CENTER for ENVIRONMENTAL ENERGY ENGINEERING

Advances in Caloric Cooling Technologies

July 2017

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The 8th International Conference on Compressors and Refrigeration, Xi'an, China, 2017

Introduction

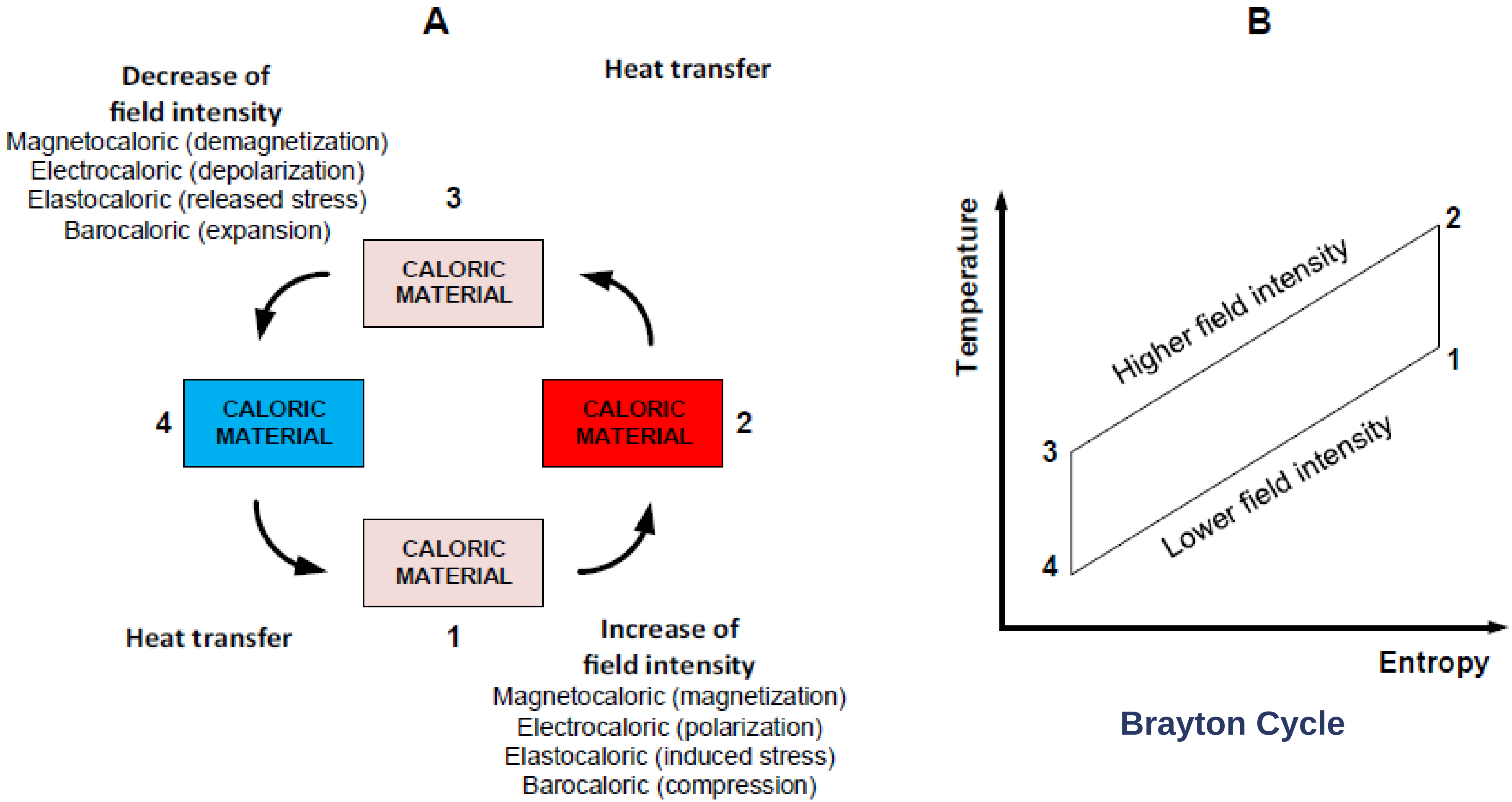
- To minimize environmental effects of HVAC systems, their direct and indirect GHG emissions should be reduced.
- Use working fluids with ultra-low GWPs
- Improve the efficiency of vapor compression cycles
- Develop a new cooling technology, which uses working fluids with ultra-low GWPs and is more efficient.
- This work presents the overview of caloric cooling technologies.

Introduction

Not-in-kind Cooling Technologies

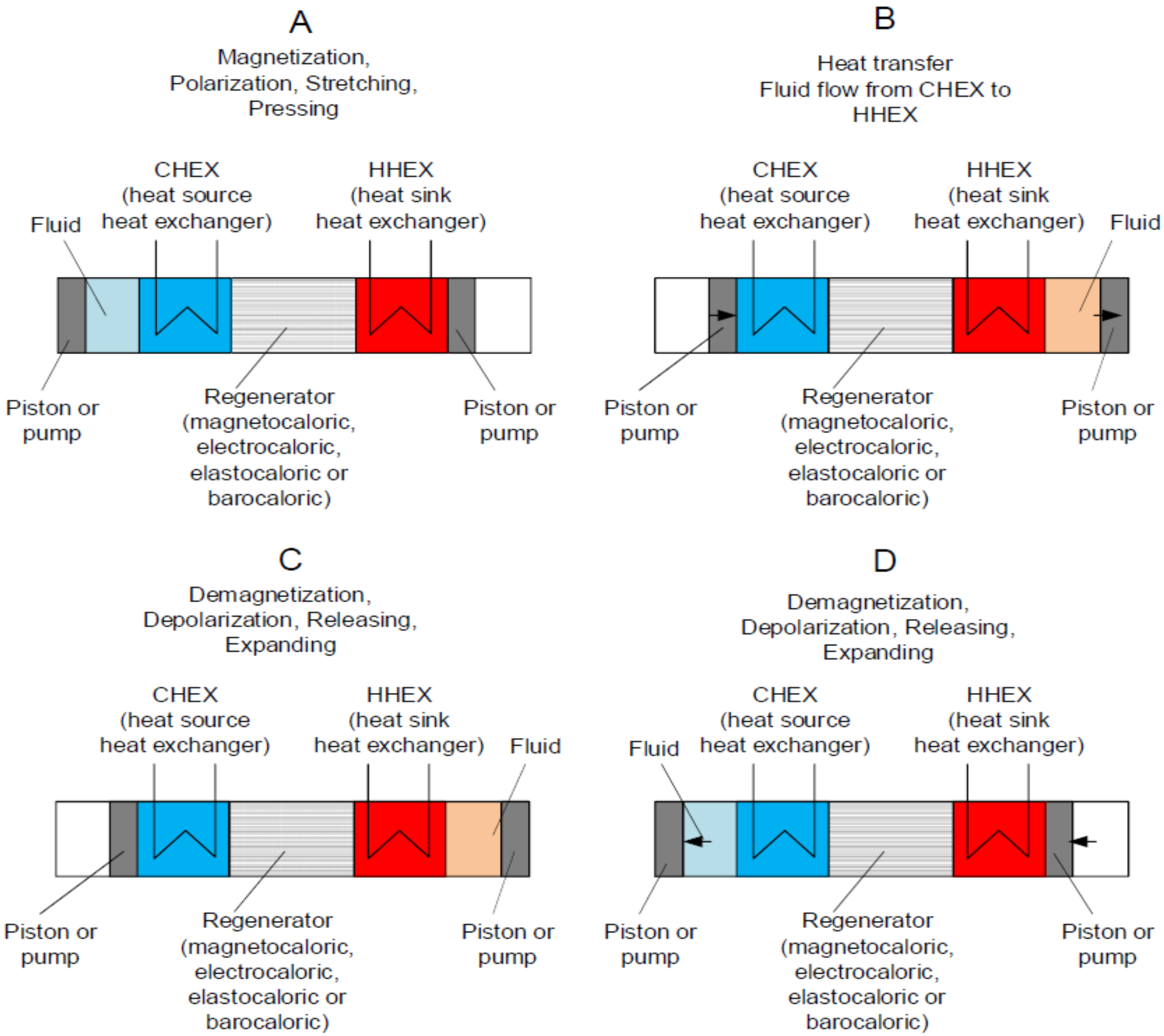
- **Solid-State**
  - **Magnetocaloric**
  - **Electrocaloric**
  - **Elastocaloric**
  - **Thermoelectric**
  - Thermoionic
- Heat activated
  - **Absorption**
  - **Adsorption**
  - Ejector
  - Vuilleumier heat pump
- Gaseous
  - Thermoacoustic
  - Brayton heat pump
  - Stirling heat pump
  - Vortex-tube
  - Pulse-tube
- Liquid-vapor
  - Membrane heat pump
  - Metal hydride
  - **Electro-chemical compression**
- Others
  - Malone cycle

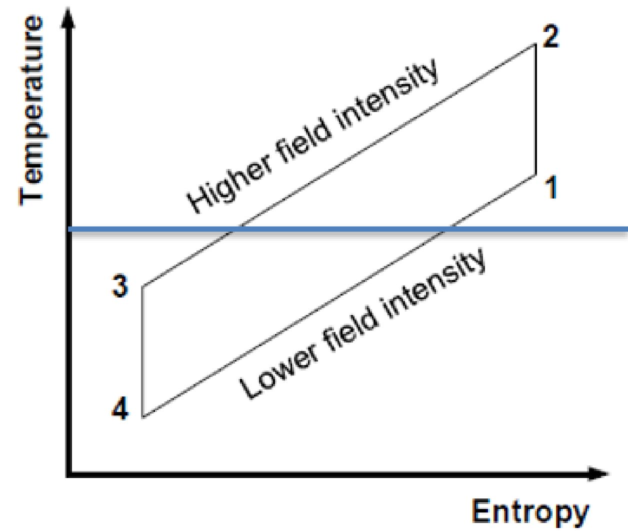
Caloric Cooling Process



Kitanovski et al., IJR, 57 (2015)

