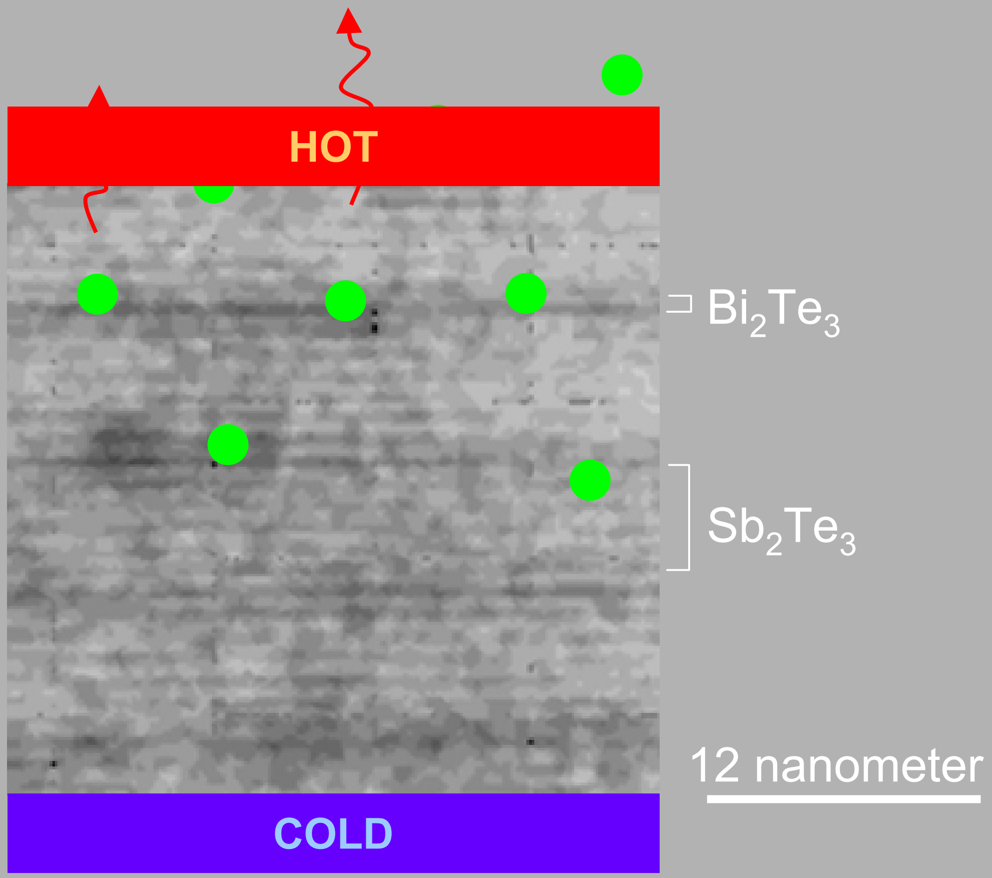


The RTI breakthrough arises from reducing heat transmission without disrupting electron flow

RTI's Superlattice Material



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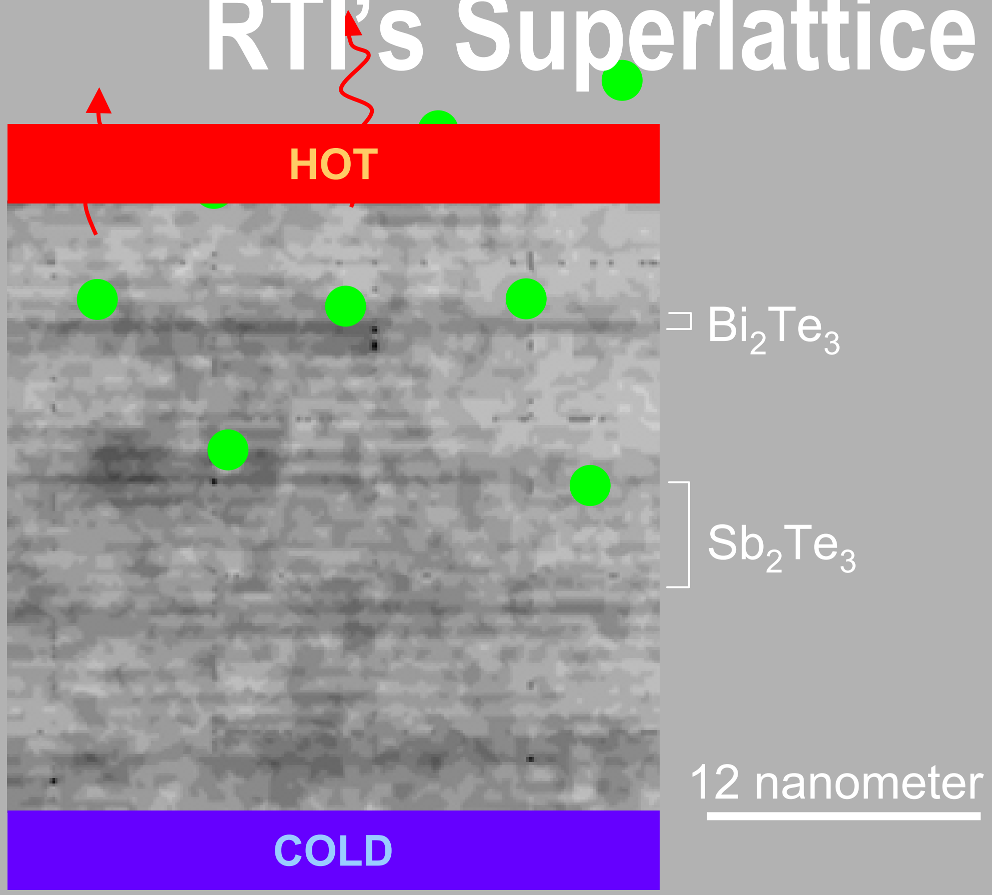
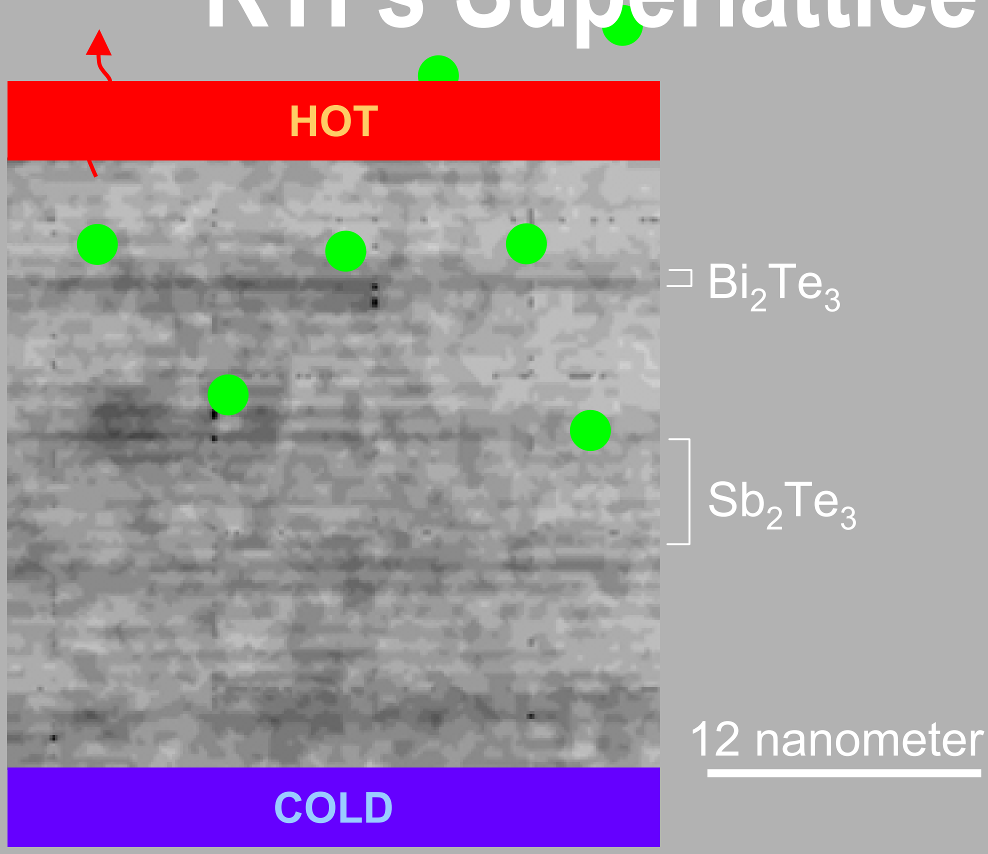


