The direct conversion of heat to electricity using multiferroic materials

A completely new method of energy conversion for the small temperature difference regime

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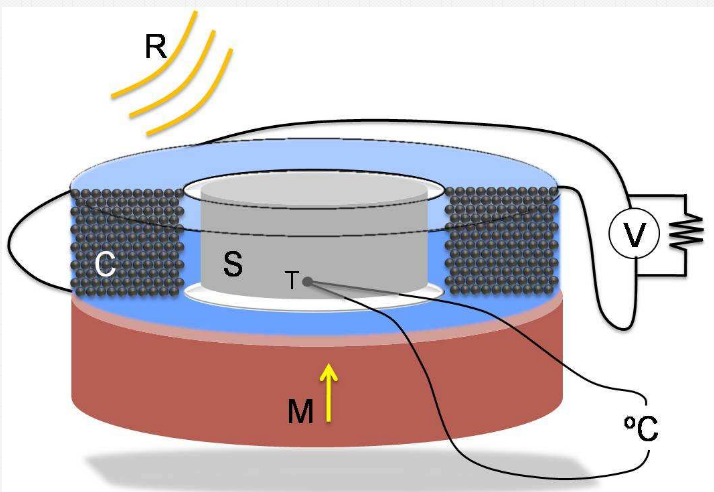
Workshop on the Potential Threat of Future Power and Energy Technology Breakthroughs
MITRE Corporation, March 27-28, 2012

Main Idea

- Use a material with a highly reversible first order martensitic phase transformation
- Arrange the two phases to have different electromagnetic properties such as magnetization or polarization

V. Srivastava, Y. Song, K. Bhatti and R. D. James, *Advanced Energy Materials* **1** (2011), 97-104



Fact Sheet on this technology available from R. D. James, james@umn.edu

Features

- **A completely new idea for energy conversion (2011).** Many ways to use the idea based on the choice of electromagnetic properties
- Adapted to **energy conversion at small temperature difference, ~10-100 C. There is no existing energy conversion device for this regime**
- **Highly tunable**, based on tuning the transformation temperature and the operating temperature range
- Key scientific breakthroughs that enable these devices:
  - An understanding of the **origins of hysteresis** in phase transformations, and **a way to make exceptionally low hysteresis alloys**
  - A correlation between low hysteresis and **reversibility**
  - An understanding of the "lattice parameter sensitivity" of electromagnetic properties and its use in phase transformations. **Multiferroic materials by phase transformation**

There are many sources of energy on earth stored at small temperature difference

- The natural sources: **deserts** and the **arctic**
- **US Industry** consumes a terawatt, ~1/15 of all the power consumed on earth (DOE, 2008): 25-50% rejected as waste heat. 60% of this is “low grade” waste heat, rejected at < 232 C
- Computers: **US data centers** now consume 2.5% of the national energy budget
- Waste heat from **laptop** and **desktop computers**
- **Hand held electronic devices** (phones, videogames)
- The waste heat from **automobile exhaust systems**
- The waste heat from **air conditioning systems** and **power plants**
- Accumulated heat in **attics and roofs**
- The rapidly growing list of **solar thermal plants**

Thin film devices: **chip level integration**

The huge sources

- **The major existing and planned solar thermal plants**

Seville, Spain

- **The arctic and deserts of the world**

< 3 m ice sheet

-40 to -20°C for 10 months/year

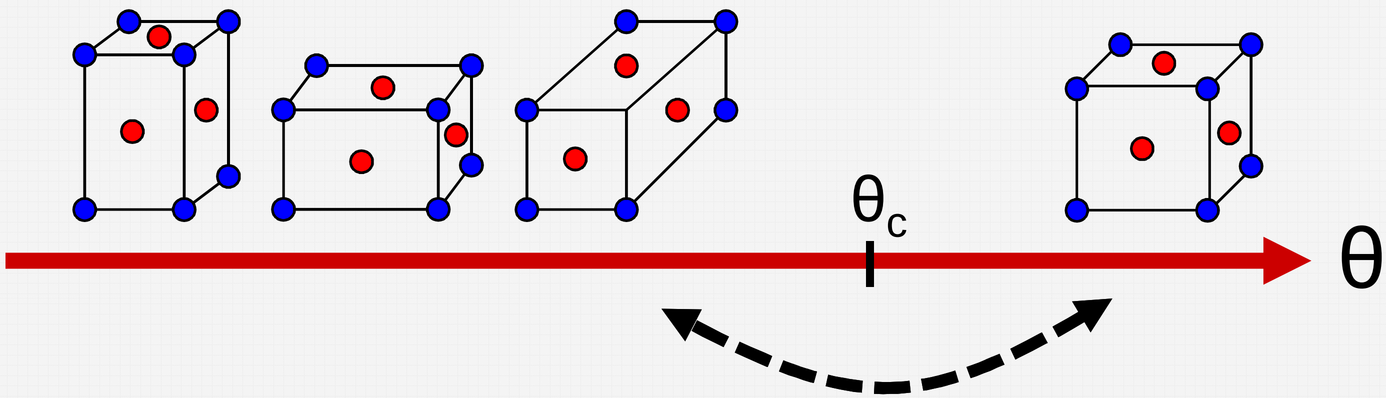
≈ 0°C

First order phase transformations + magnetism (or other collective property)

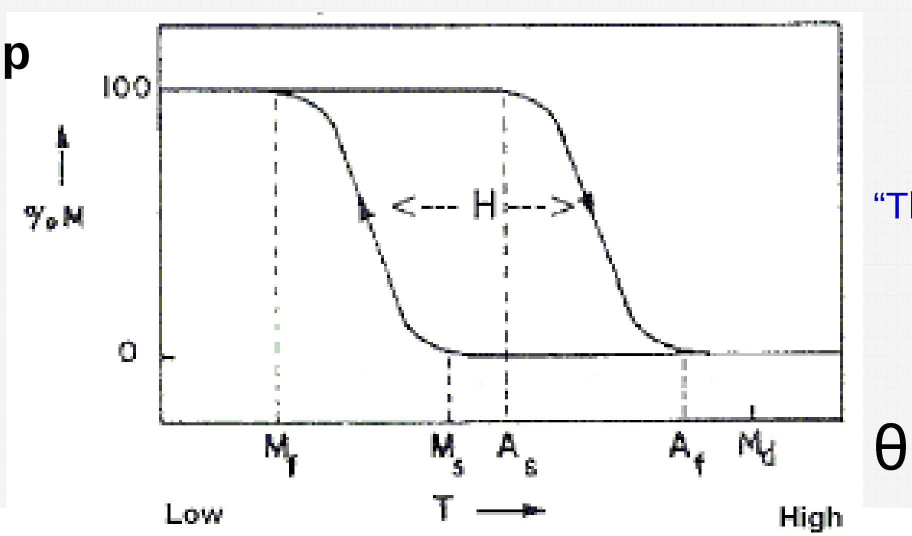
- Why?
  - Magnetic properties are sensitive to the lattice parameters. Fe + N
  - First order phase transformations have a change of lattice parameters: martensitic transformations
  - Can switch back and forth between "completely different materials"
  - Martensitic phase transformations are fast: no diffusion
  - Latent heat
- Many first order phase transformations are not reversible: what governs **reversibility** of martensitic transformations?

Main advance1: origins of hysteresis*

Martensitic phase transformation



Hysteresis loop

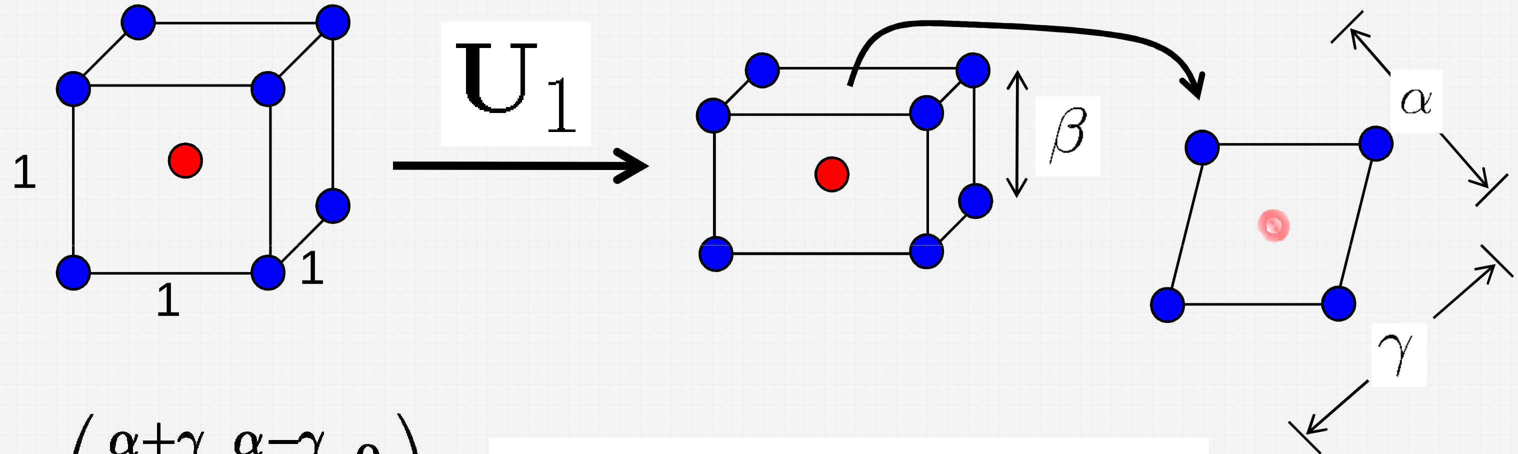


"Thermal hysteresis"