Active Caloric Regeneration Process

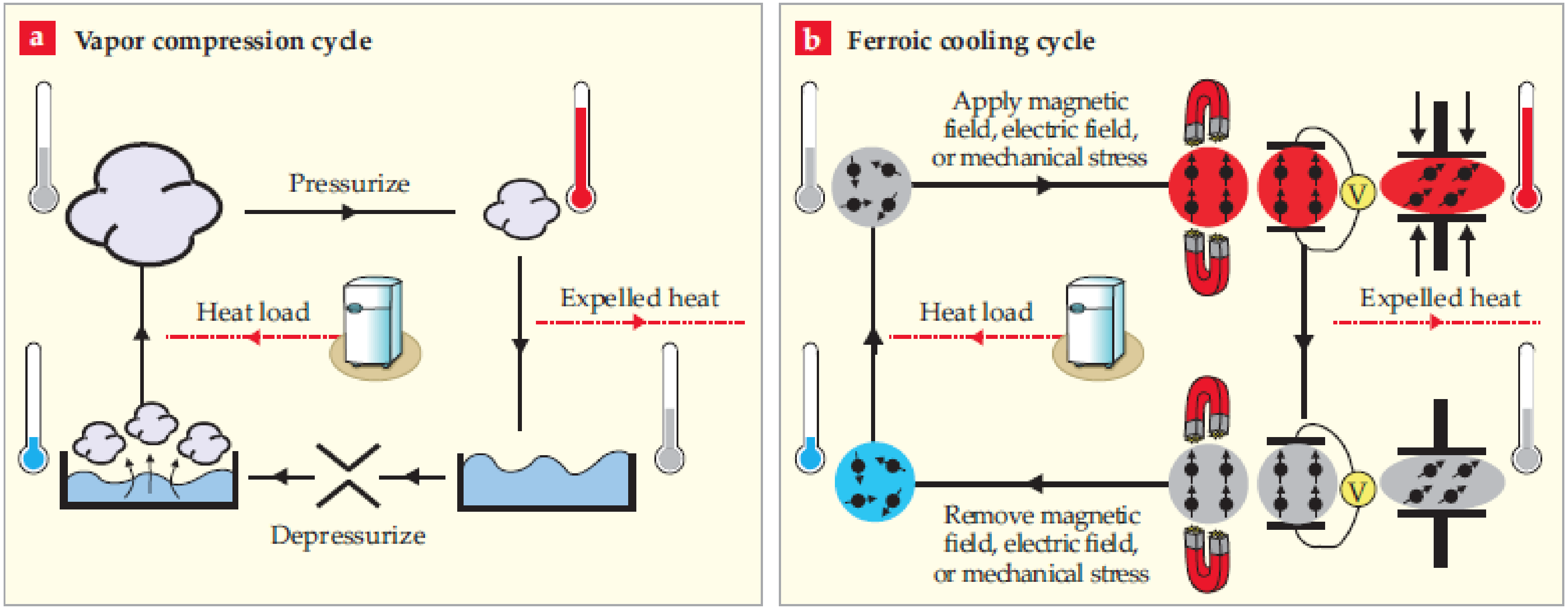




Kitanovski et al., IJR, 57 (2015)

Magnetocaloric (MC)

MC Working Principle



Refrigerant is fluid and moves through the conditioned space to exchange heat.	Refrigerant is solid, and the system requires a heat transfer fluid to exchange heat with the conditioned space.

List of Magnetocaloric Cooling Projects

EU projects

DRREAM – Drastically Reduced Use of Rare Earths in Applications of Magnetocalorics (2013–2016), http://www.drream.eu/

ICE – MagnetoCaloric Refrigeration for Efficient Electric Air Conditioning (2010–2014), http://www.ice-project.webs.upv.es/home

ELICiT "Environmentally Low Impact Cooling Technology", (2014–2016), http://elicit-project.eu/

FRISBEE, Food Refrigeration Innovations for Safety, consumers' Benefit, Environmental impact and Energy optimization along the cold chain in Europe, (2010–2014), http://www.frisbee-project.eu/

FRIMAG: "Demonstrator of drinks cooler running by means of magnetic refrigeration". France & Switzerland (INTERREG IV A), http://www.frimag.net/en-gb/home/Pages/home.aspx

US projects

Air Conditioning With Magnetic Refrigeration, Program: BEETIT, ARPA-E AWARD (2010–2014), http://arpa-e.energy.gov/?q=slick-sheet-project/air-conditioning-magnetic-refrigeration

Magnetocaloric Refrigeration, US DOE – CRADA PROJECT (ORNL + GE), (2013–2016), http://energy.gov/eere/buildings/downloads/magnetocaloric-refrigeration

Novel magnetocaloric air conditioner, project founded by U.S. Department of Energy, announced in 2015, http://energy.gov/eere/articles/energy-department-invests-nearly-8-million-develop-next-generation-hvac-systems

Larger National projects in Europe

ENOVHEAT project which is funded by the Danish Council for Strategic Research within the Programme Commission on Sustainable Energy and Environment (2013–2017), Denmark, http://www.enovheat.dk/

SPP 1599 "Ferroic Cooling", Caloric Effects in Ferroic Materials: New Concepts for Cooling (Magnetocaloric, electrocaloric, elastocaloric), Start in 2012, Germany, http://www.ferroiccooling.de/

MagCool: "New giant magnetocaloric materials round room temperature and applications to magnetic refrigeration, (2011–2015), France, http://www.agence-nationale-recherche.fr/?Project=ANR-10-STKE-0008

Kitanovski et al., IJR, 57 (2015)

Magnetic Material: La(Fe-Mn-Si)13

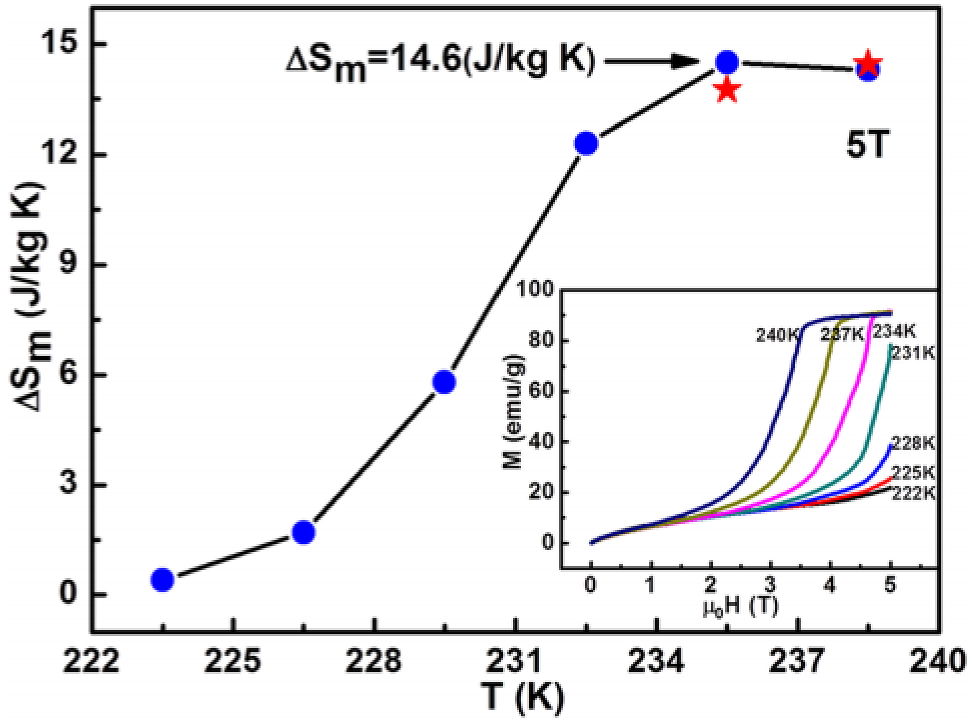


FIG. 4. The reversible magnetic entropy change (ΔS_m) under a magnetic field of 5 T shown as a function of temperature. The solid stars denote the data estimated from the Clausius-Clapeyron relation. The inset shows the *M(H)* curves measured at different temperatures from 222 to 240 K with an interval of 3 K. For clarity, only the curves recorded during increasing magnetic fields are displayed.

L. Huang, D. Y. Cong, L. Ma, Z. H. Nie et al., Large reversible magnetocaloric effect in a Ni-Co-Mn-In magnetic shape memory alloy, Appl. Physics Letters, 108 032405 (2016).

Magnetic Material: La(Fe-Mn-Si)13

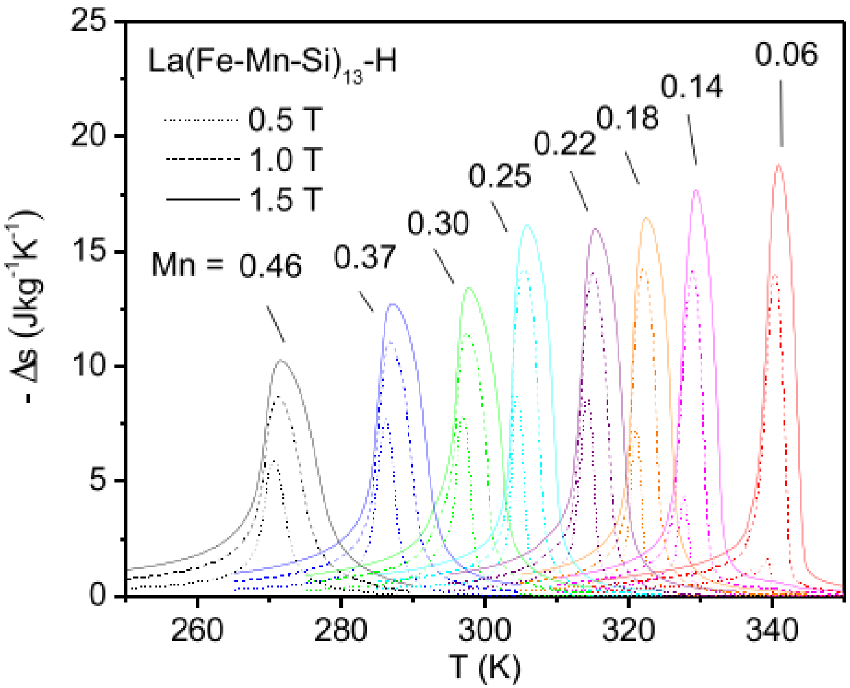


FIG. 7. Isothermal entropy change $-\Delta s_{iso}$ for cyclic processes of hydrogenated La(Fe-Mn-Si)$_{13}$ with different Mn content.

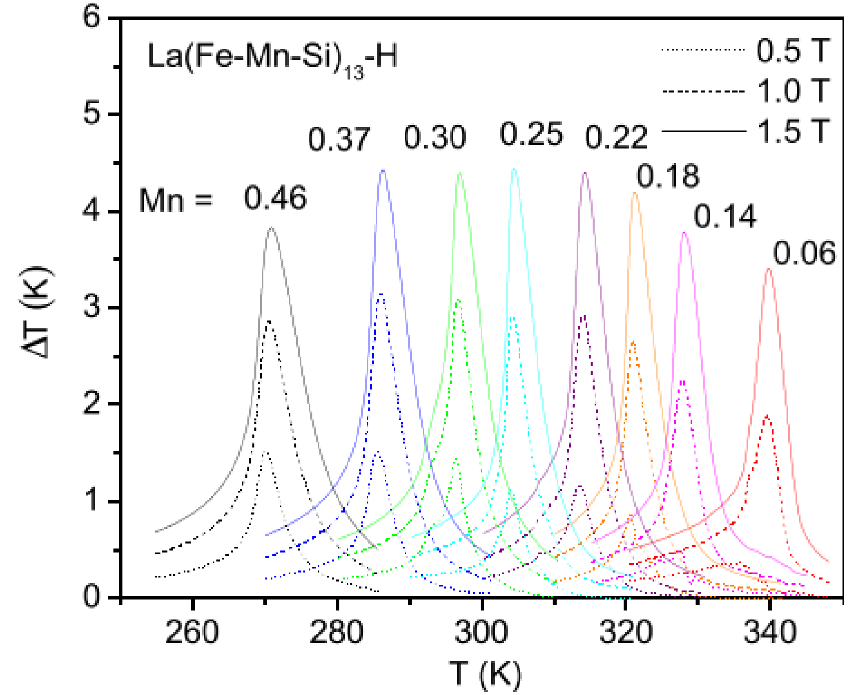


FIG. 8. Adiabatic temperature change ΔT_{ad} for cyclic processes of hydrogenated La(Fe-Mn-Si)$_{13}$ with different Mn content.