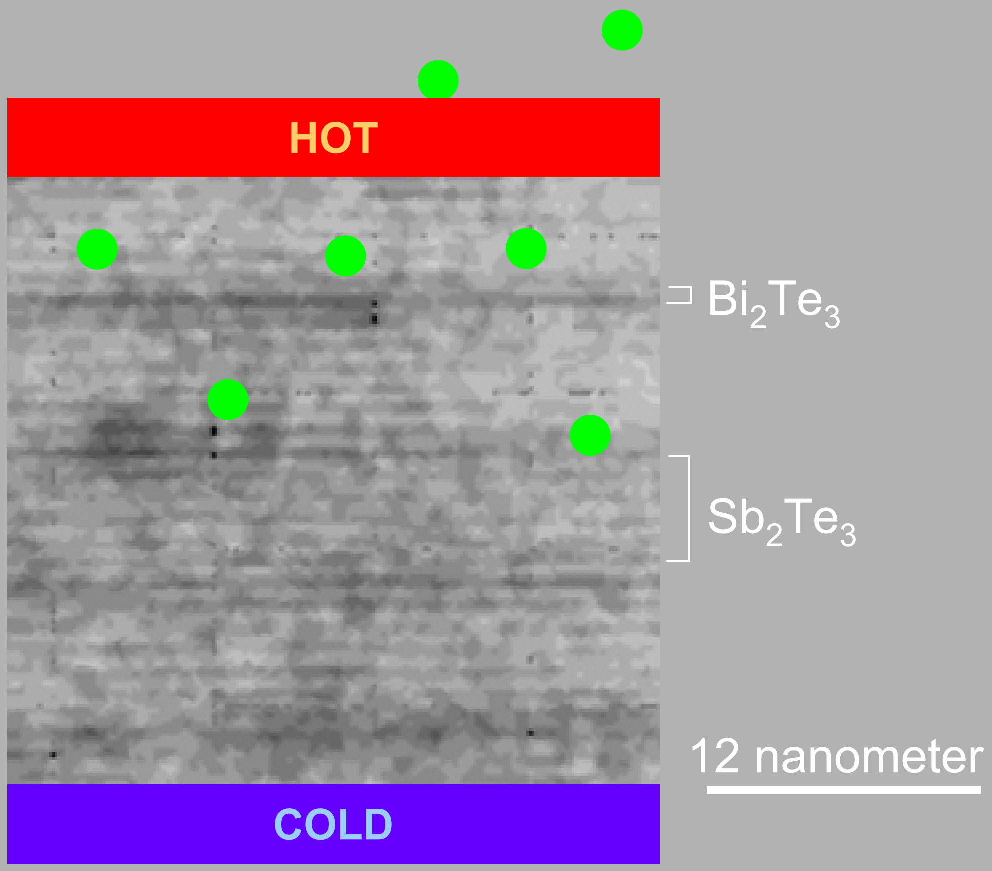
The RTI breakthrough arises from reducing heat transmission without disrupting electron flow

RTI's Superlattice Material



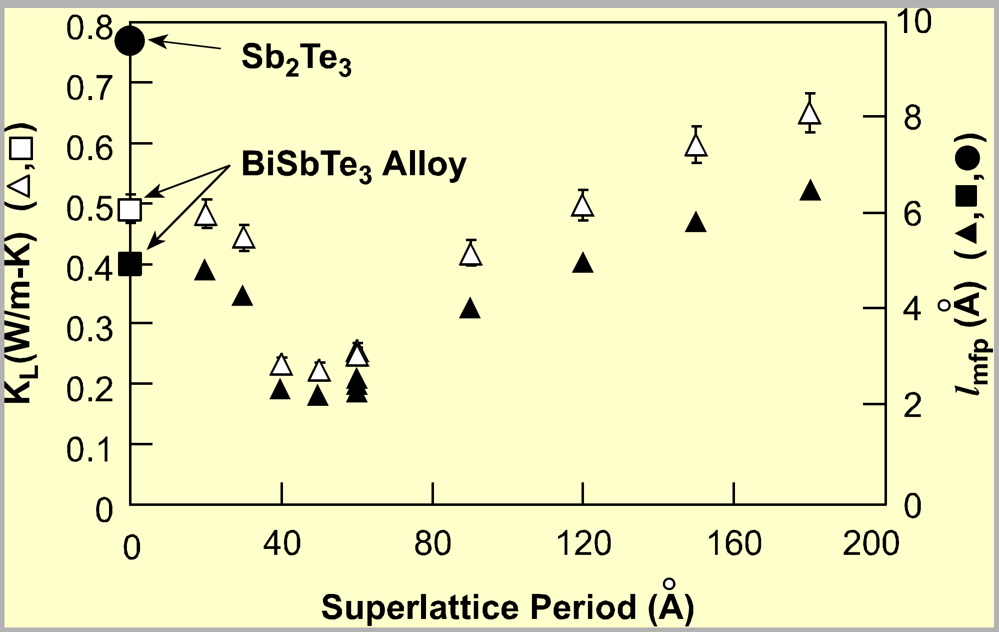
The RTI breakthrough arises from reducing heat transmission without disrupting electron flow

RTI's Superlattice Material

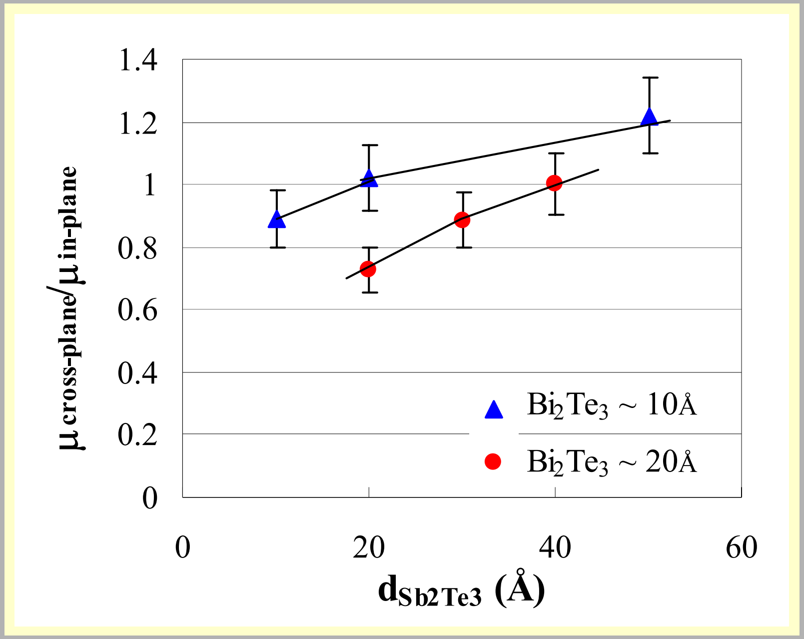


The RTI breakthrough arises from reducing heat transmission without disrupting electron flow

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

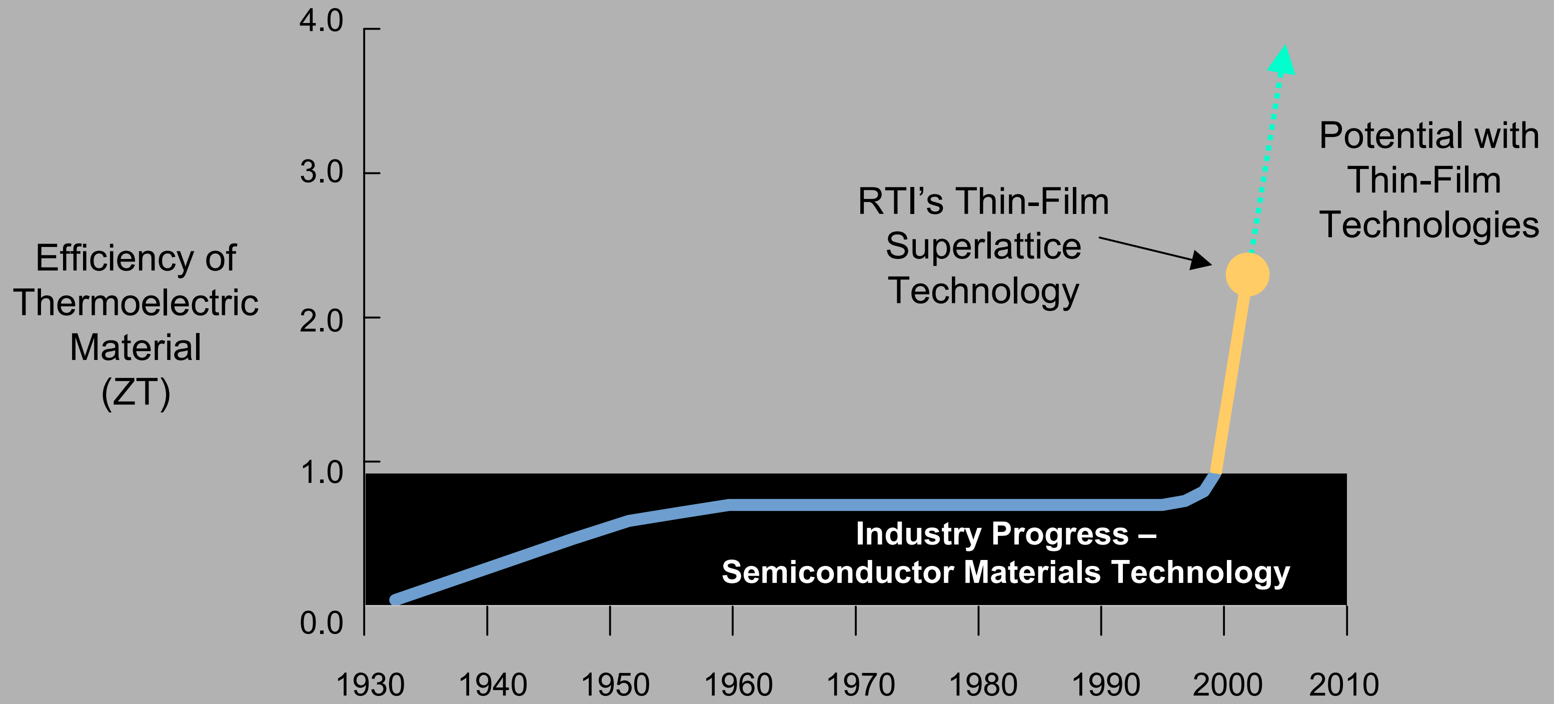


Physical Review B, 61, 3091 (2000)