*This part of the research supported by a MURI program, "MURI on the Brink" (grant monitor: John Prater, ARO)

Transformation matrix

(Transformation stretch matrix)

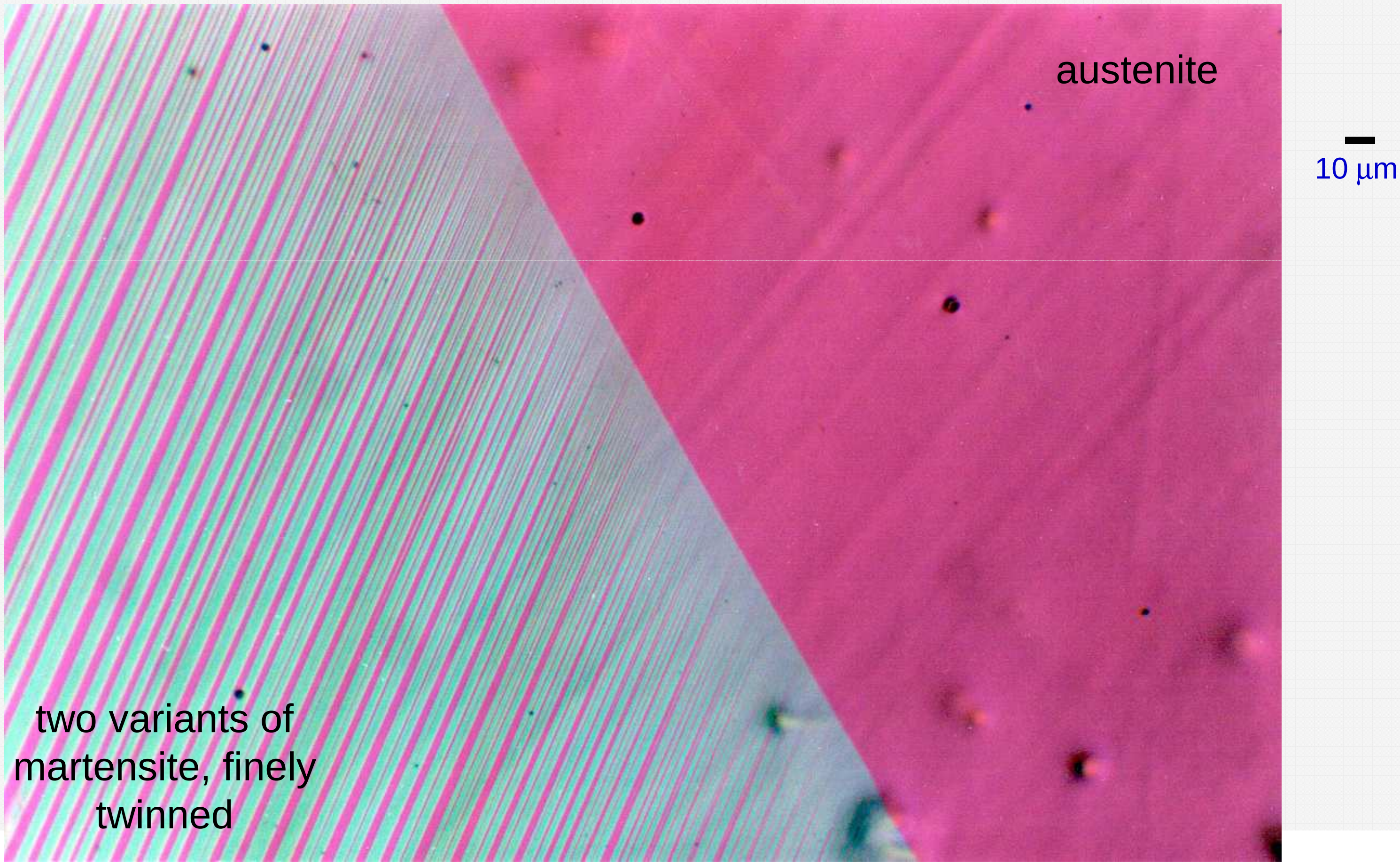


$$\mathbf{U}_1 = \begin{pmatrix} \frac{\alpha+\gamma}{2} & \frac{\alpha-\gamma}{2} & 0 \\ \frac{\alpha-\gamma}{2} & \frac{\alpha+\gamma}{2} & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

eigenvalues $\lambda_1 \leq \lambda_2 \leq \lambda_3$

The austenite/martensite interface from the perspective of energy minimization

The typical mode of transformation when $\lambda_2 \neq 1$:



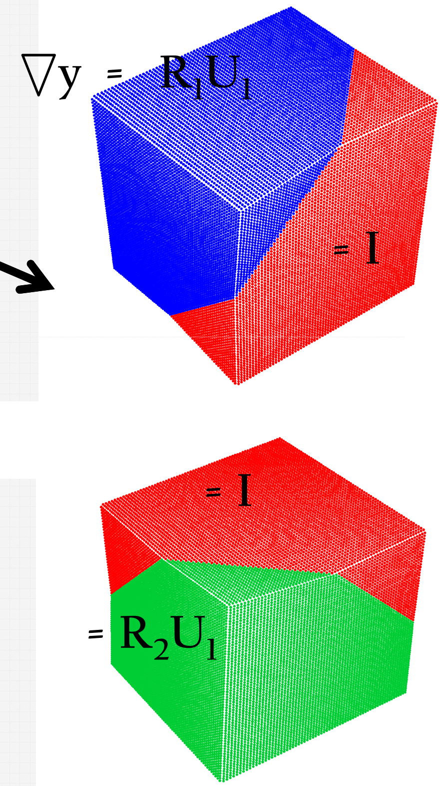
Origins of hysteresis

$$\mathbf{U}_1 \overset{\text{for example}}{=} \begin{pmatrix} \frac{\alpha+\gamma}{2} & \frac{\alpha-\gamma}{2} & 0 \\ \frac{\alpha-\gamma}{2} & \frac{\alpha+\gamma}{2} & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

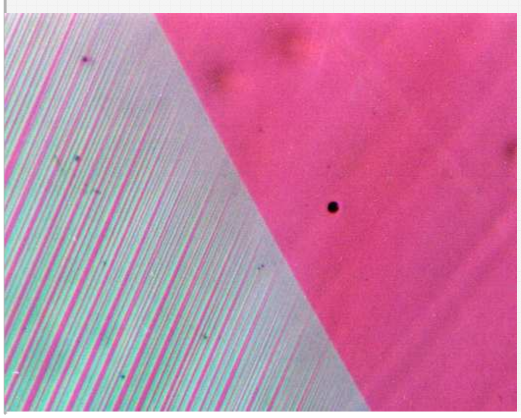
$$\text{eigenvalues } \lambda_1 \leq \lambda_2 \leq \lambda_3$$

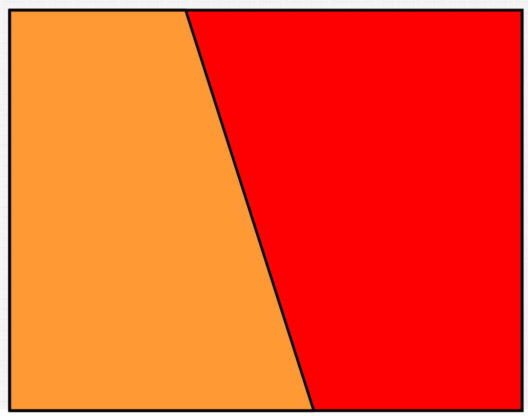
$$\lambda_2 = 1$$

Is necessary and sufficient that the phases fit together perfectly, without a stressed transition layer