M. Krautz, K. Skokov, T. Gottschall, C.S. Teixeira, A. Waske, J. Liu, L. Schultz, O. Gutfleisch, Systematic investigation of Mn substituted La(Fe,Si)13 alloys and their hydrides for room-temperature magnetocaloric application, AIP. 118, 053907 (2015).

ELICit: EU's Research Project

- European Union (EU) started the three year research project, ELICiT "Environmentally Low Impact Cooling Technology" in 2014 to enhance the commercialization of magnetic cooling.
- The ELICiT Project focused on applying magnetic cooling to domestic refrigeration.
- Objectives are:
  - Life Cycle Optimization
  - System Optimization
  - Benchmarked Validation
  - Regulations and Standards

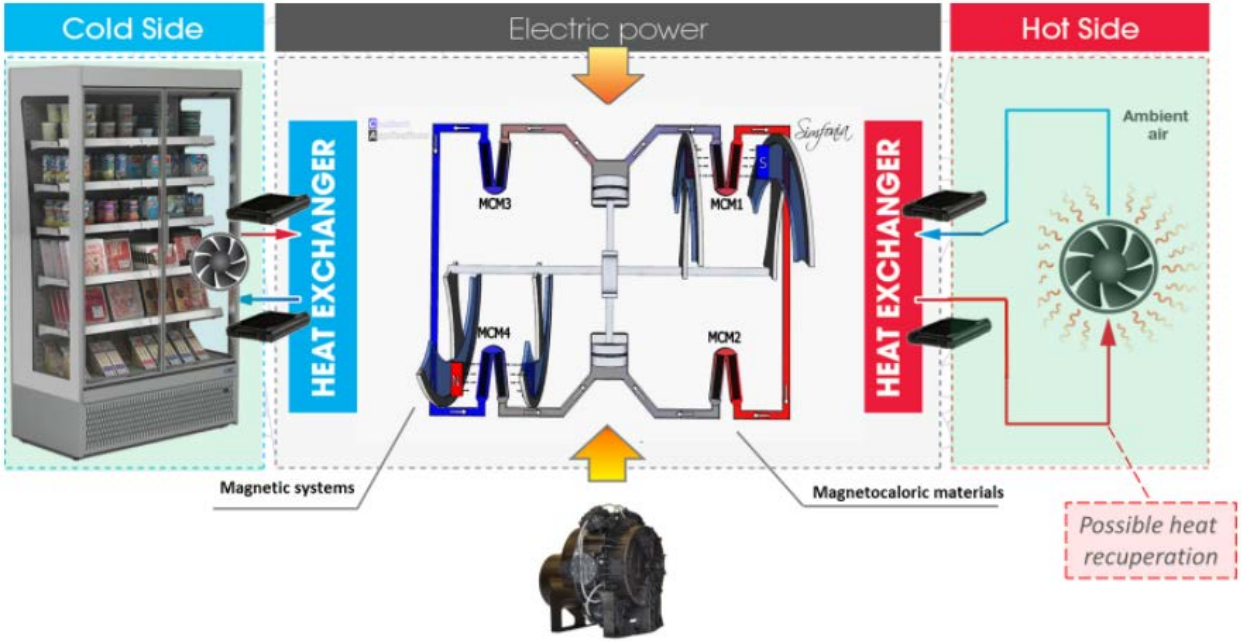
ELICit: Camfridge

- Magnetic cooling can double COP than R600a freezer
- Pump efficiency doubled.
- Optimized HXs
- Volume of three magnetic cooling systems:
  - Camfridge: 5,292 cm^3
  - Astronautics: 86,400 cm^3
  - CoolTech: 784,000 cm^3
- Used shaped magnetic material/HXs (others use sphere or powder) to make a compact system

Source: ICR 2015, Yokohama, Japan

ELICit: CoolTech

- 2 heat exchangers and 2 small pumps to circulate HTF
- For 380 liter volume cabinet, achieved 3.5-4.2°C T_{cabin} at 21.5°C T_{amb}, Power 38 W with direct HX loop
- Designed for wine cooler: capacity 200 W, COP 4.54, Achieved -4°C T_{low} and 40°C T_{high} at 20°C T_{ini}



http://www.cooltech-applications.com/magnetic-refrigeration-system.html

MC Challenges

- Magnetocaloric effect decreases as temperature moves away from Curie temperature, thus efficiency of all cycles degrades with increasing temperature lift.
- Need multi-stage cycles using different Curie temperatures as each stage can make only 1-2 K.
- Pumping power is a larger contributor to loss than in vapor compression; systems require 25~60X more pumping power.

Electrocaloric (ETC)

List of Electrocaloric and Elastocaloric Cooling Projects

Electrocaloric

EU projects

METCO – European Metrology Research Programme EURAMET - Electrocaloric cooling for clean refrigeration, http://projects.npl.co.uk/METCO/index.html (until end of 2016)

US projects

Solid State Cooling With Advanced Oxide Materials, AFRL-OSR-VA-TR-2014-0134, (2011–2014)

Electrocaloric heat pump, project founded by U.S. Department of Energy, announced in 2015, http://energy.gov/eere/articles/energy-department-invests-nearly-8-million-develop-next-generation-hvac-systems

Larger National projects in Europe

SPP 1599 "Ferroic Cooling", Caloric Effects in Ferroic Materials: New Concepts for Cooling (Magnetocaloric, electrocaloric, elastocaloric), Start in 2012, Germany, http://www.ferroiccooling.de/

Elastocaloric

US projects

Thermoelastic cooling, Department of Energy (DOE) Advanced Research Projects Agency—Energy (ARPA-E), (2010–2016), http://arpa-e.energy.gov/?q=slick-sheet-project/elastic-metal-alloy-refrigerants

Compact thermoelastic cooling, project founded by U.S. Department of Energy, announced in 2015, http://energy.gov/eere/articles/energy-department-invests-nearly-8-million-develop-next-generation-hvac-systems

Larger National Projects in Europe

SPP 1599 "Ferroic Cooling", Caloric Effects in Ferroic Materials: New Concepts for Cooling (Magnetocaloric, electrocaloric, elastocaloric), Start in 2012, Germany, http://www.ferroiccooling.de/

Kitanovski et al., IJR, 57 (2015)

Electrocaloric: Polymer

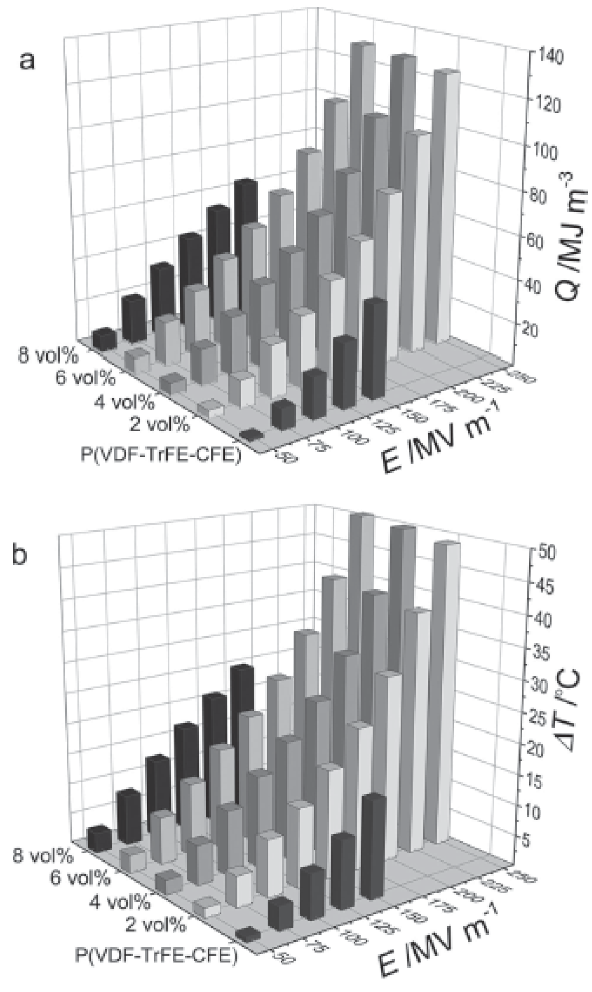


Figure 3. ECE of P(VDF-TrFE-CFE)/BNNSs/BST67 ternary polymer nanocomposites. a) Q, b) ΔT, and c) ΔS of the nanocomposites at 9 vol% BNNSs and different BST contents versus P(VDF-TrFE-CFE).

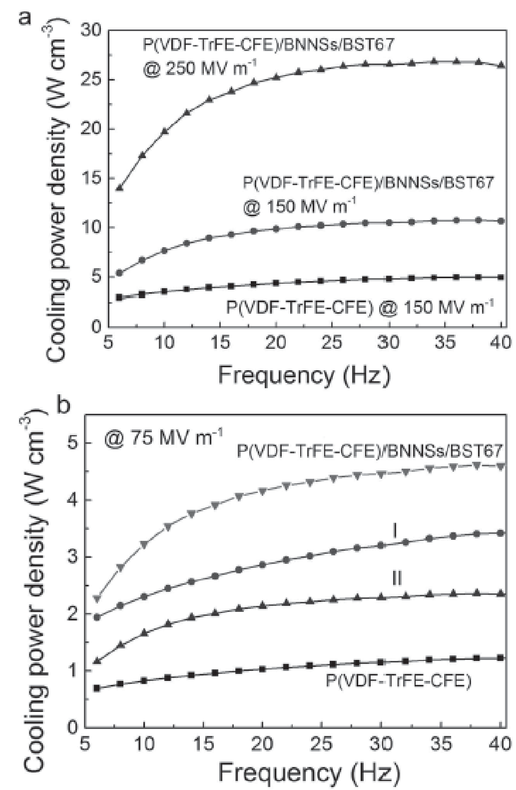


Figure 4. Cooling power densities of the nanocomposites at various operating frequencies. a) The ternary polymer nanocomposite (9 vol% BNNSs and 6 vol% BST67) at 150 and 250 MV m^{-1} versus P(VDF-TrFE-CFE) measured at 150 MV m^{-1}. b) The ternary polymer nanocomposite and P(VDF-TrFE-CFE) measured at 75 MV m^{-1}. Curve I illustrates the simulated cooling power densities of the polymer nanocomposite with the assumption that the polymer nanocomposite has the same thermal conductivity as the polymer matrix. Curve II is the cooling power densities of the polymer nanocomposite with the assumption that the polymer nanocomposite possesses the same Q as the polymer matrix.