Nature, 413, 597-602 (2001)

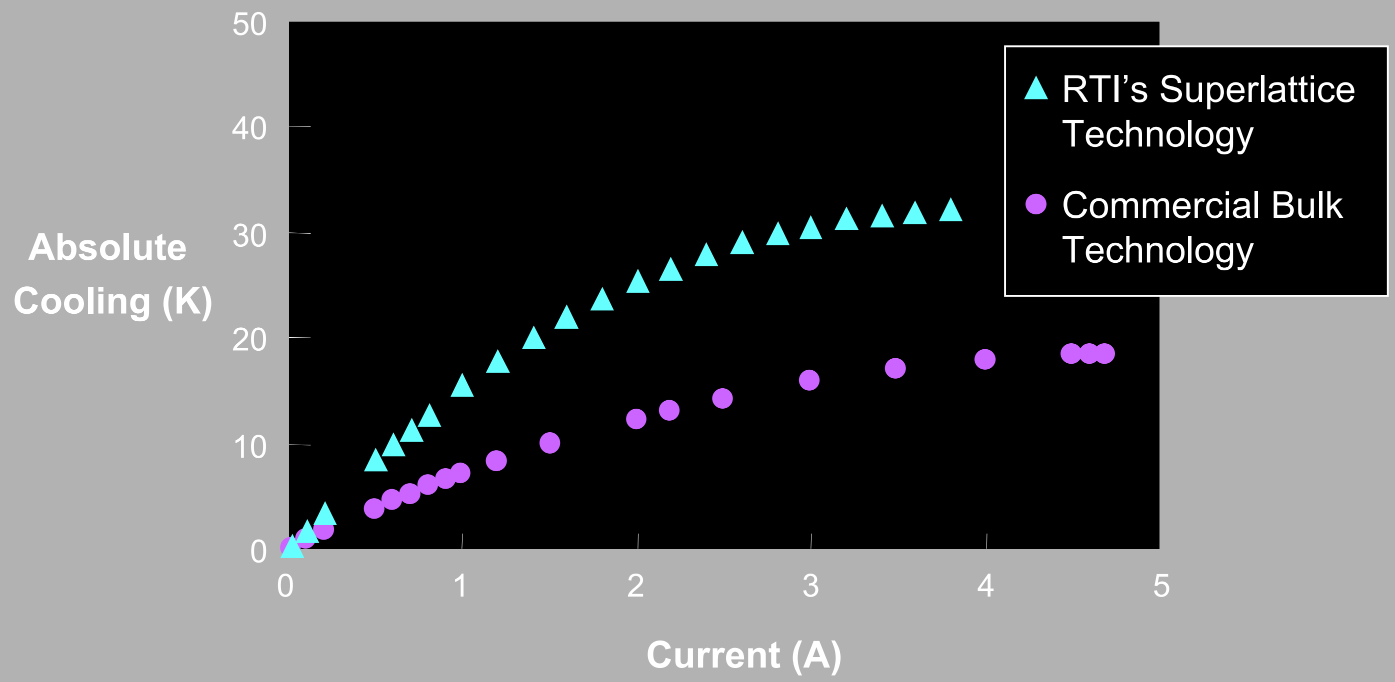
Big Jump in ZT with the Phonon-Blocking, Electron-Transmitting Structures



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

Advantages of Superlattice Thermoelectric Technology

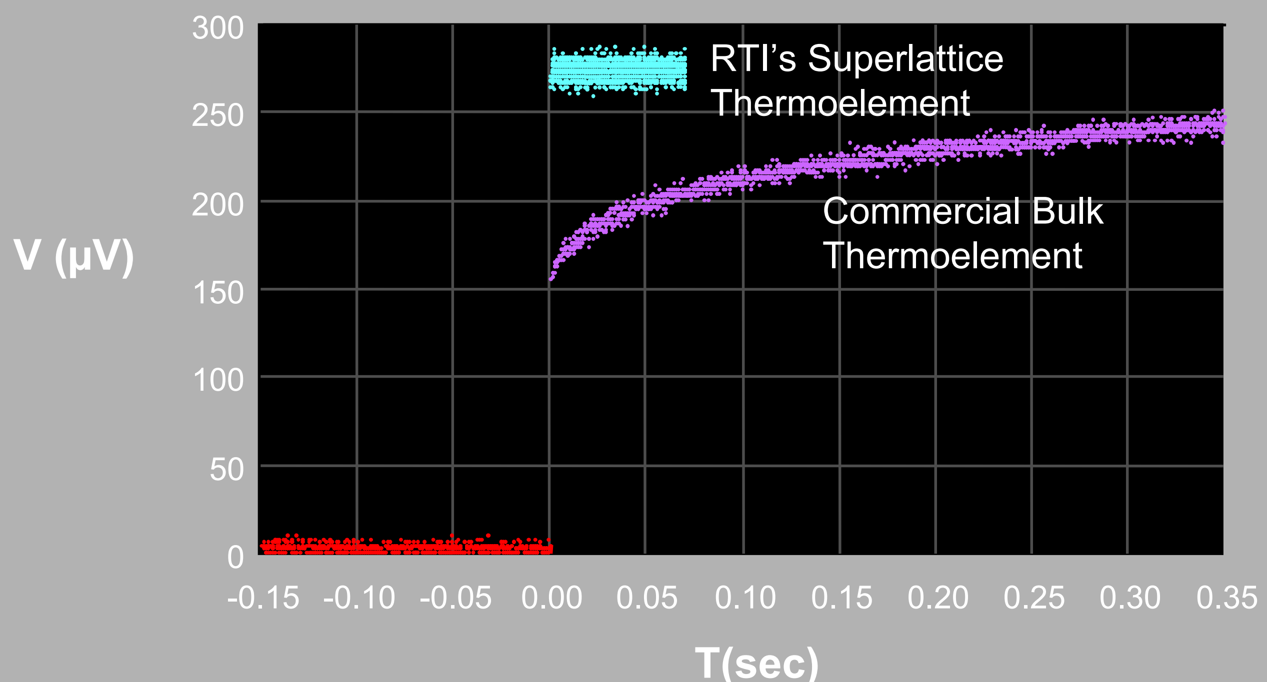
- Enhanced efficiency compared to bulk TE element under similar test conditions