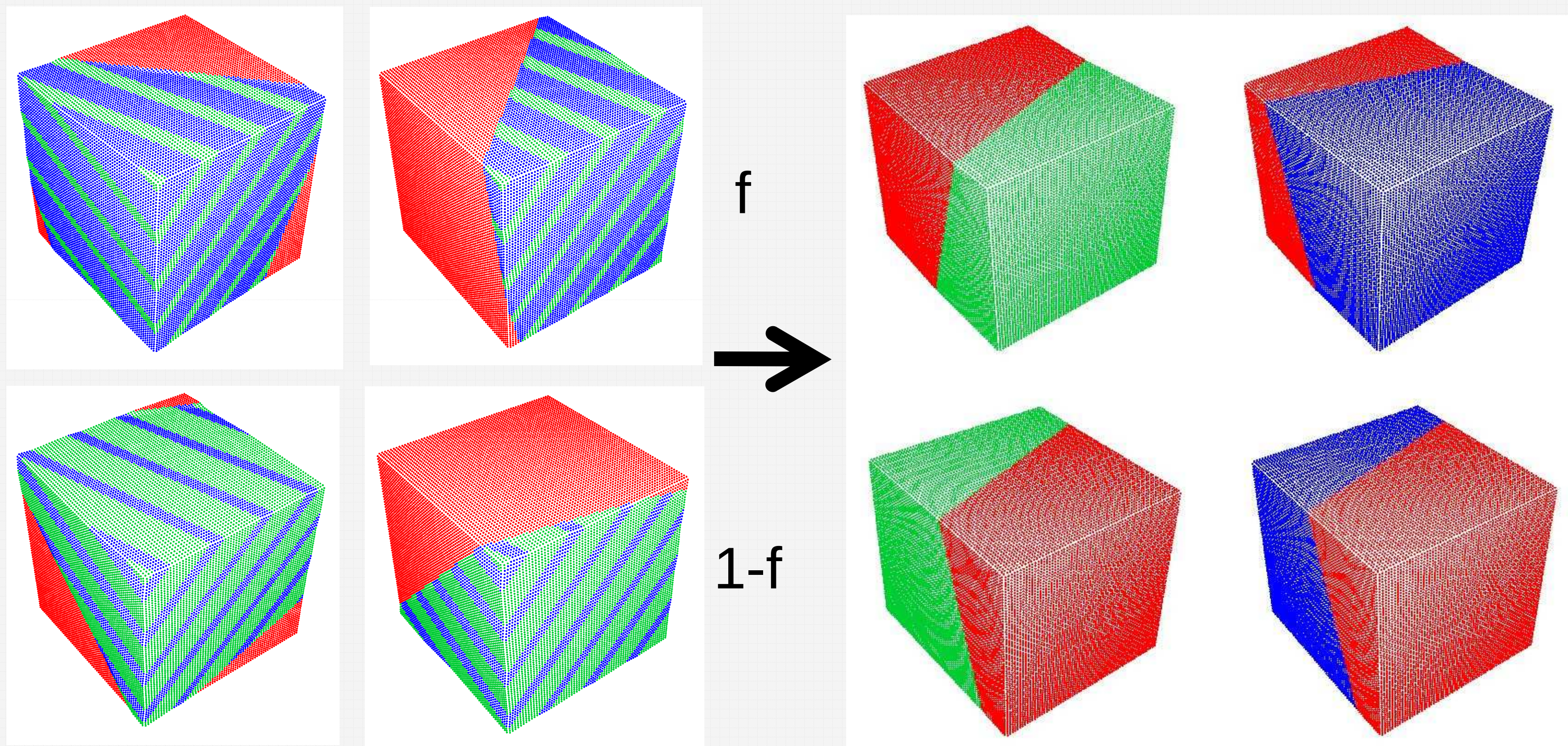
Alloy development: **tune the composition to make** $\lambda_2 = 1$





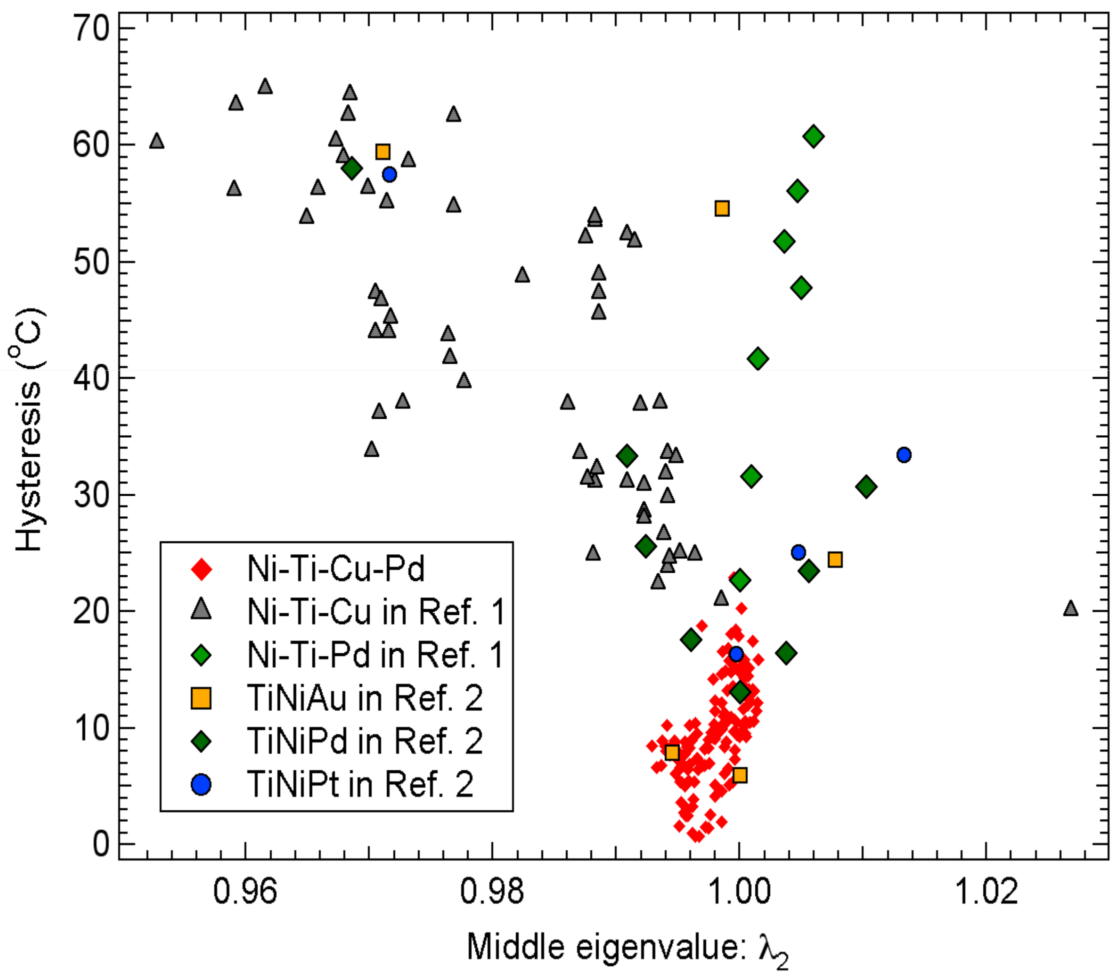
When $\lambda_2 = 1$…

…the 4 solutions degenerate to:



(no loss of the number of strains)