Zhang et al, 2015. Adv. Materials.

Electrocaloric: Ceramic

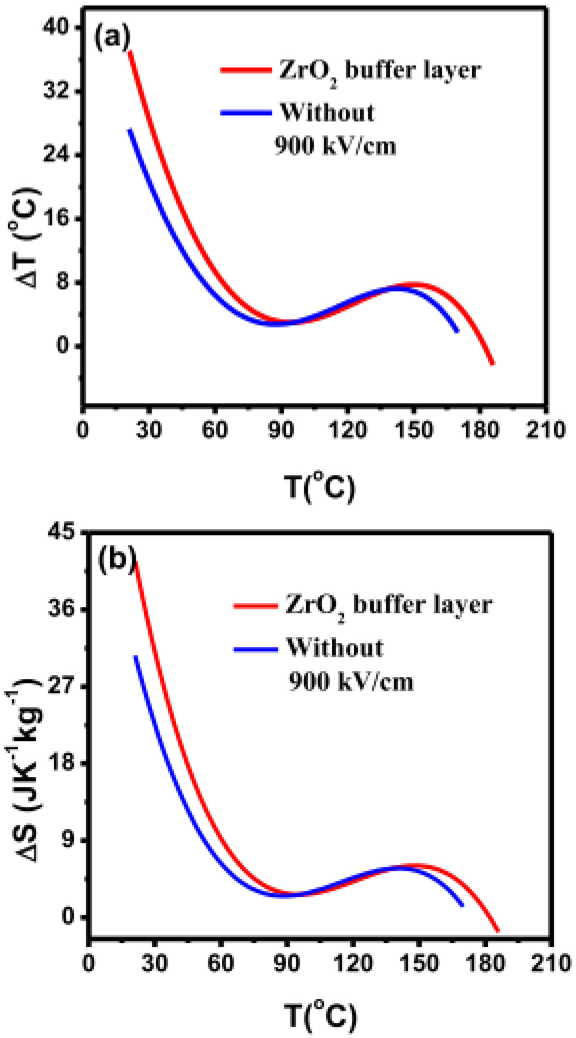


Fig. 4. (a) Temperature change of ΔT as a function of temperature at 900 kV/cm of the PLZST 2/57/38/5 AFE thick films with and without ZrO_2 buffer layer, respectively, and (b) the corresponding adiabatic changes in entropy ΔS of the films.

- Developed PLZST 2/57/38/5 anti-ferroelectrics (AFE) thick films with ZrO_2 buffer layer on LNO bottom electrodes
- Achieved an enhanced relative dielectric constant and a reduced leakage current. Improved ECE by about 10 K from 27.3°C to 37.1°C at room temperature 21°C.
- The corresponding entropy changes are 31 and 42 J/kg-K.

Zhao et al, 2015. J. Alloys & Compounds. 653 (2015).

Electrocaloric: Ceramic

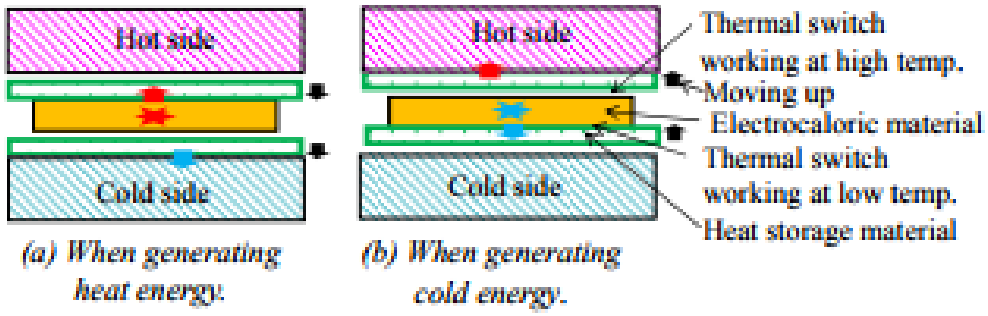


Figure 7. Model of electrocaloric refrigeration system with thermal switch by changing contact thermal conductance.

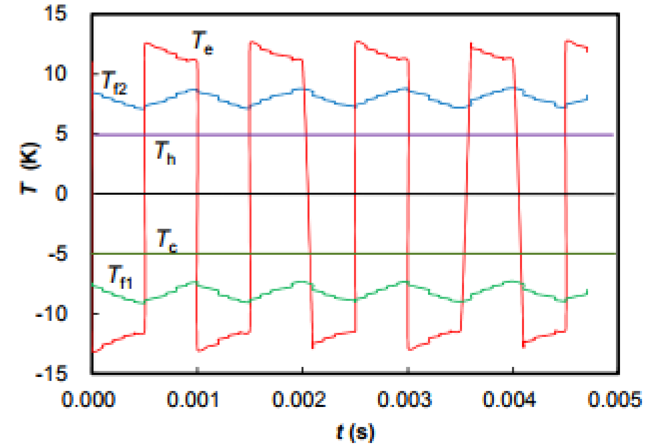


Figure 8. Temperature change for thermal switch by changing contact thermal conductance.

Predicted average heat flux performance was 70 kW/m^2 with 1,000 Hz frequency and the 20 µm thicknesses of the electrocaloric material and 20 µm heat storage material.

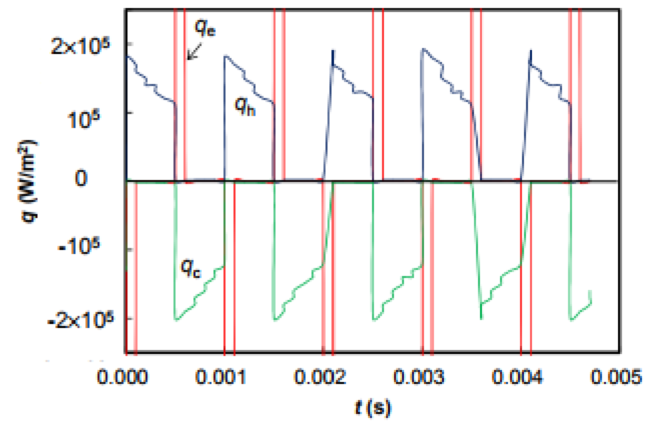


Figure 9. Change of heat flux for thermal switch by changing contact thermal conductance.

S. Hirasawa, T. Kawanami, K. Shirai,, American J. of Physics and Applications, 4 (2016) 134-139.

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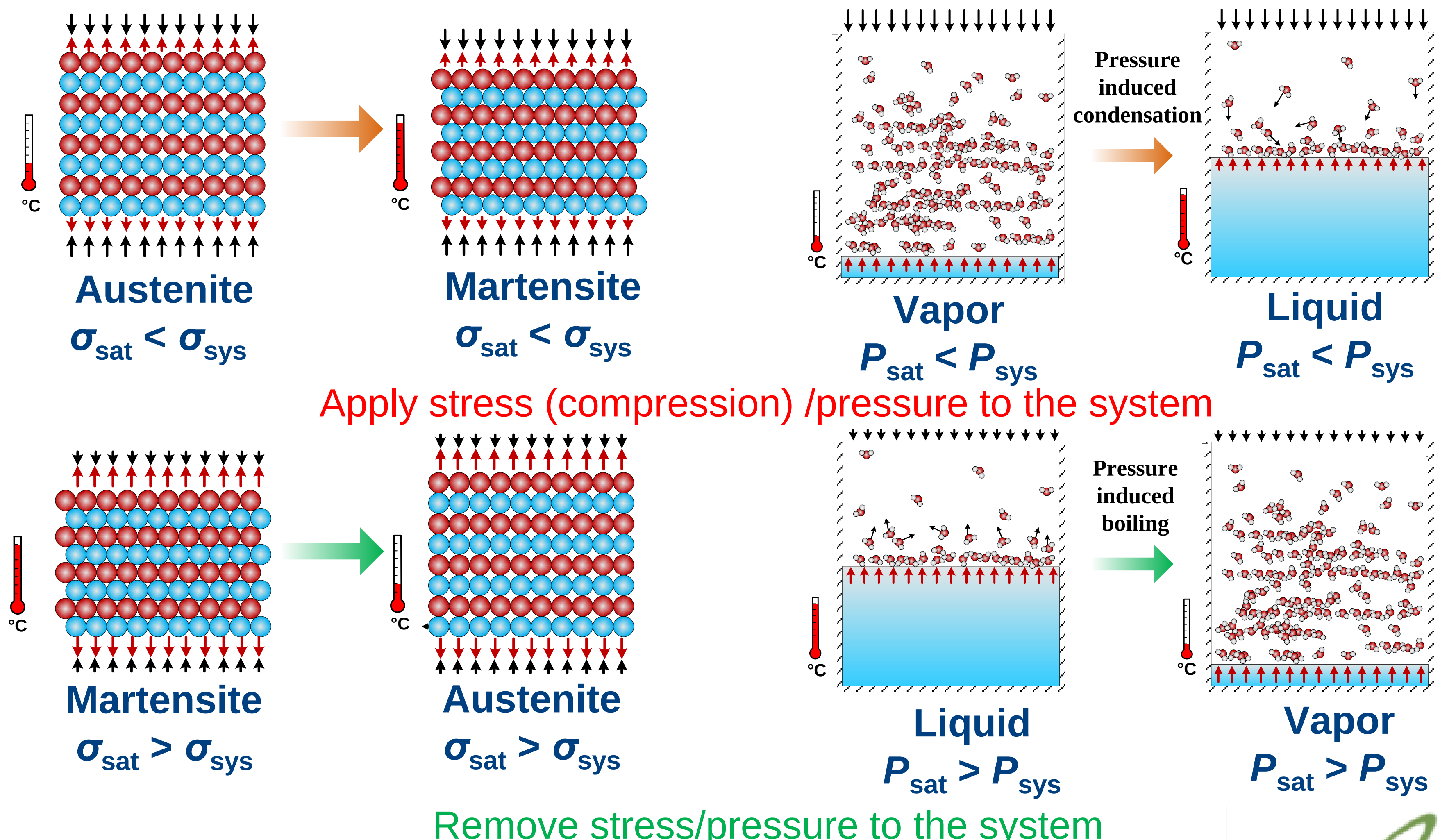
ETC Challenges

- The limitation in the shape of the materials. Only thin films can be applied since a high electric field is needed (hundreds of MV/m).
- Lacking of ETC multilayer modules with high reliability (> 100 cycles) and high ETC performance (DT > 5 K),
- There is no ETC device demonstration reported showing large temp. span (> 10 K) with any cooling power.