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

Advantages of Superlattice Thermoelectric Technology

- Enhanced efficiency
- Super-fast cooling and heating



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

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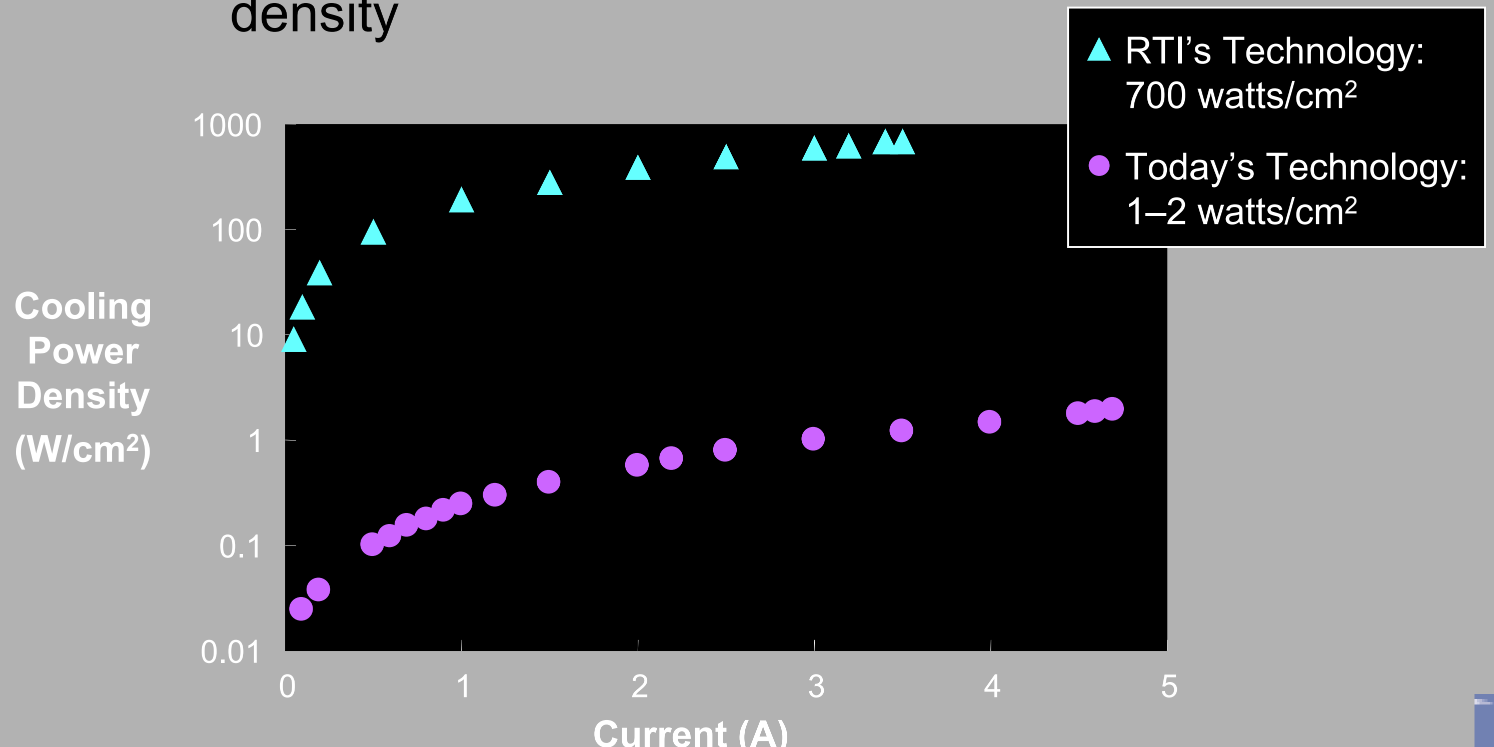
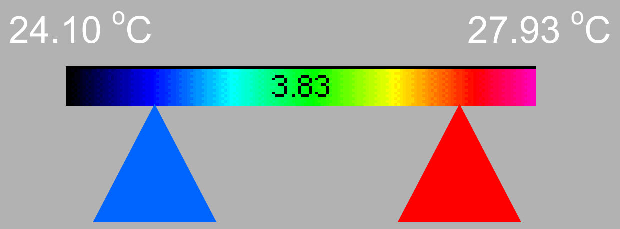
Advantages of Superlattice Thermoelectric Technology

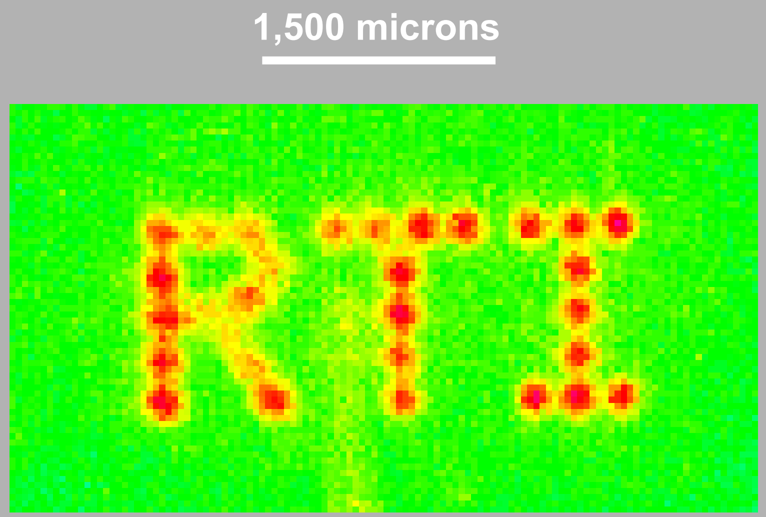
- Enhanced efficiency
- Super-fast cooling and heating
- Enhanced cooling power density



Advantages of Superlattice Thermoelectric Technology

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

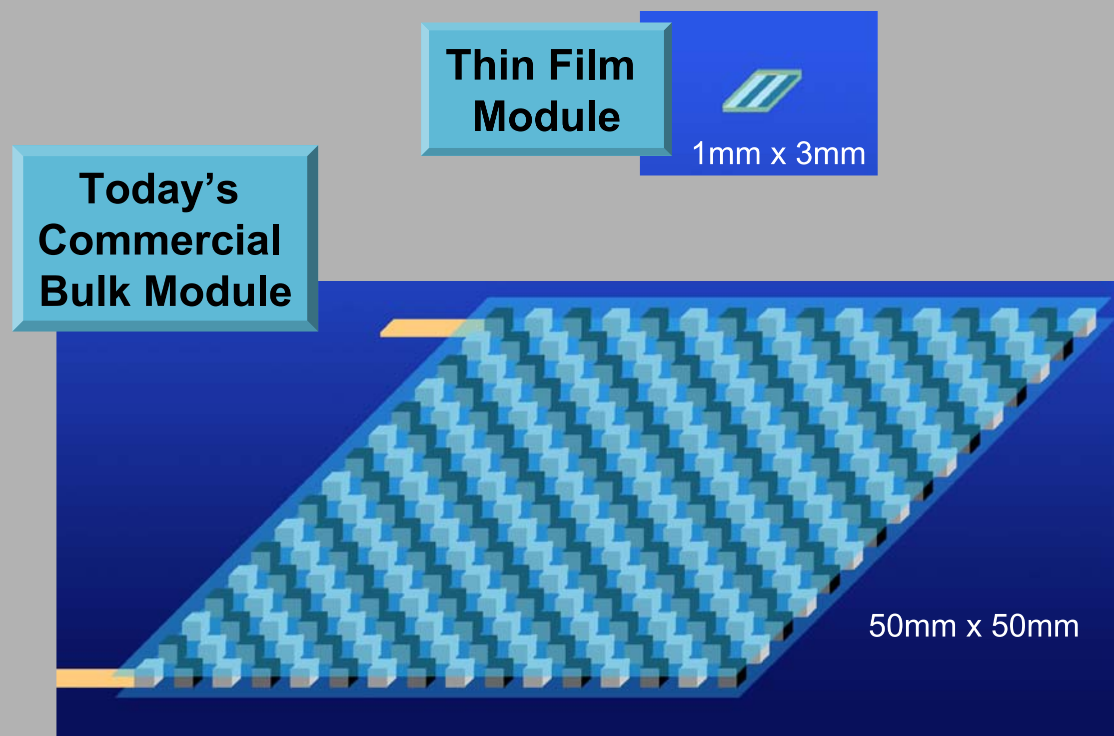




Nature, **413, 597 (2001)**

Advantages of RTI's Superlattice Thermoelectric Technology

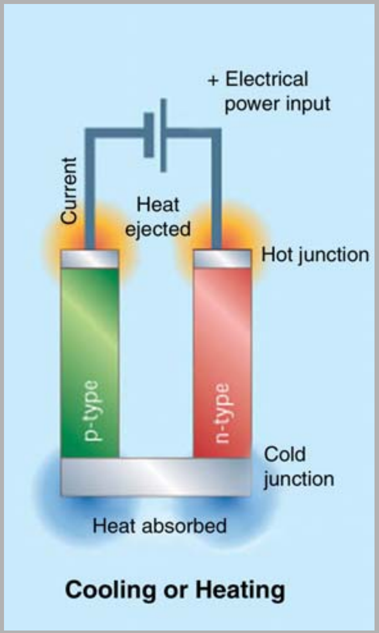
- Enhanced efficiency
- Super-fast cooling and heating
- Enhanced power density
- Localized cooling/ heating technology
- 1/40,000th the actual TE material requirement of bulk technology for same functionality – low recycle costs – Eco-friendly technology