Hysteresis vs. λ_2 using combinatorial synthesis methods

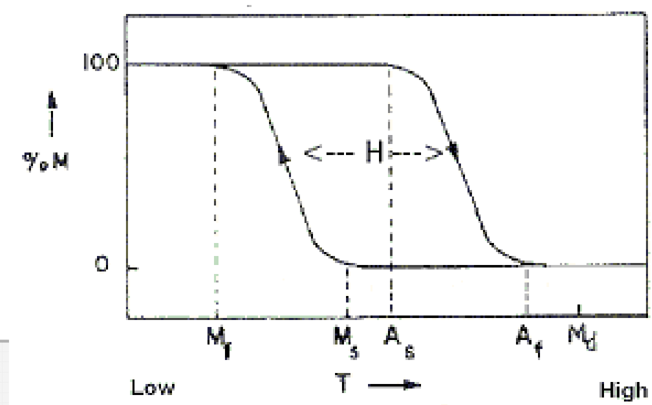


Red: Zarnetta et al., Adv. Funct. Matls, 2009

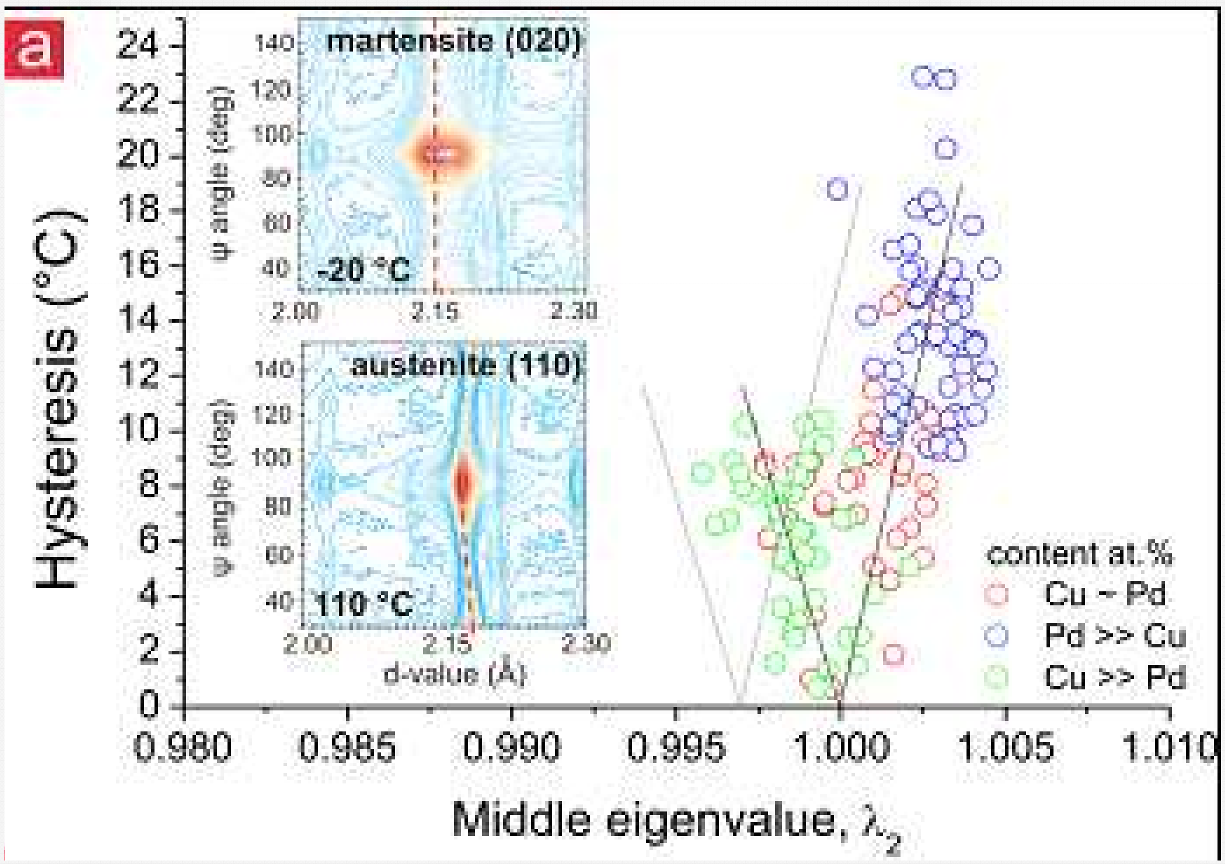
Ref. 1 J. Cui et al. *Nature Materials*, **5**, 286 (2006), Ref. 2 Z. Zhang et al., *Acta Materialia*

Correction for stress

Hysteresis = $(1/2)(A_s + A_f - M_s - M_f)$



Zarnetta et al., Adv. Functional Materials,
DOI: 10.1002/adfm.200902336

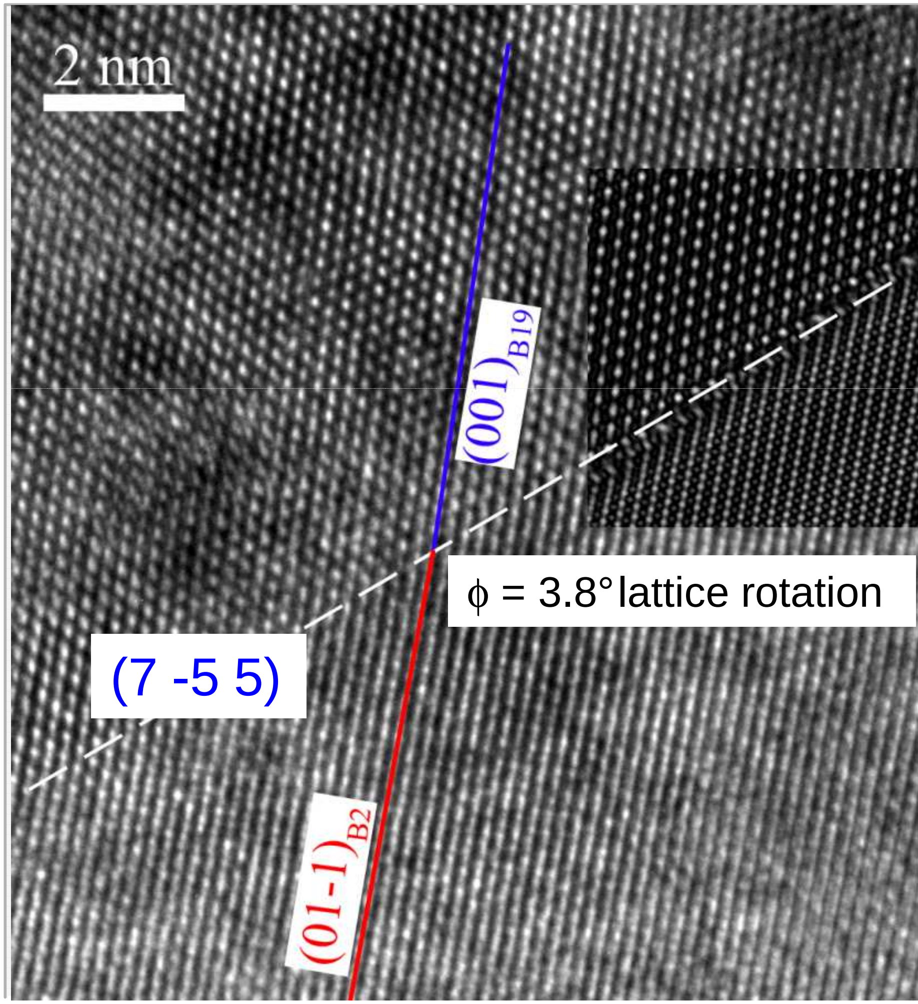


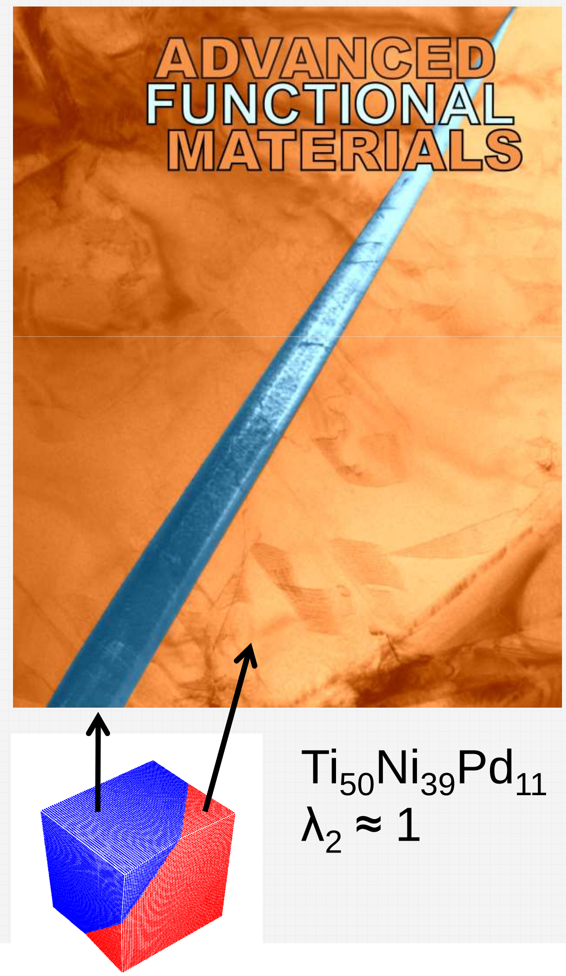
Materials with
big first order phase
transformations and
1-2 C thermal hysteresis
were extremely unusual
prior to this work