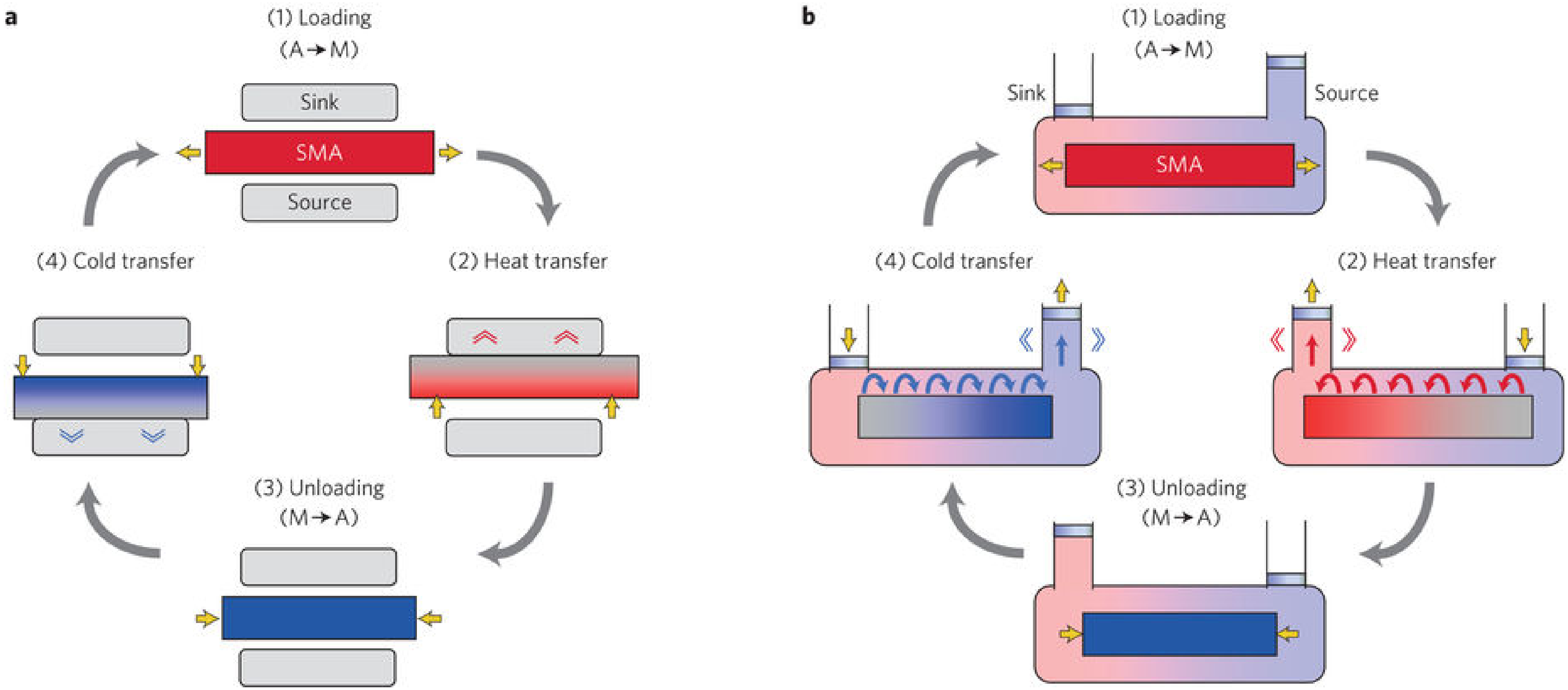
Source: Q. M. Zhang, Penn State, 2016

Elastocaloric (ESC)

Elastocaloric Effect



Elastocaloric Cooling



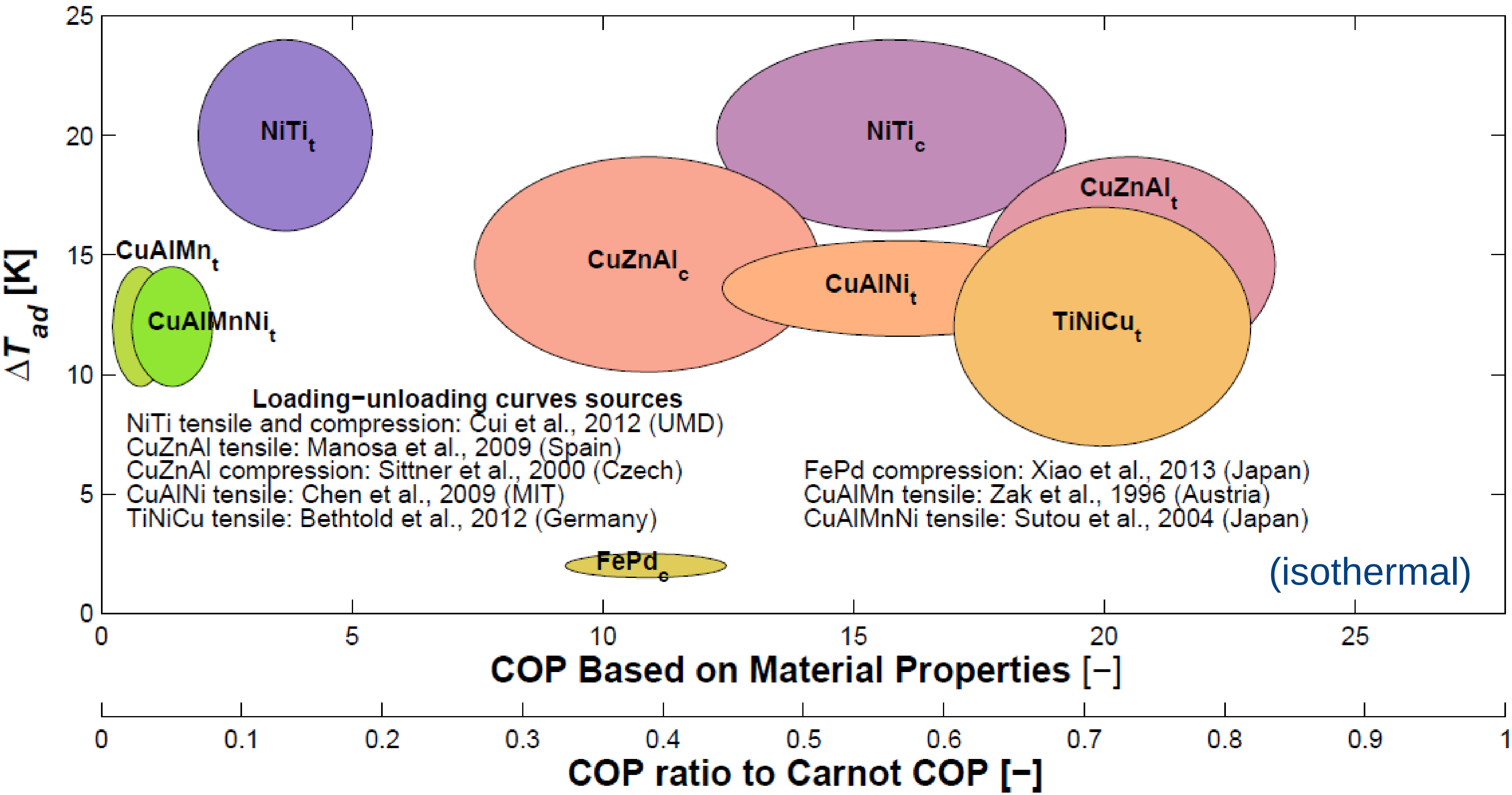
The cycle consists of four basic steps: mechanical loading (1), heat transfer (2), mechanical unloading (3) and cold transfer (4). **a**, Heat transfer is accomplished by solid mechanical contact between the SMA material and the heat sink (2) as well as the heat source (4). **b**, In a system exploiting the concept of active regeneration, a fluid is pumped along the SMA material during both the transfer of heat (2) and cold (4). By this procedure, a temperature gradient is established along the pumping direction. A, austenite; M, martensite.

https://www.nature.com/articles/nenergy2016159/figures/1

Comparison of Elastocaloric Materials

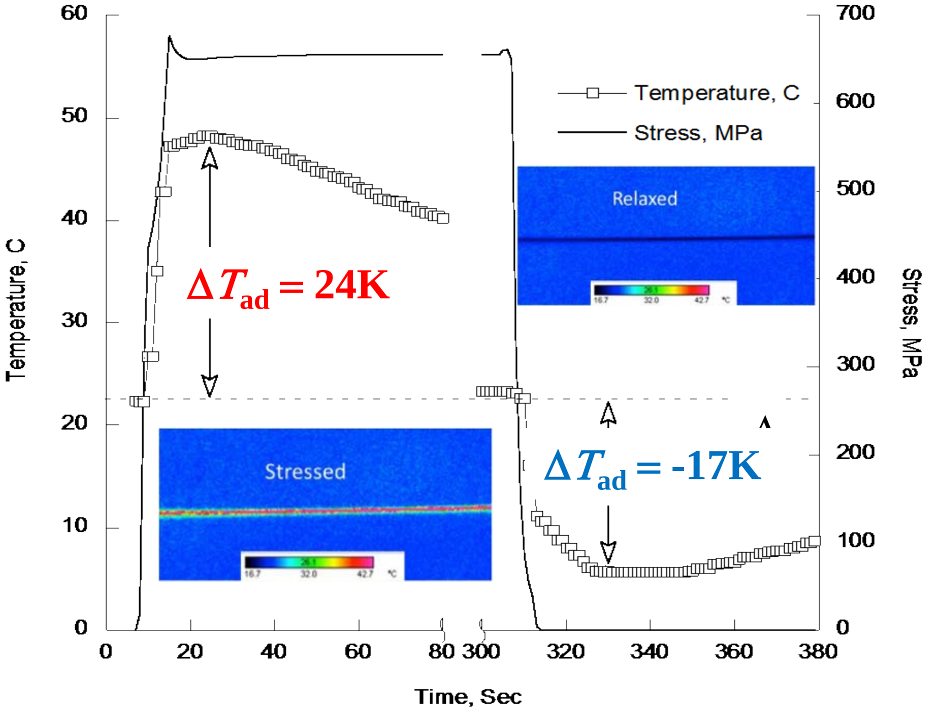
SMA		NiTi	Cu-Al-Zn	Cu-Al-Ni	Cu-Al-Mn
Latent Heat (J/g)	Reported	5~31	7~9	7~9	4~8
	From UMD	14	5.9	8.2	N/A
Specific Heat (J/g.°C)		0.450~0.620	0.390~0.400	0.373~0.574	0.390~0.440
$\Delta T_{adiabatic}$ (K)		20.8	15	14	10~15*
COP (Tension, adiabatic)		3.1 ± 1.3	15.3 ± 1.7	13.1 ± 2.4	0.8 ± 0.5
COP (Compression, adiabatic)		10.0 ± 1.4	9.1 ± 2.5	/	/
COP (Tension, isothermal)		3.7 ± 1.7	20.5 ± 2.9	15.9 ± 3.5	0.8 ± 0.5
COP (compression, isothermal)		15.8 ± 3.5	10.9 ± 3.4	/	/
Operational Tensile Stress (5% strain) (MPa)		450	100~200	100~200	100~300
Operational Compression Stress (5% strain) (MPa)		700 MPa	N/A	100~200	N/A
Thermal Conductivity (W/m*K)		10~18	84~120	30~75	30~120
Raw Materials Cost (USD/kg)		~16.40	~4.84	~6.6	~4.84
Brittleness		Fair	Very Brittle	Very Brittle	Fair

Comparison of Elastocaloric Materials



Can we increase latent heat, reduce heat capacity, lower operational stress, and increase work recovery?