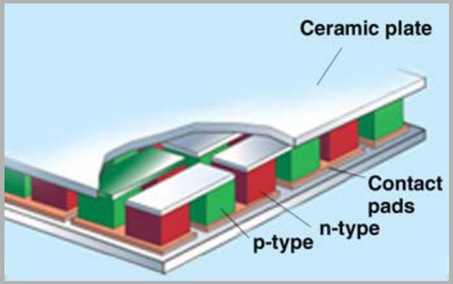


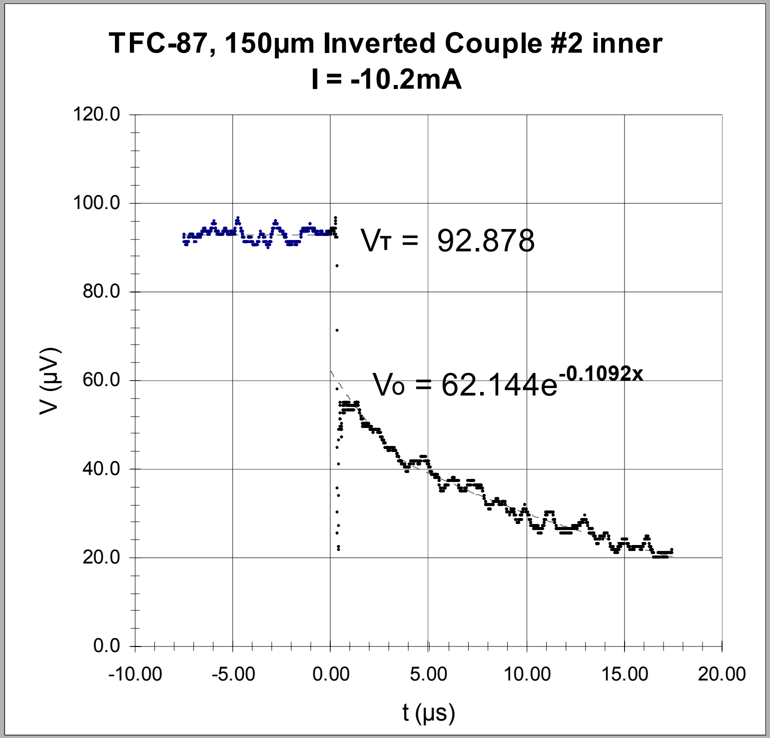
Technology Overview

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



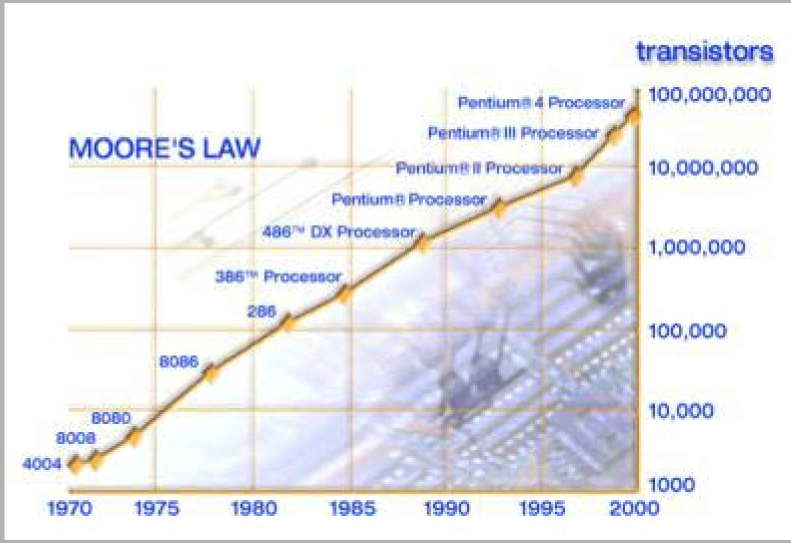


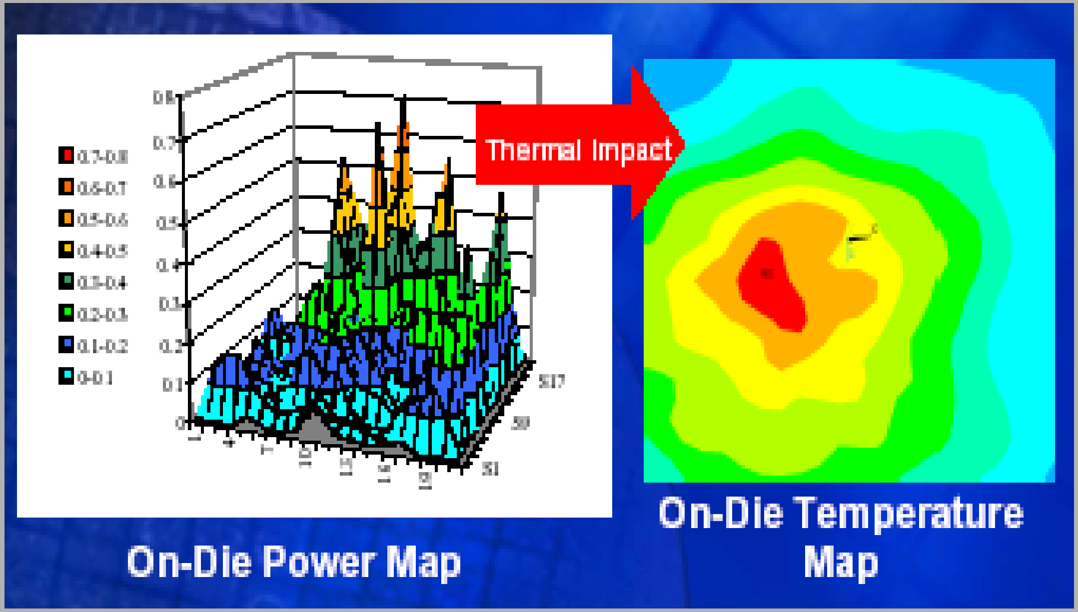


- ZT ~ 2 at 300K
- The individual ZT of p- and n- SL materials has been transitioned to the ZT of couple

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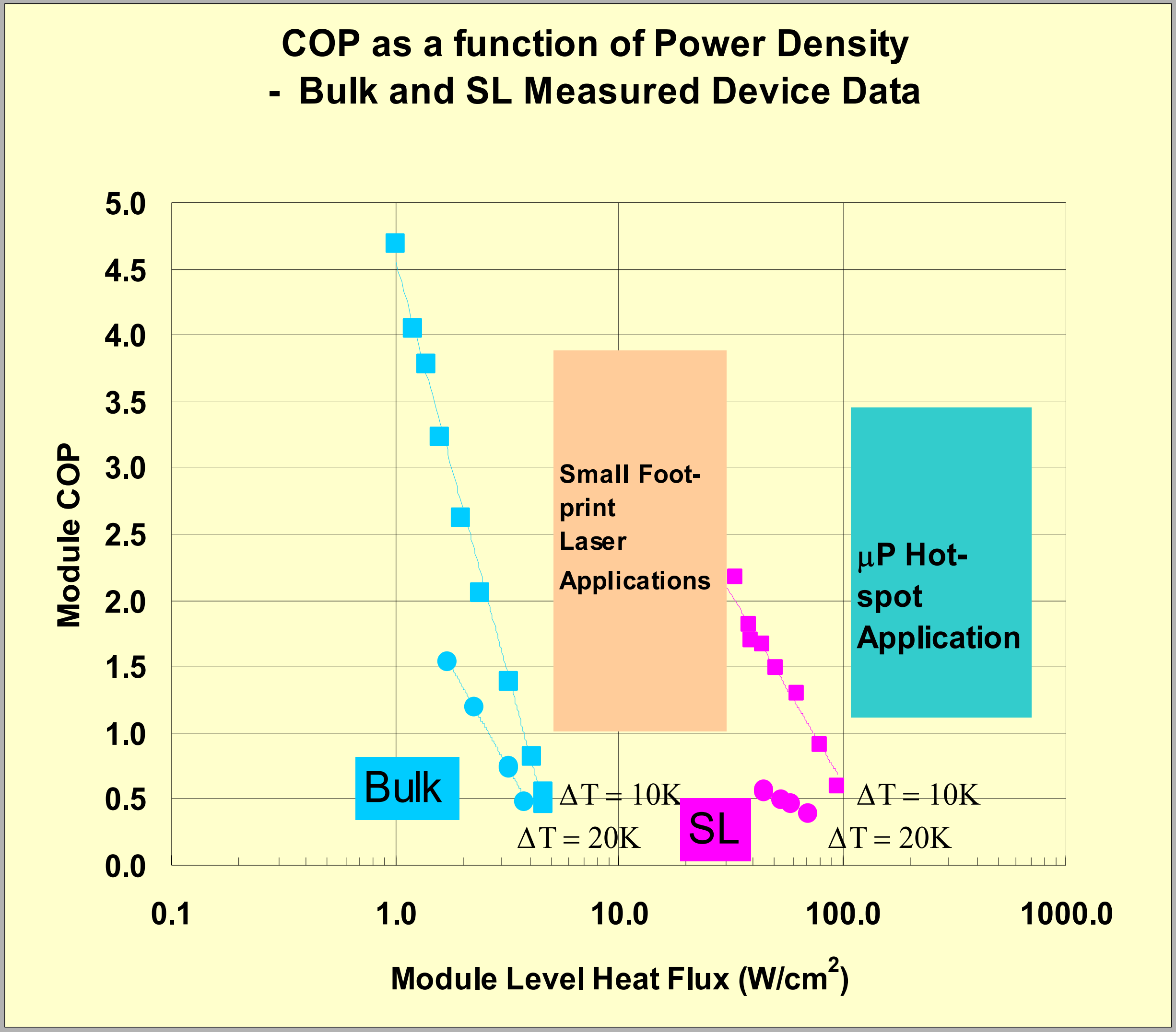
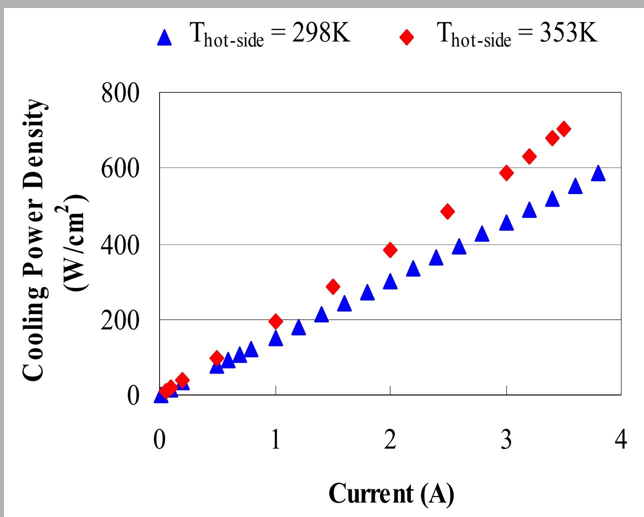
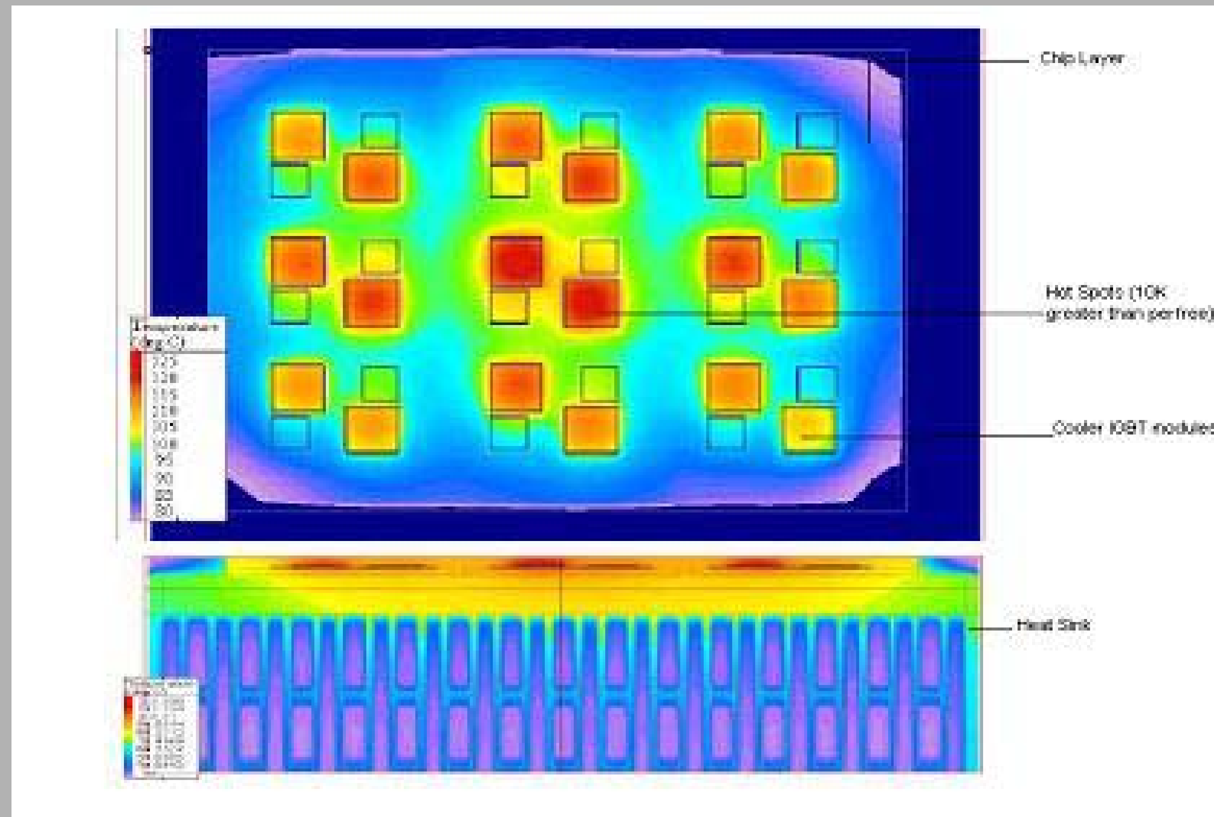
Thermal Management of High Heat Fluxes – Better Efficiencies at High Heat Fluxes with State-of-the-art Superlattice Devices