HRTEM austenite / single variant martensite interface

$Ti_{50}Ni_{39}Pd_{11}$ $\lambda_2 \approx 1$

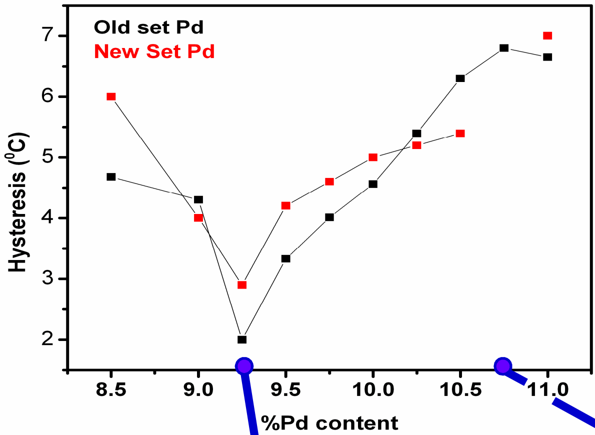
Delville, Schryvers



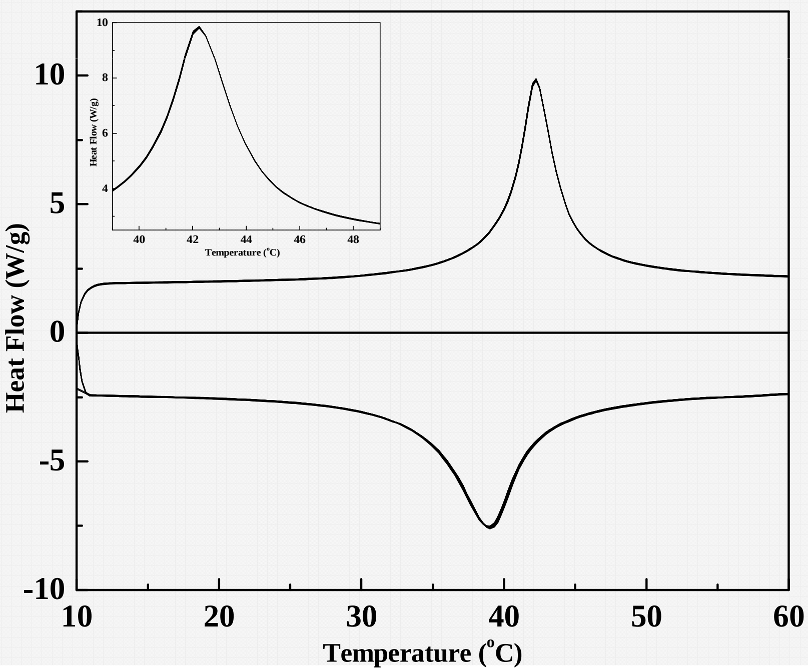


$Ti_{50}Ni_{39}Pd_{11}$
$\lambda_2 \approx 1$

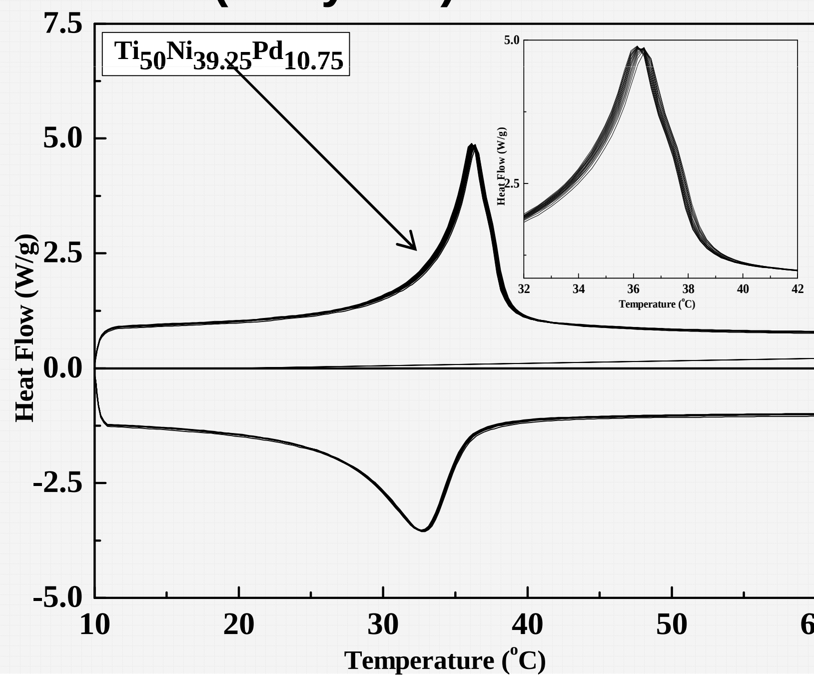
Main advance 2: hysteresis and reversibility



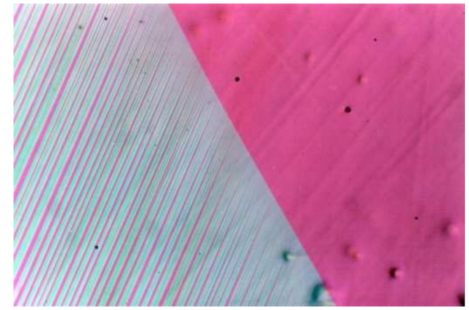
$Ti_{50}Ni_{40.75}Pd_{9.25}$ (30 cycles) λ_2 = 1.0000



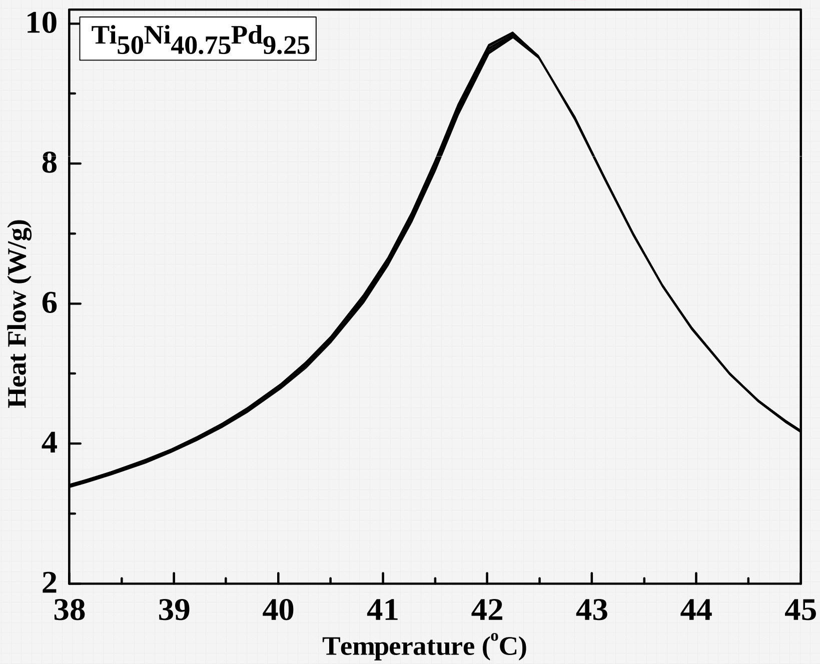
$Ti_{50}Ni_{39.25}Pd_{10.75}$ (30 cycles) λ_2 = 1.0060



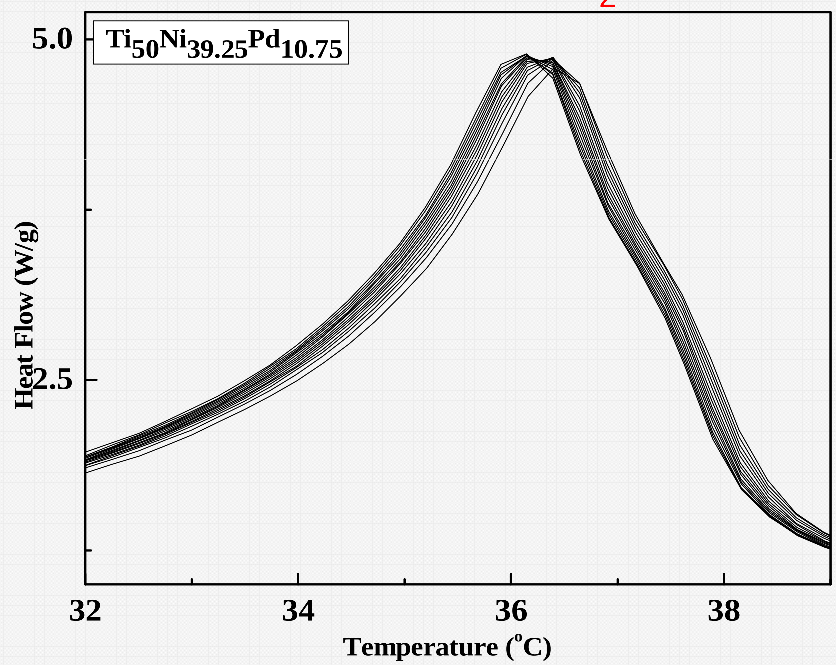
Close up view



$Ti_{50}Ni_{40.75}Pd_{9.25}$
(30 cycles) λ_2 = 1.0000



$Ti_{50}Ni_{39.25}Pd_{10.75}$
(30 cycles) λ_2 = 1.0060



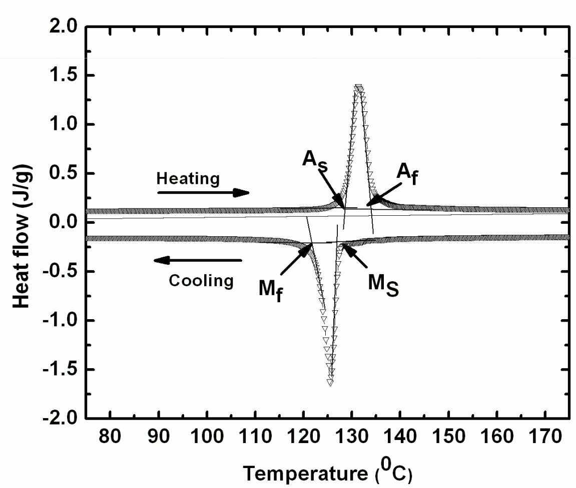
Main advance 3: multiferroic materials by phase transformation