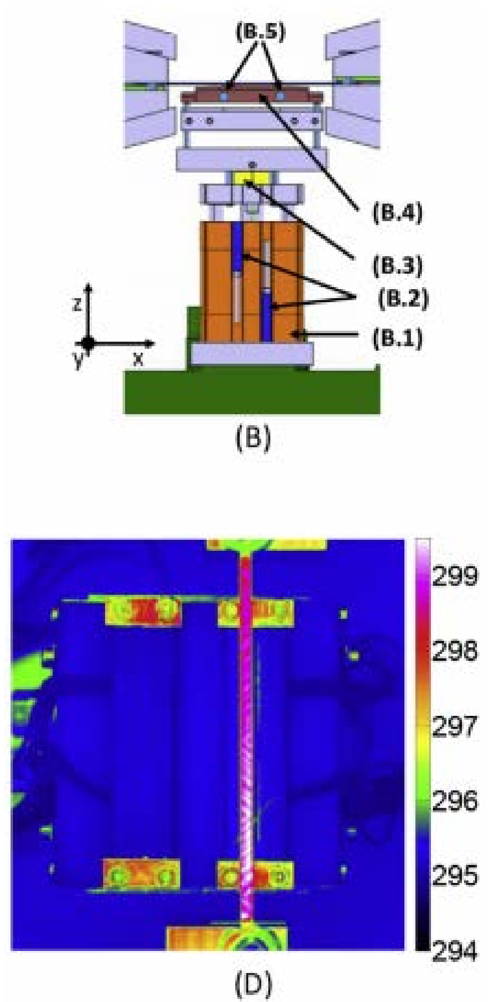
Elastocaloric Effect in Ni-Ti Wire



- 3 mm Nitinol (Ni-Ti alloy)
- 3 mm NiTi wire
- ΔT_{ad} ~ 17K Martensite – Austenite phase change (solid)
- Direction for material developments
  - High latent heat (Ni-Ti 12 J/g)
  - Low transitional stress (Ni-Ti 700 MPa)
  - Long fatigue life (Ni-Ti > 360,000 cycles)
  - Low hysteresis to reduce loss (Ni-Ti 1 J/g)

Cui et al., 2012, App. Phy. Lett., 101, 073904

Elastocaloric Effect in Ni-Ti Ribbon



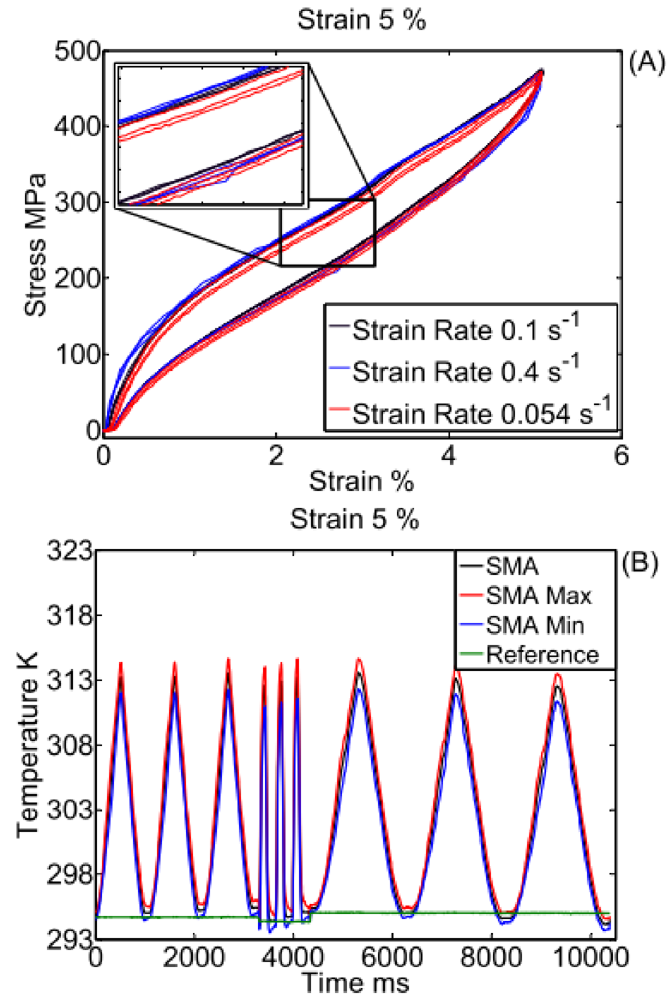


Fig. 3 – Rate dependent stress-strain diagram (A) and temperature-time diagram showing min, max and mean SMA temperature (B) with three cycles at each strain rate.

Ni-Ti (50.8/49.2)
DT_{ad} ~ 9.5 K

M. Schmidt, A. Schutze, S. Seelecke, Int. J. Refrig. 54 (2015) 88-97.

Elastocaloric Effect in NiTiFe Film

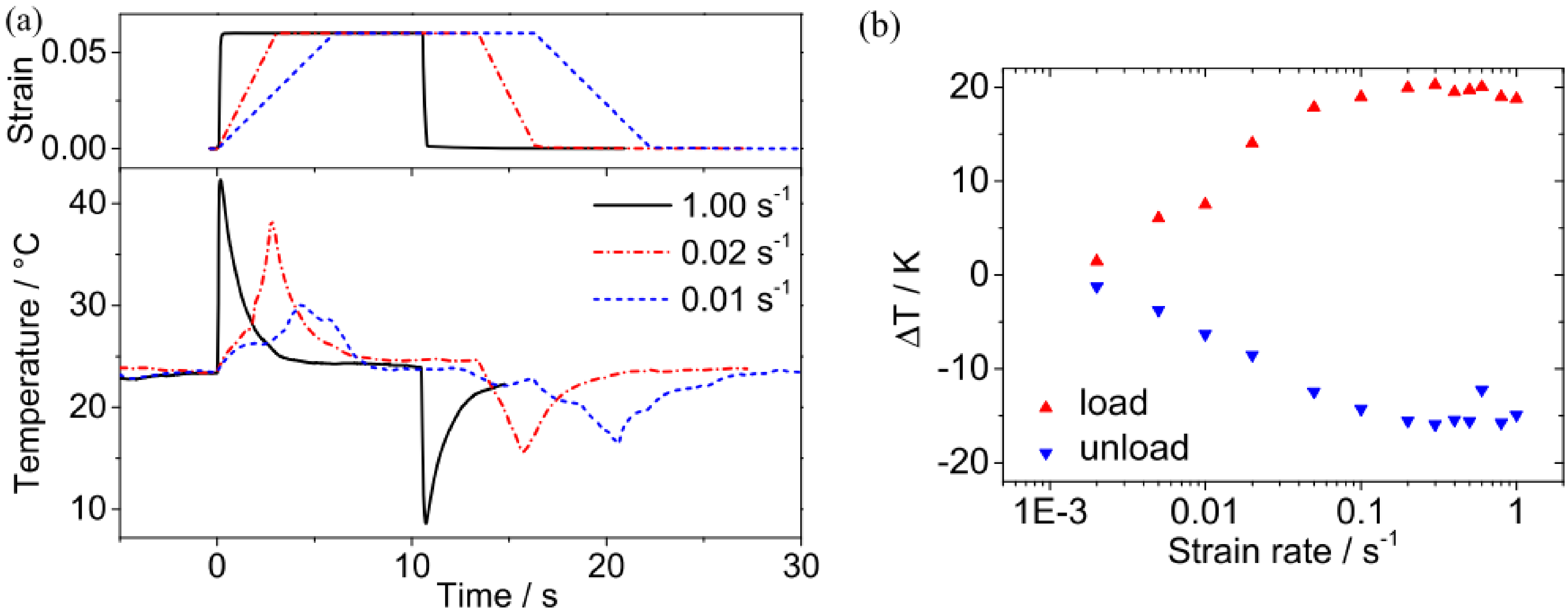


Figure 2. (a) Temperature change determined by IR thermography of a TiNiFe tensile test sample for different strain rates. Between loading and unloading step, the strain is held constant for 10 s to allow for temperature equalization with the environment. (b) Corresponding maximum temperature changes during mechanical loading and unloading as a function of strain rate. The adiabatic limit is reached at a strain rate of 0.2 s^{-1}.

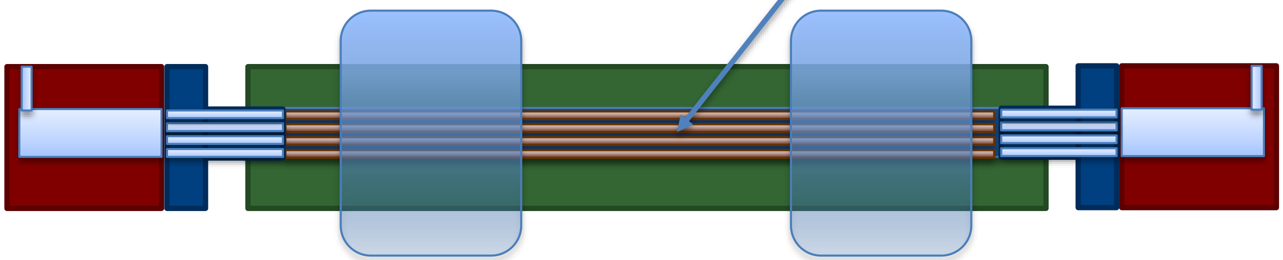
- **NiTiFe (49.1/50.5/0.4)**
- **3 micron foil**
- **DT_{ad} ~ 9.4 K**

Ossmer et al., Smart Mater. Struct. 25 (2016) 085037.