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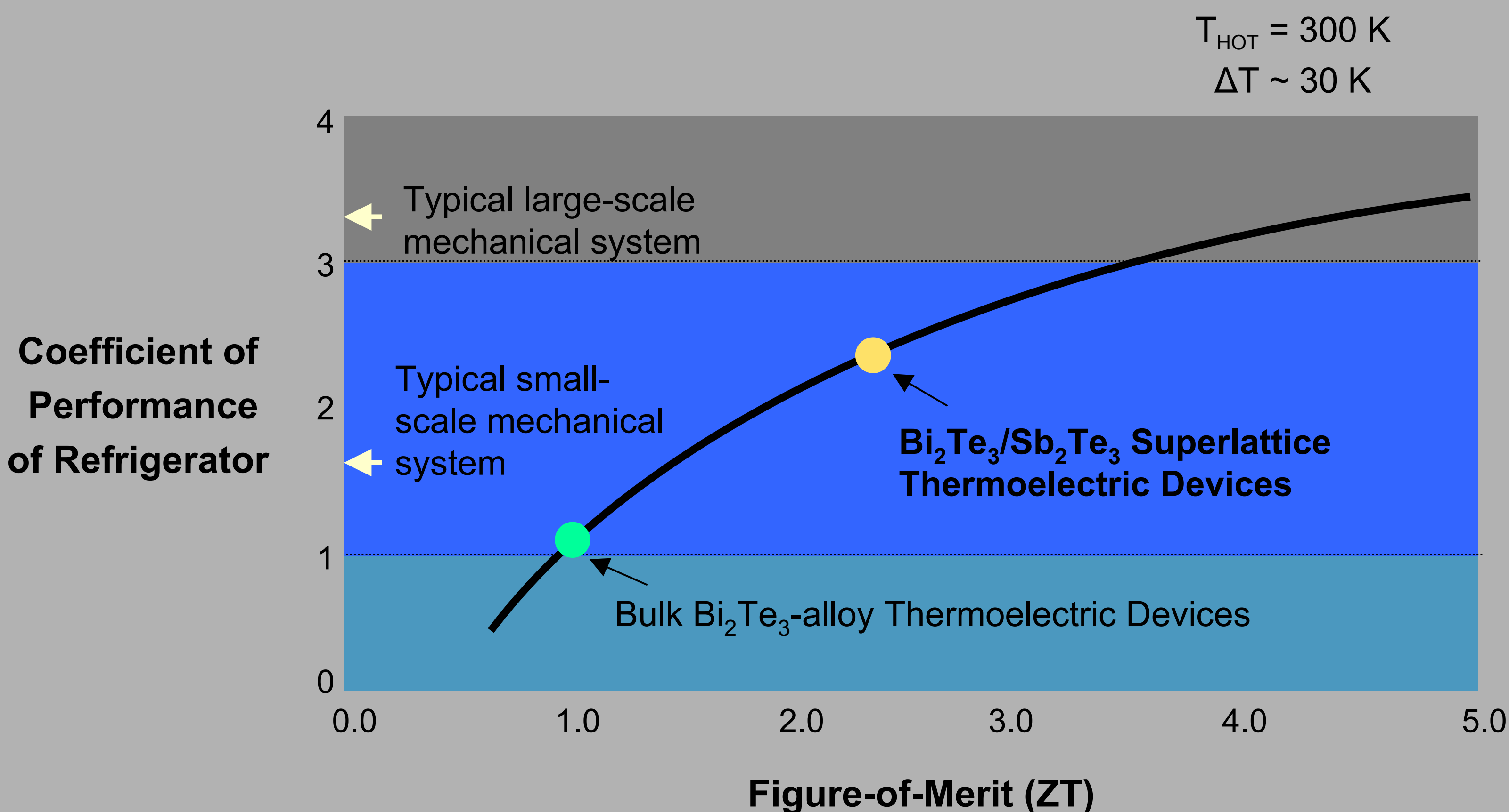
Advanced System-Level Concepts to further leverage nano-materials advancements