V. Srivastava, X. Chen, James

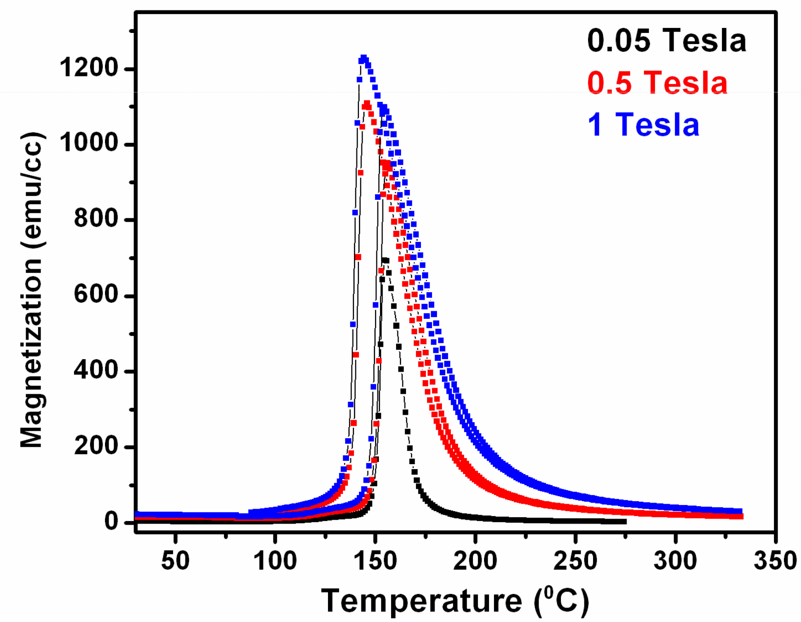
$Ni_{43}Co_7Mn_{40}Sn_{10}$

$\lambda_2 = 1.0032$

calorimetry

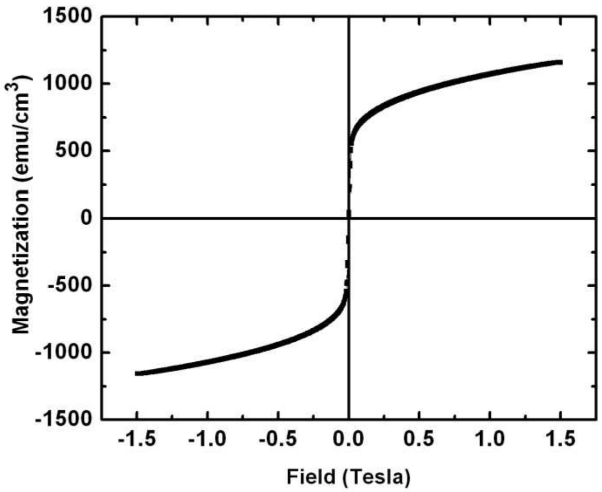


magnetization vs. temperature



$Ni_{43}Co_7Mn_{40}Sn_{10}$: a soft magnet

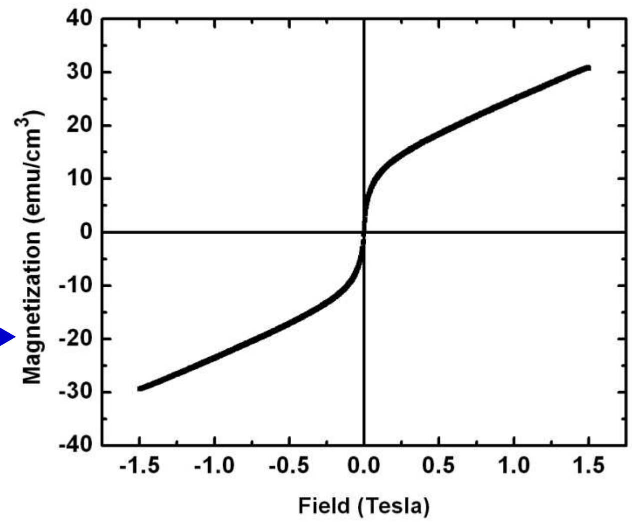
V. Srivastava, X. Chen, James



magnetization vs. field

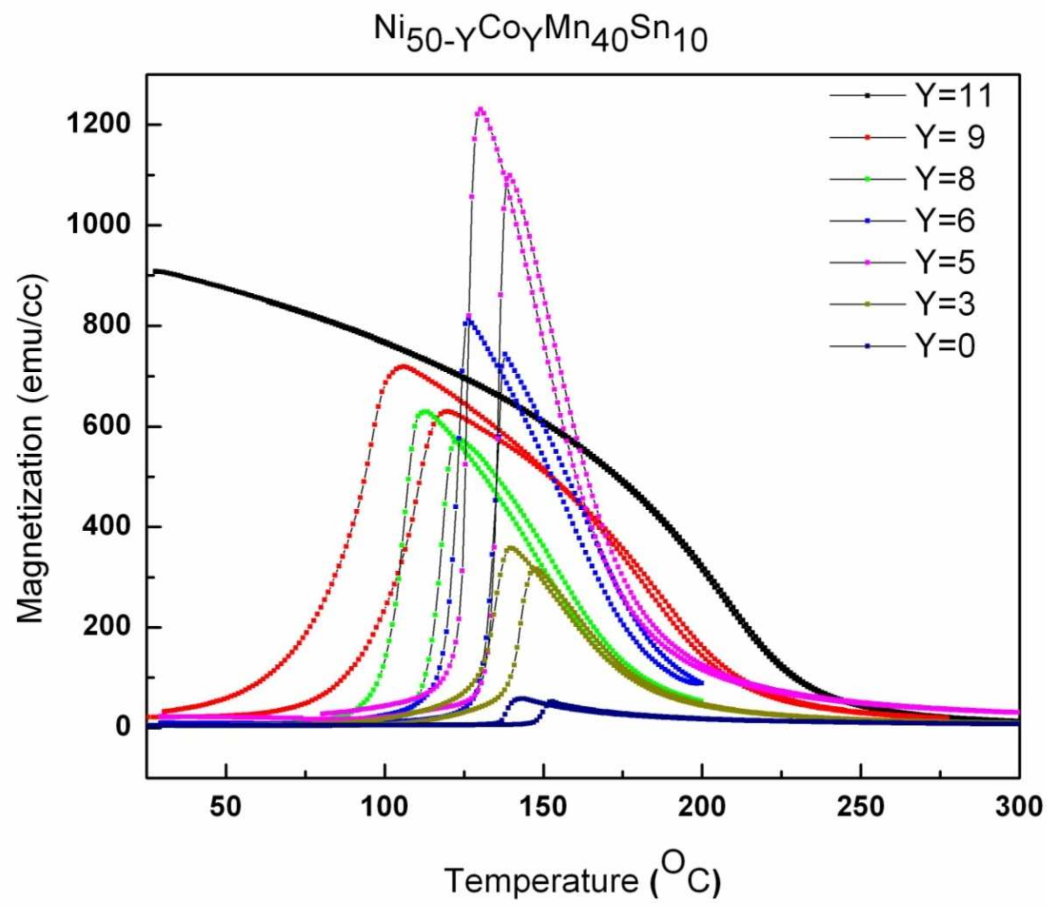
austenite

martensite



$Ni_{43}Co_7Mn_{40}Sn_{10}$ and nearby alloys

V. Srivastava, X. Chen, James

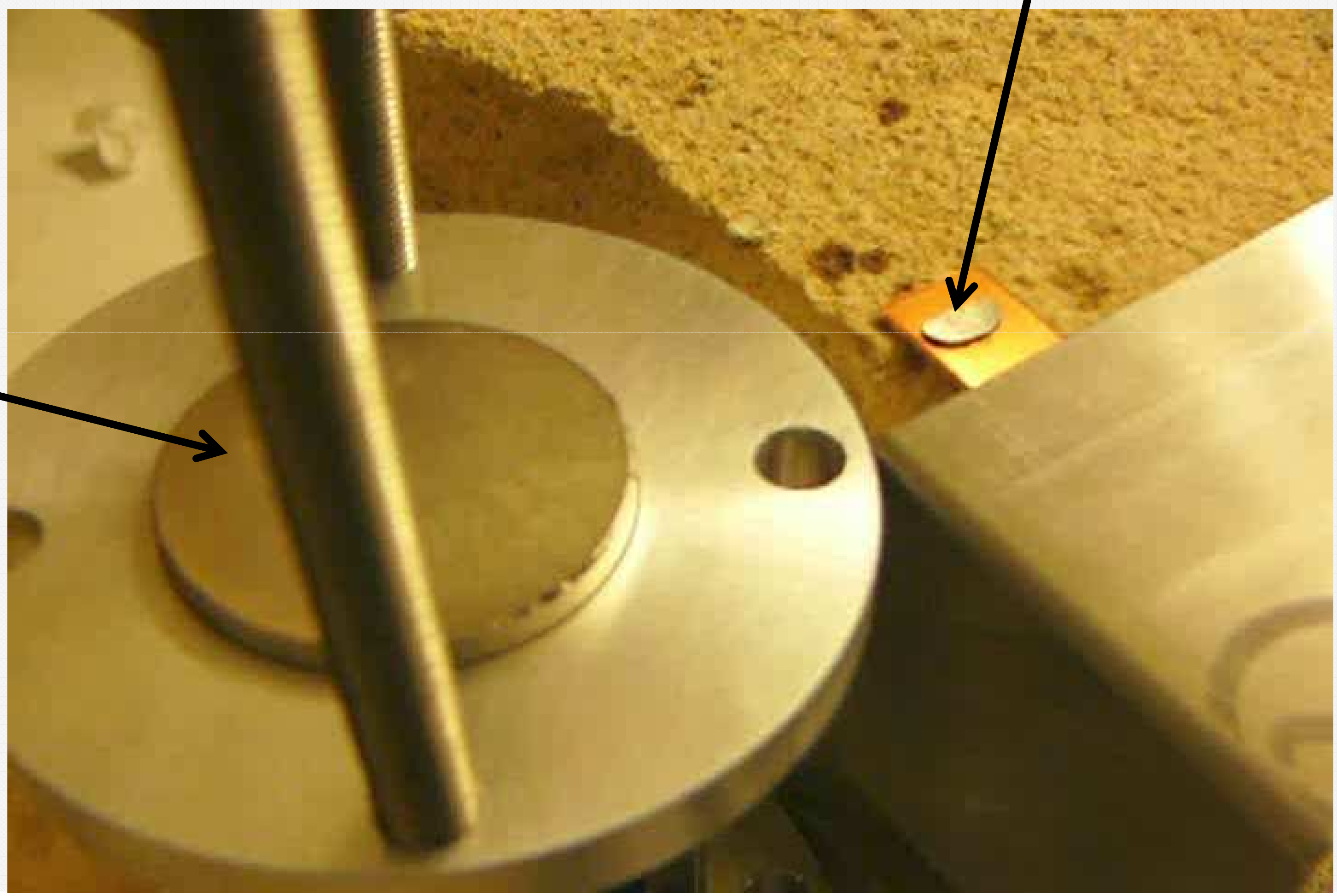


$Ni_{43}Co_7Mn_{40}Sn_{10}$

Specimen of $Ni_{43}Co_7Mn_{40}Sn_{10}$ on a copper finger. The copper is being heated