ESC Prototype: NiTi Tube

OD = 4.72 mm
ID = 3.76 mm

Nitinol tubes



Hexagon arranged NiTi (SMA) tubes in each bed

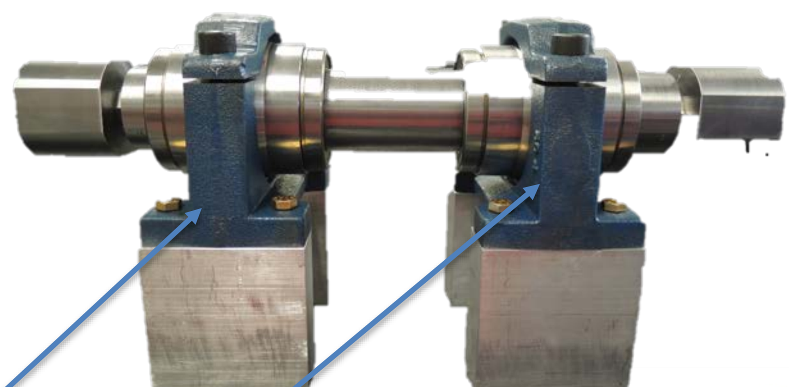
Compressible solid:

- **Deformation: 0.5" (12.7 mm), which is 5% of 10" (254 mm) tube**
- **Force: each tube requires 1,350 lbf (6 kN)**

Water in

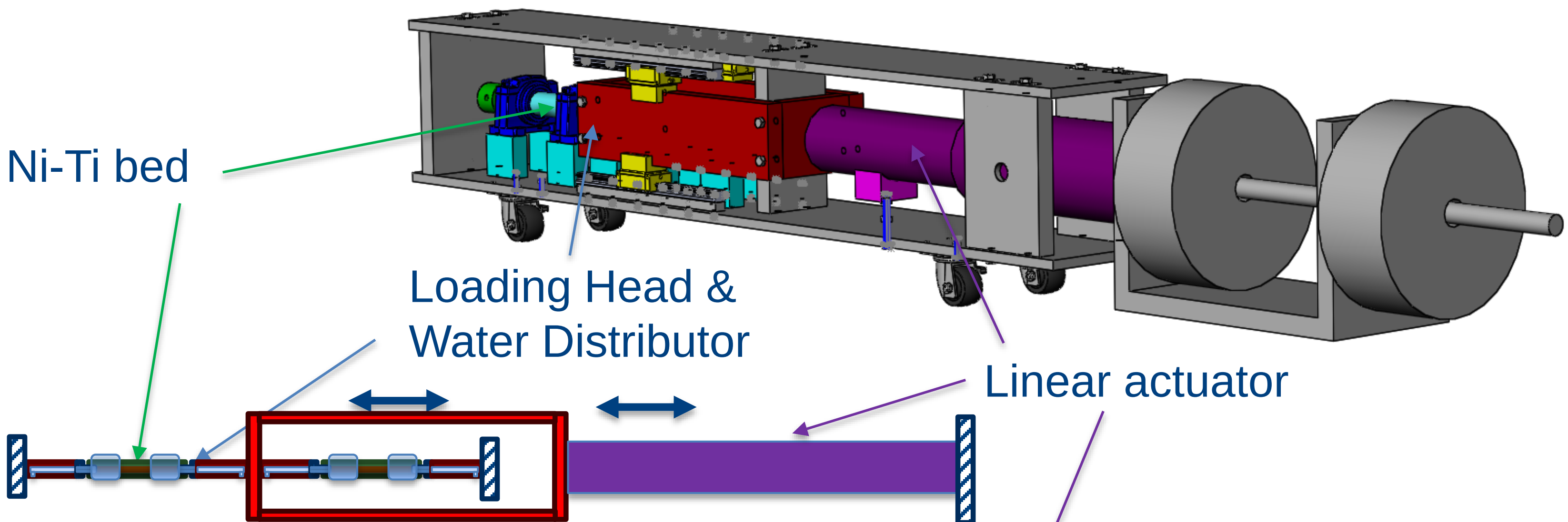
Water out

Nitinol tube holder



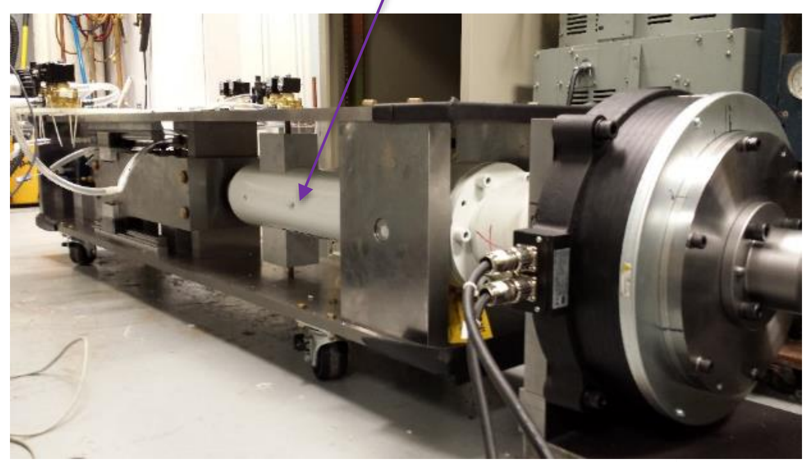
Linear bearing

ESC Prototype: Ni-Ti Tube

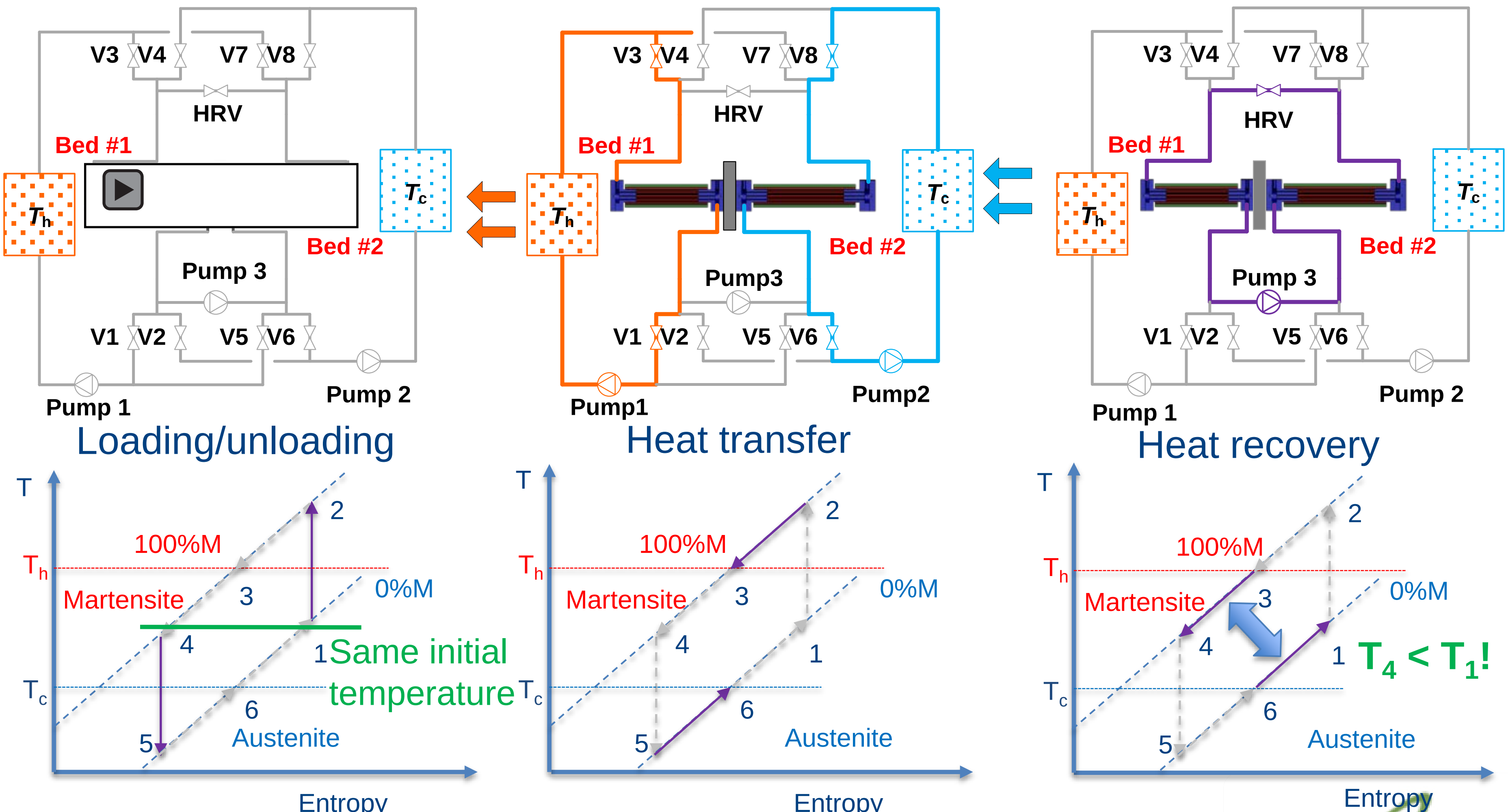


Top view

- **Work recovery: two beds were 50-50 percent pre-compressed**
- **Linear actuator attached to the “moving box”**