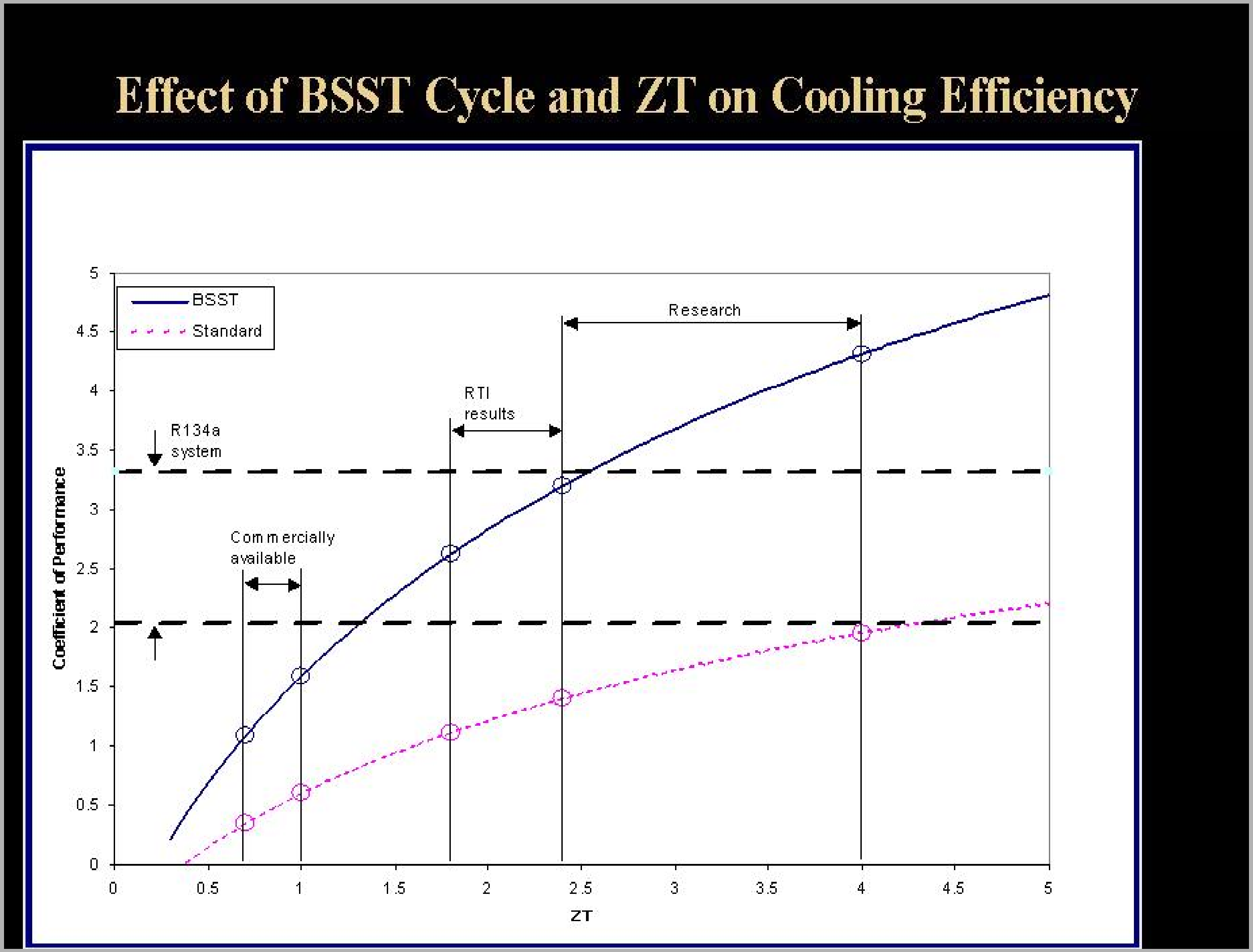
RTI's Superlattice Device on Cooling Efficiency



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

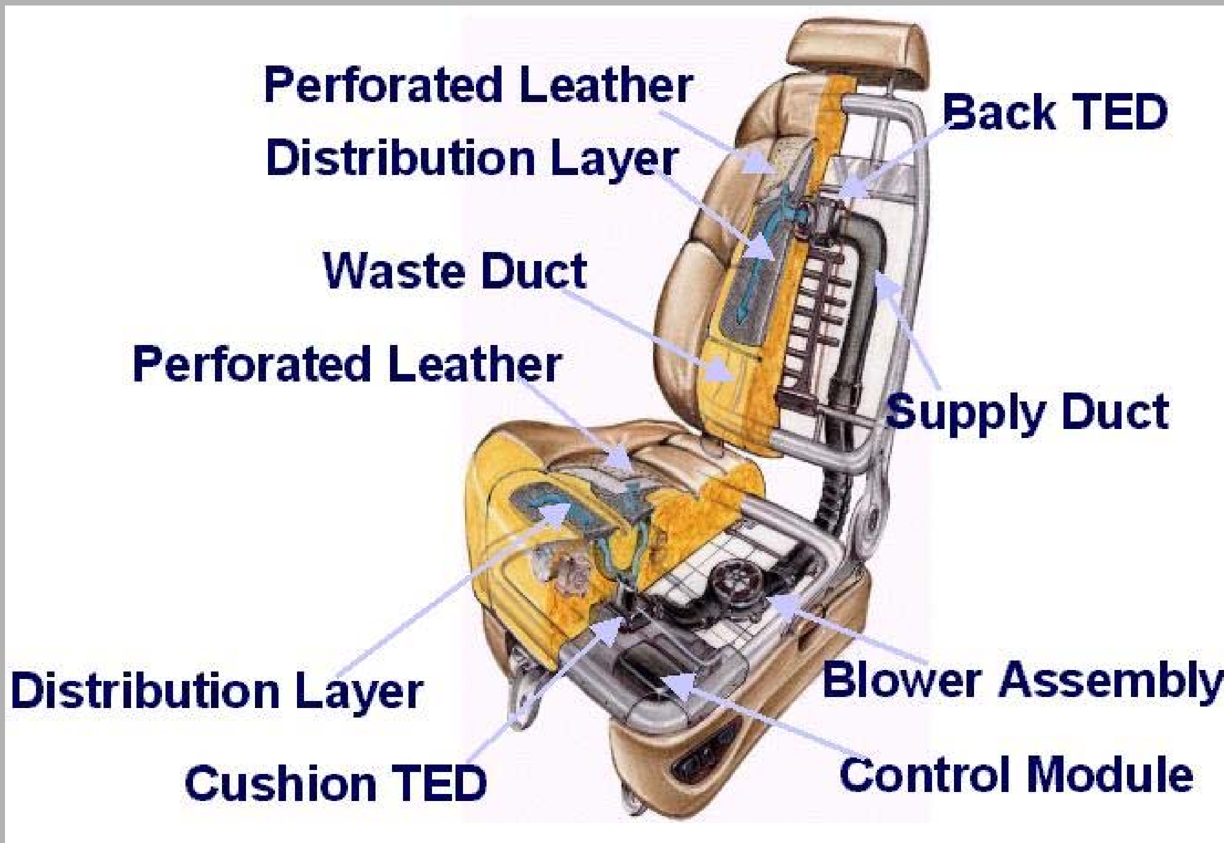
- **Higher ZT – Incentives for New Approaches to Implement Higher COP Concepts like Novel Thermodynamic Cycles and Novel Heat-Transfer Approaches**

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

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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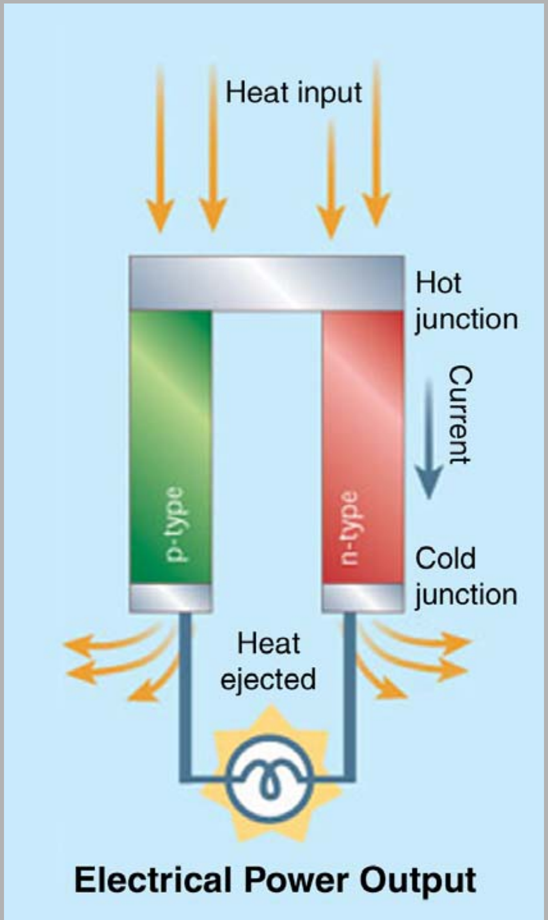
Direct Thermal-to-Electric Energy Conversion