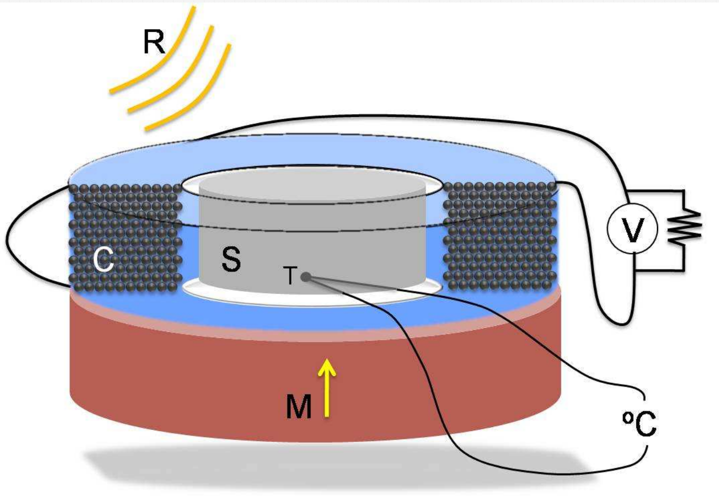
7.5 cm

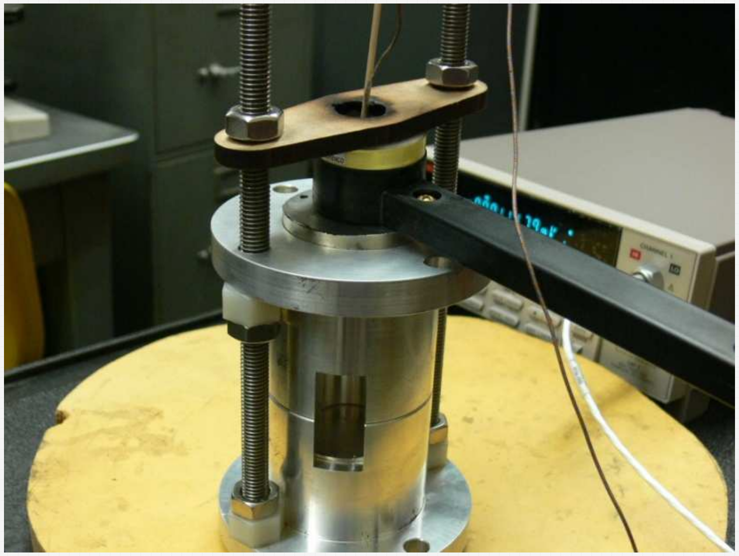
permanent magnet



Energy conversion demonstration

Adv. Energy Materials 1 (2011), 97-104





$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$$

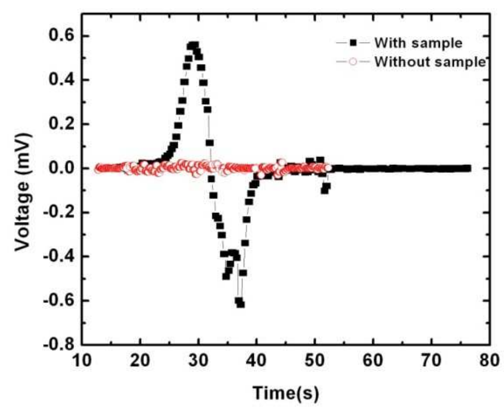
$$\mathrm{curl}\mathbf{E} = \frac{-1}{c}\frac{d\mathbf{B}}{dt}$$

$$\left(\frac{4\pi AN(1+(4\pi-\delta)\chi(t))}{c^2 L_{eff}}\right) I'(t) + \left(\frac{8r_c}{d^2\sigma} + \frac{R}{N} + \frac{4\pi AN(4\pi-\delta)\chi'(t)}{c^2 L_{eff}}\right) I(t) + \frac{A(4\pi-\delta)\chi'(t)h_0}{c} = 0$$