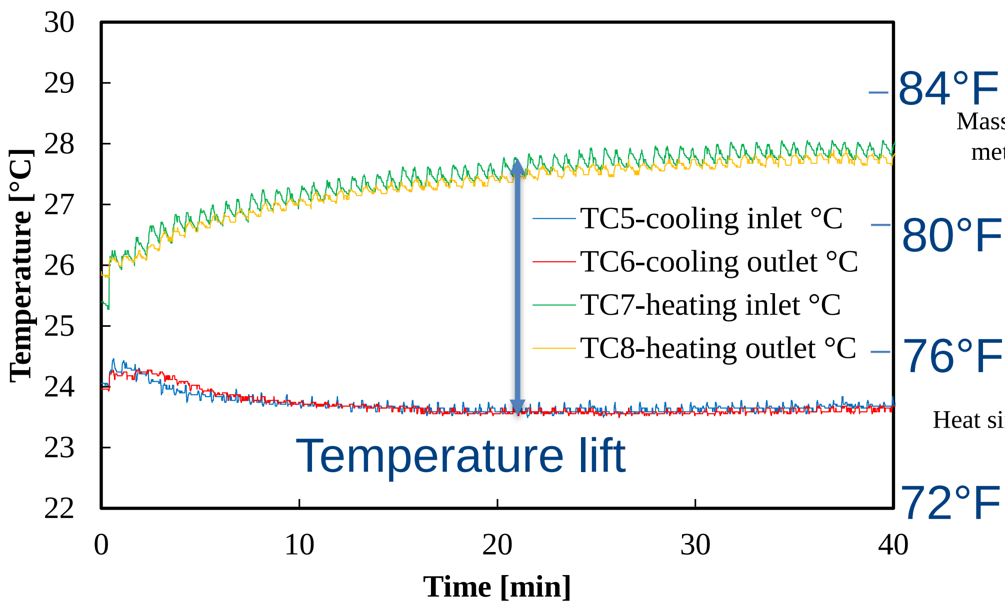


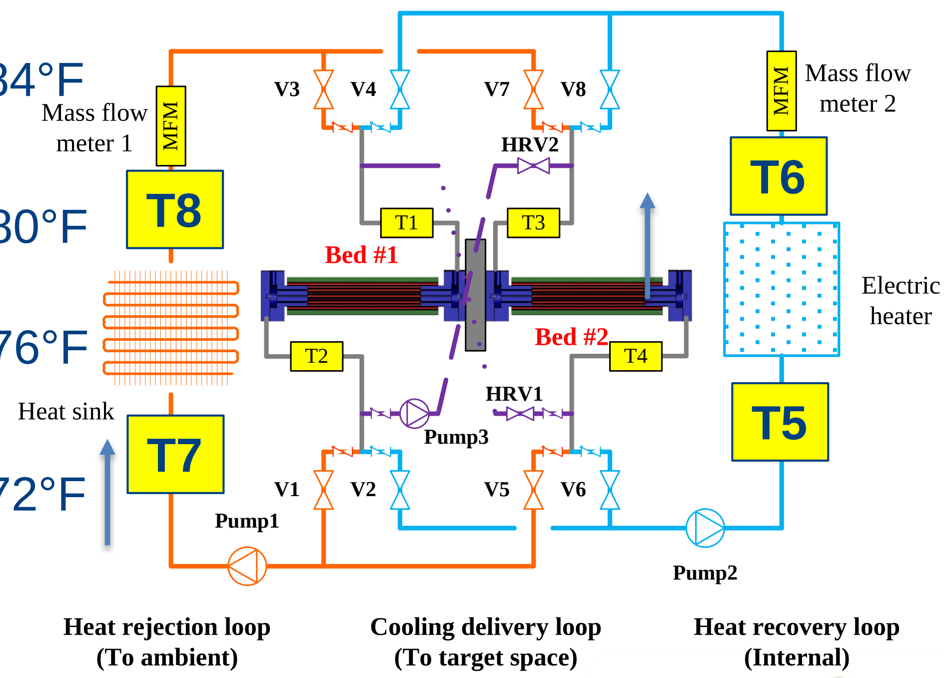
ESC From Material to System



ESC-NiTi Tube: Temperature Lift

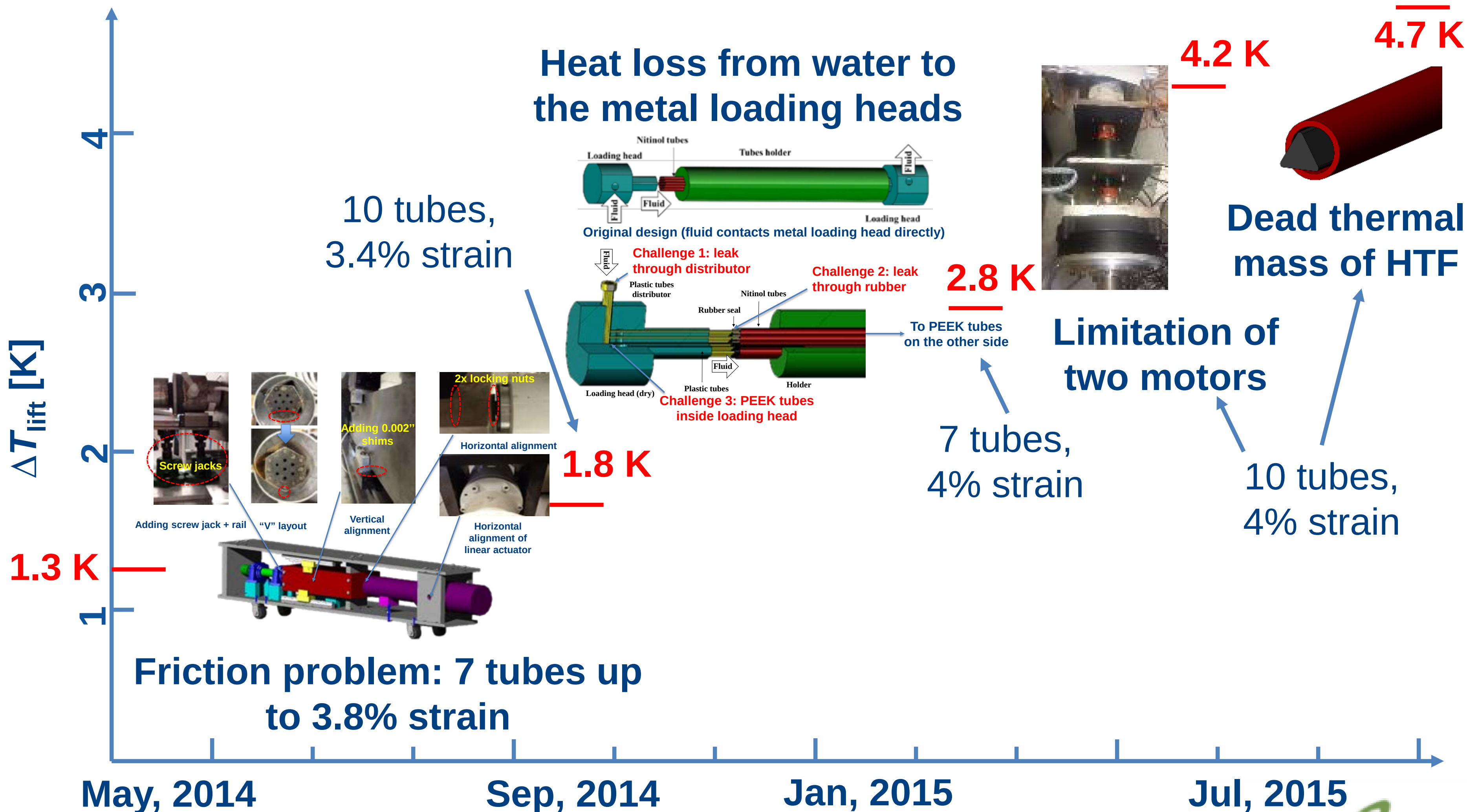
- Without compression: all fluid temperatures are following the same trend
- With compression: temperature lift exists





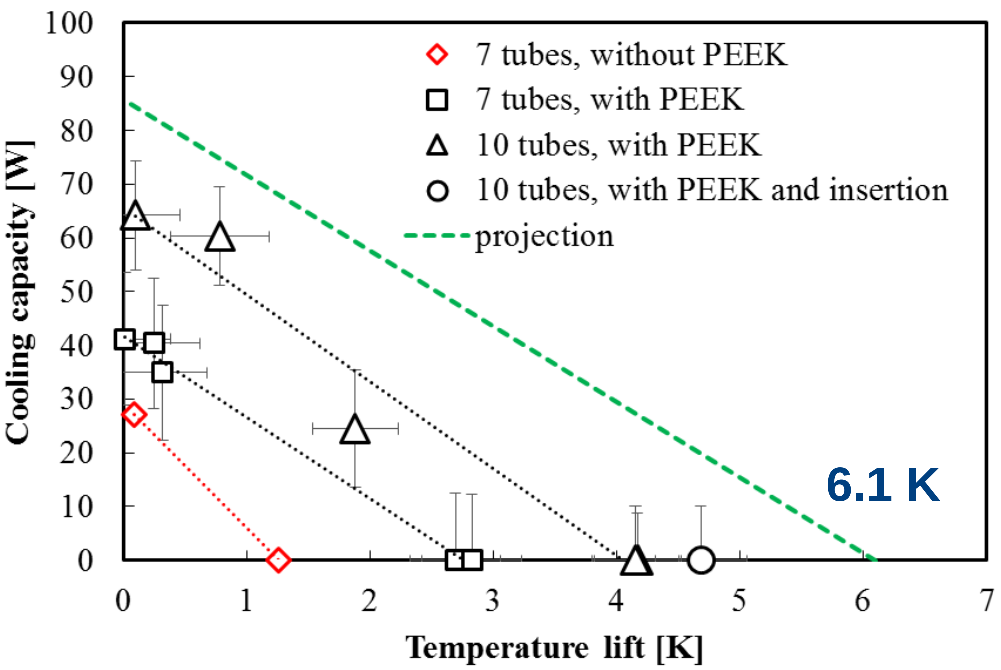
Measured fluid temperature variations

ESC-NiTi Tube: Performance Progress



ESC-NiTi Tube: Test Results

- **Maximum cooling capacity: 65 ± 10 W**
- **Maximum temperature lift: 4.7 ± 0.4 K**



- **Achieved 4.7 K ΔT_{lift} when using plastic insertions to block 50% HTF inside tubes**
- **Measured 9% heat loss from Ni-Ti tubes to the holder**
- **Adding 12 W parasitic heat generated from pumps + 9% heat loss → 6.1 K ΔT_{lift}**

"PEEK" means plastic insulation tubes to reduce heat loss to the metal loading heads

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ESC Challenges

- Material development
  - Large latent heat, low transitional stress, low hysteresis and long fatigue life
  - Custom shape/structure manufacturing capability
- Cycle design: high frequency heat transfer feature
- System integration
  - Compact and light system
  - High efficient heat transfer
  - High efficient heat recovery/regeneration
  - Cost down

Performance Comparison

Technology	Φ_{mat} @ ΔT_{lift} = 10 K	Φ_{sys} @ ΔT_{lift} = 10 K	$\Phi_{sys,max}$ @ ΔT_{lift}
Vapor compression	0.88	0.20	0.27 @ 24 K
Magnetocaloric	0.91	0.29	0.30 @ 9 K
Electrocaloric	0.41	n/a	n/a
Elastocaloric	0.63	0.14	0.16 @ 17 K

$$\Phi_{mat} = COP_{mat} / COP_{carnot} \quad (1)$$

$$\Phi_{sys} = COP_{system} / COP_{carnot} \quad (2)$$

$$COP_{mat} = \frac{q_c}{w_{mat}} \quad (3)$$

$$COP_{Carnot} = \frac{T_c}{\Delta T_{lift}} \equiv \frac{T_c}{T_h - T_c} \quad (4)$$

Summary of Cooling Technologies

Technology	R&D status	Cost/ complexity	Refrigerant	Work input form	Possible heat recovery method	Possible work recovery method
Vapor compression (baseline)	Mature	Low	R410A	$\int p dv$	Suction-line heat exchanger	Expander
Magnetocaloric	Advanced R&D	High	Gd	$\int \mu_0 H dm$	Active magnetic regenerator	Multi-bed rotary bed design
Electrocaloric	R&D, recently started	Moderate	P(VDF-TrFE-CFE)	$\int E dD$	Passive external regenerator	n/a
Elastocaloric	R&D, recently started	Moderate	Ni-Ti	$\int \sigma d\varepsilon$	Thermowave heat recovery	Multi-bed symmetric design

Conclusions

- Solid-state caloric cooling technologies are advancing among NIKs because of new material development.
- Summarized the working principles and recent advancements of caloric cooling technologies.
- Solid-state caloric technologies are applicable to small temperature lift applications if single stage is used and require more development in both materials and system integration.

Thanks for your attention!

感謝您的關注

Any Questions?

有問題嗎？