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

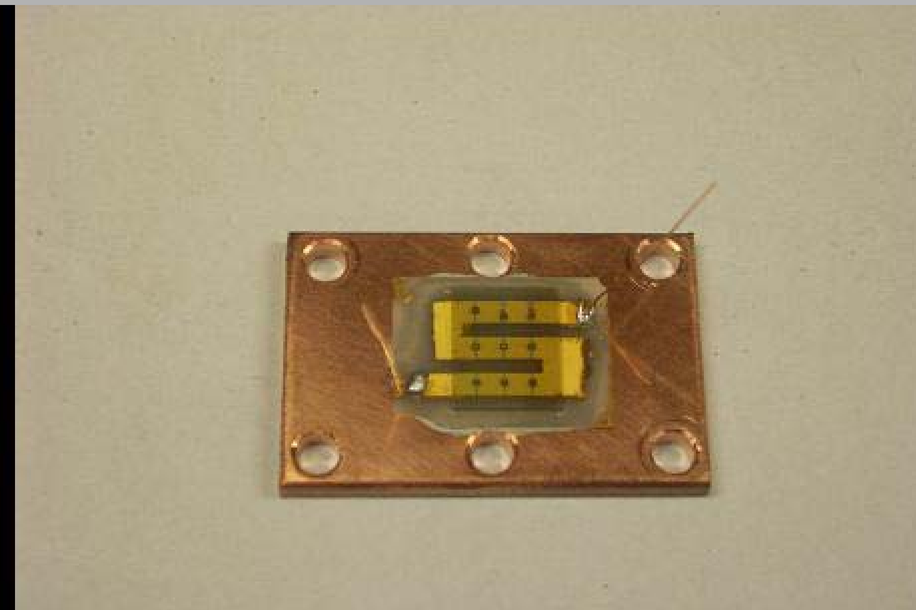
Thermoelectric Power Conversion



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

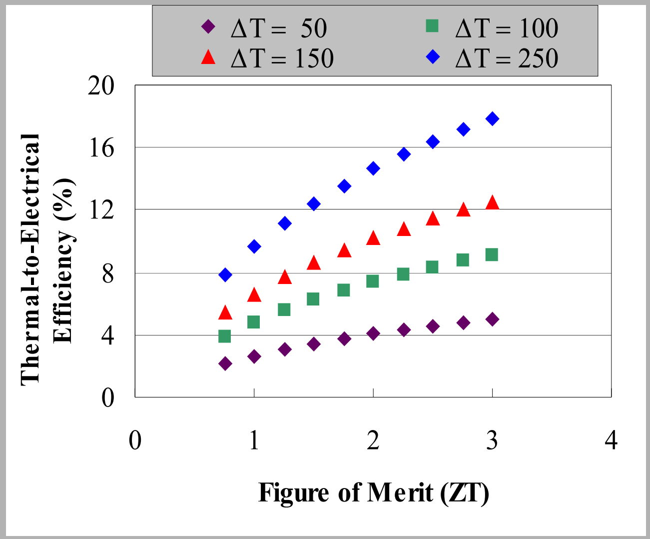
- Power Conversion Efficiency critically dependent on the material Figure of Merit (ZT)
- Maximize ΔT
  - Thermal management (getting the heat out from the heat-sink) is important to generating the maximum ΔT

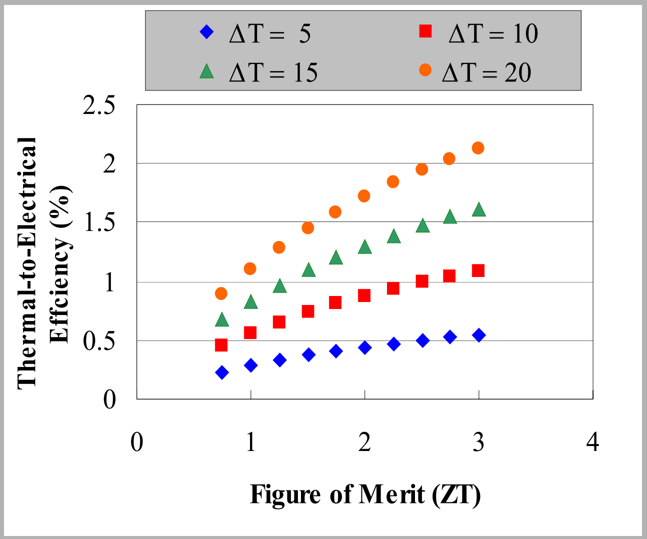
Power Conversion with Modules



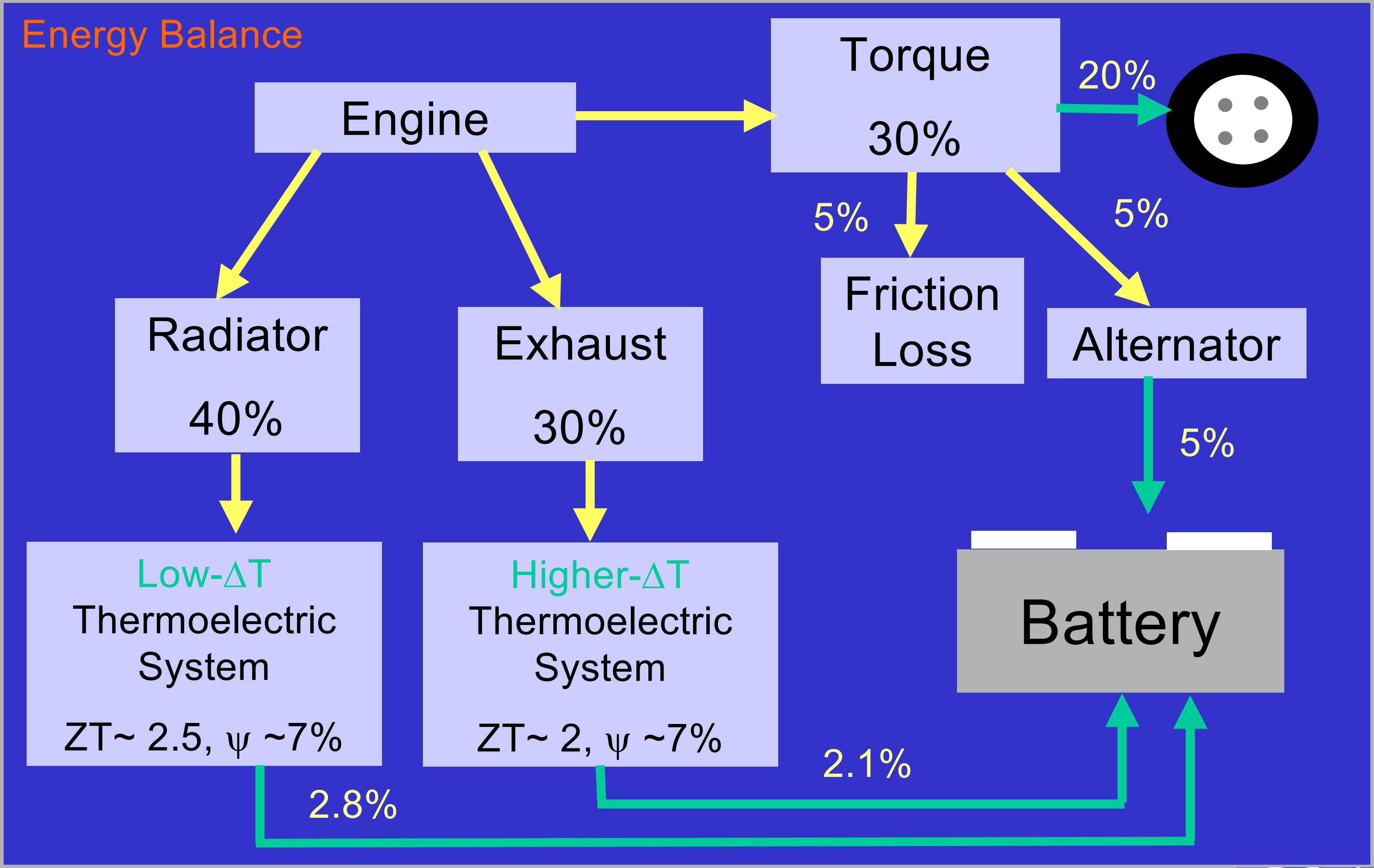
Implications for Power

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





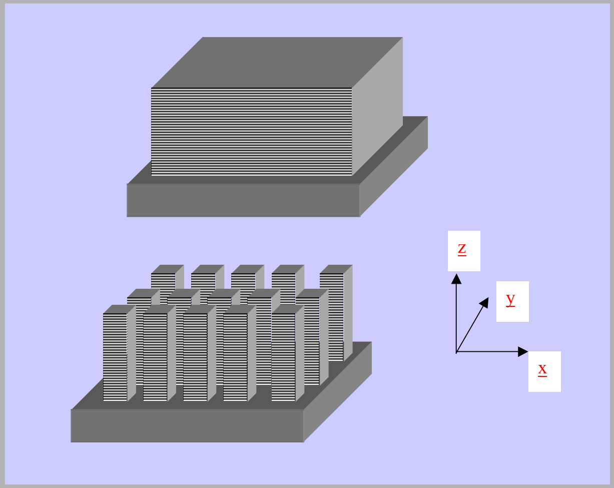
Impact of Light-weight, High-Efficiency Thermoelectric Technology with Waste-Heat Recovery



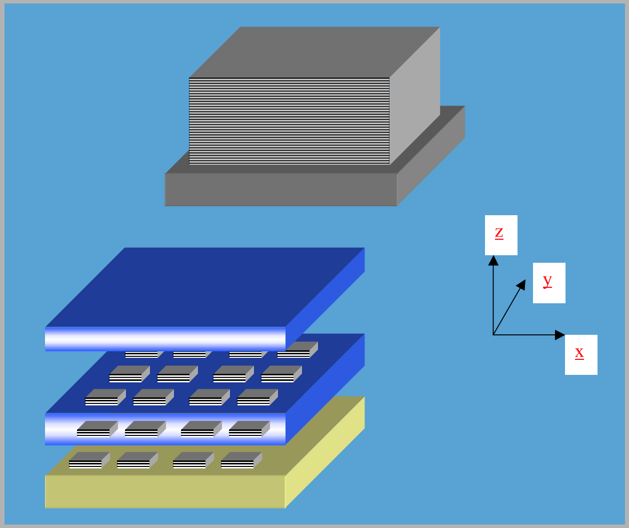
Further Possibilities with Nano-scale Thermoelectrics

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**