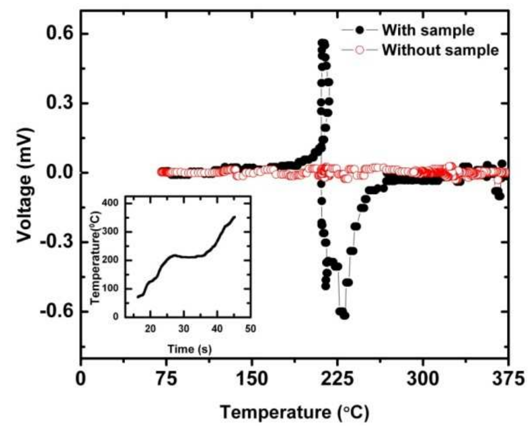
Yintao Song

Measured voltage, and comparison with the simple model: heating

Measured voltage vs. time

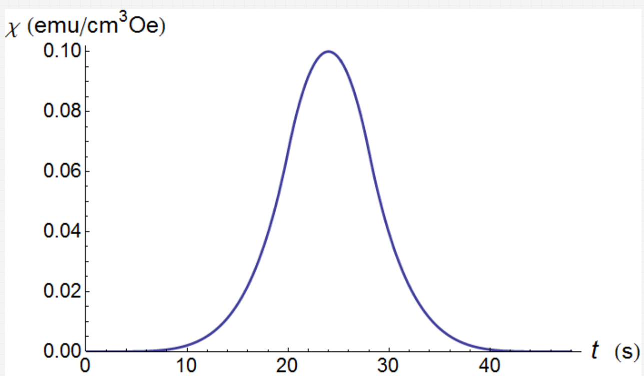


Measured voltage vs. temperature

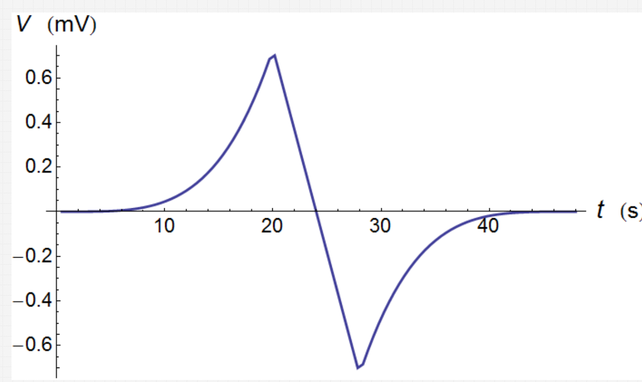


compare

Assumed susceptibility vs. time



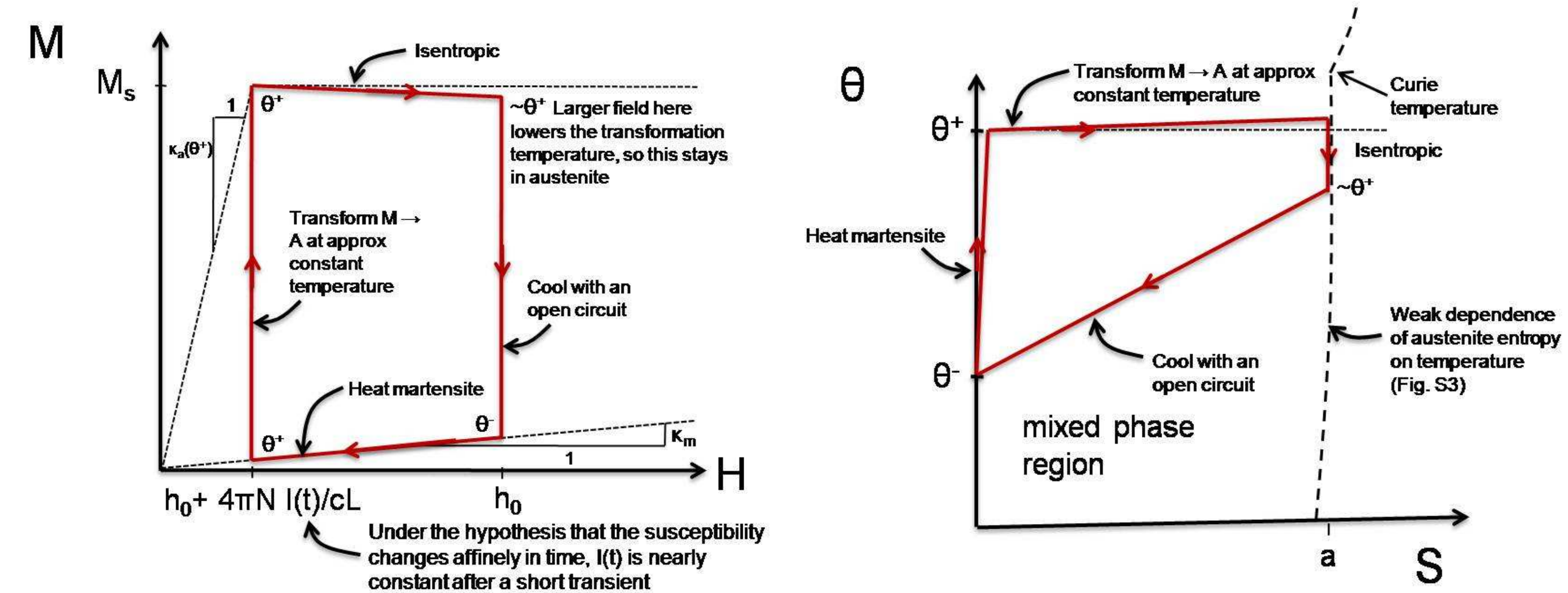
Calculated voltage vs. time



Thermodynamic cycles

Y. Song, K, Bhatti, V. Srivastava, C. Leighton, R. James, preprint

Based on a simple thermomagnetic free energy, φ(M,θ), calibrated from experiment…



- Concept adapted to energy conversion at small temperature difference
- The **effect of magnetic field on transition temperature** is a key parameter

Other ways to convert heat to electricity using multiferroic materials

Phase 1	Phase 2	Physics	Notes
1. Ferromagnetic	Nonmagnetic	Faraday's law	Biasing by a permanent magnet; external coil
2. Ferroelectric	Nonferroelectric	Ohm's law	Biasing by a capacitor; polarization-induced current
3. Ferromagnetic; high anisotropy	Ferromagnetic; low anisotropy	Faraday's law	Biasing by a permanent magnet, intermediate magnetic field; external coil
4. Ferroelectric; high permittivity	Ferroelectric; low permittivity	Ohm's law	Biasing by a capacitor, intermediate electric field; polarization-induced current
5. Ferroelectric; large P_s near T_c (large pyroelectric coefficient)	Nonpolar	Ohm's law	Second-order transition; biasing by a capacitor
6. Ferromagnetic; large M_s near T_c (small critical exponent)	Nonmagnetic	Faraday's law	Second-order transition; biasing by a permanent magnet
7. Nonpolar; nonmagnetic	Nonpolar; nonmagnetic	Stress-induced transformation; Faraday's law	Shape-memory engine driving generator; biased by stress

Multiferroic energy conversion: questions

- **Does this technology have the potential to disrupt the energy landscape in the next 5-30 years?**
  - Yes. Most likely near term: solar thermal plants, small solar thermal distributed energy conversion, waste heat in computers and from air conditioning systems
- **Who will develop them?**
  - Scientists and engineers in the country that is willing to fund **basic and applied research, and development,** in this area. US? China? Germany?
- **When will they mature?**
  - 5-30 years
- **How will their cost and performance compare to current technologies?**
  - Not known. The useful ΔT regime for multiferroic energy conversion is not currently being exploited

Multiferroic energy conversion: questions, continued

- **What are the economic, military, geopolitical, environmental and social implications?**
  - **Economic**: governments are currently willing to spend >$ 10^9 on solar thermal plants. Distributed energy conversion also possible. Many other possible uses of highly reversible, multiferroic phase change materials in microelectronics, information storage, actuation, refrigeration
  - **Military**: A completely new method. Potential for use as a light, small, quiet energy conversion system for surveillance systems, requiring no fuel or light. Autonomous sensors and communication devices requiring no batteries. A new source of space power. A new material for thermal management.
  - **Geopolitical**: No obvious geopolitical restrictions, but the deserts and polar regions of the world may have special significance. No rare materials use in the current devices
  - **Environmental**: No toxic material used in current or projected demonstrations. No significant greenhouse gas emissions
  - **Social**: A green technology. Apparently acceptable to society. Does not seem to necessitate major behavioral changes

Multiferroic energy conversion: questions, continued

- **What are the threats of either developing or not developing the technology?**
  - No obvious threat resulting from the development of the technology
  - Threat of not developing the technology is loss of a potentially broad economic driver, potential dependence on unfriendly countries for important power-producing devices and systems, loss of leadership in technology, inability to play a leadership role in worldwide green energy production, inability to meet worldwide standards of greenhouse gas emissions

Literature

- V. Srivastava, Y. Song, K. Bhatti and R. D. James, The direct conversion of heat to electricity using multiferroic alloys, *Advanced Energy Materials* **1** (2011), 97-104
- V. Srivastava, X. Chen and R. D. James Hysteresis and unusual magnetic properties in the singular Heusler alloy $Ni_{45}Co_5Mn_{40}Sn_{10}$ alloy, *Applied Physics Letters* **97** (2010), 014101
- R. D. James and Z. Zhang, A way to search for multiferroic materials with 'unlikely' combinations of physical properties, in *Magnetism and Structure in Functional Materials* (ed., Lluis Manosa, Antoni Planes, Avadh Saxena), Springer Series in Materials Science **79**, 159-174, Springer (2005)
- R. Zarnetta, et al., Identification of quaternary shape memory alloys with near-zero thermal hysteresis and unprecedented functional stability, *Advanced Functional Materials* **20** (2010), 1-7
- R. James, **Fact Sheet:** New Energy Conversion Concept, available from james@umn.edu