# Magnetocaloric Materials and Devices

## A Brief Review of the Past and the Present and a Peek Into the Future

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# Outline

- The magnetocaloric effect – what is it?
- First applications of the magnetocaloric effect and why is it important?
- Giant magnetocaloric effect and where we are today?
- What does the future hold?

# The magnetocaloric effect: Discovery

Pour le nickel étudié ce point est à 629°,6 abs. A 634°9 nous avons trouvé, en faisant varier le champ de zéro aux valeurs de la première colonne, et inversement de ces valeurs à zéro :

| H | $\Delta t^o$ | $\sigma^2$ | $\frac{\Delta t}{\sigma^2}$ |
|---|---|---|---|
| 990 | 0,011 | 2,18 | (0,00505) |
| 1.320 | 0,014 | 4,04 | (0,00347) |
| 7.820 | 0,264 | 74,5 | 0,00355 |
| 8.780 | 0,317 | 85,5 | 0,00371 |
| 10.050 | 0,370 | 100,8 | 0,00367 |
| 14.960 | 0,569 | 151,0 | 0,00377 |

For the nickel studied, this [Curie] point is at 629.6º absolute. At 634.9º we found, by varying the field from zero to the values in the first column, and conversely from these values to zero:

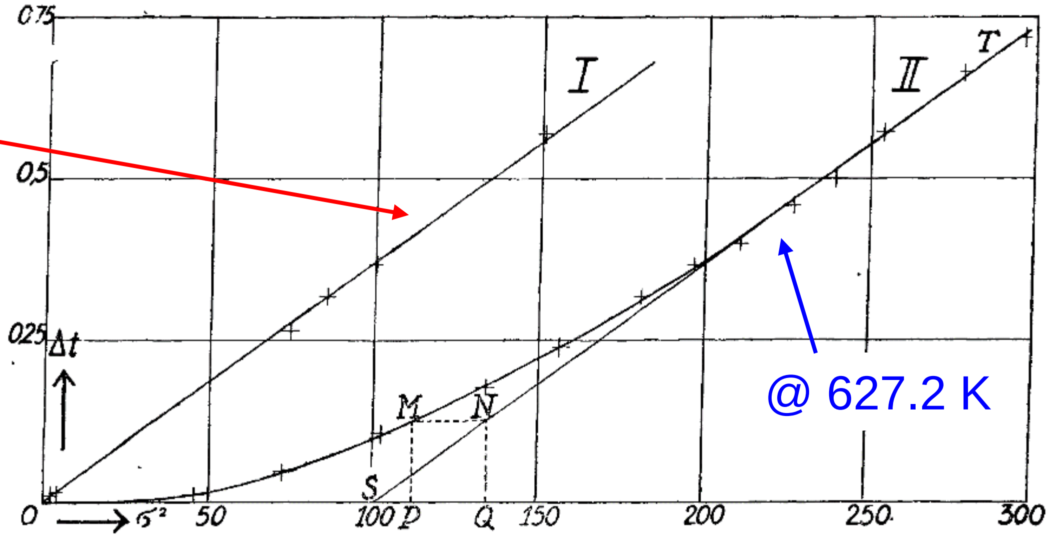


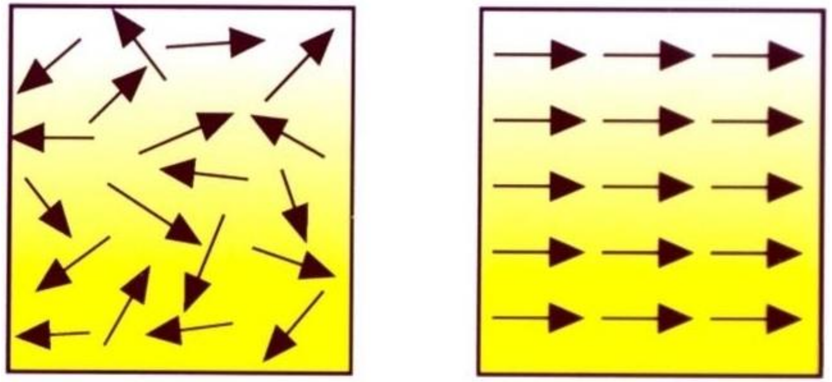

Fig. 1.

P. Weiss, A. Piccard. Le phénomène magnétocalorique. J. Phys. Theor. Appl. **7**, 103 (1917)

# The magnetocaloric effect. Why is there a ΔT?

$B_1 = 0$
$S_1$, $T_1$

$B_2 >> 0.1$ T
$S_2 = S_1$, $T_2 > T_1$

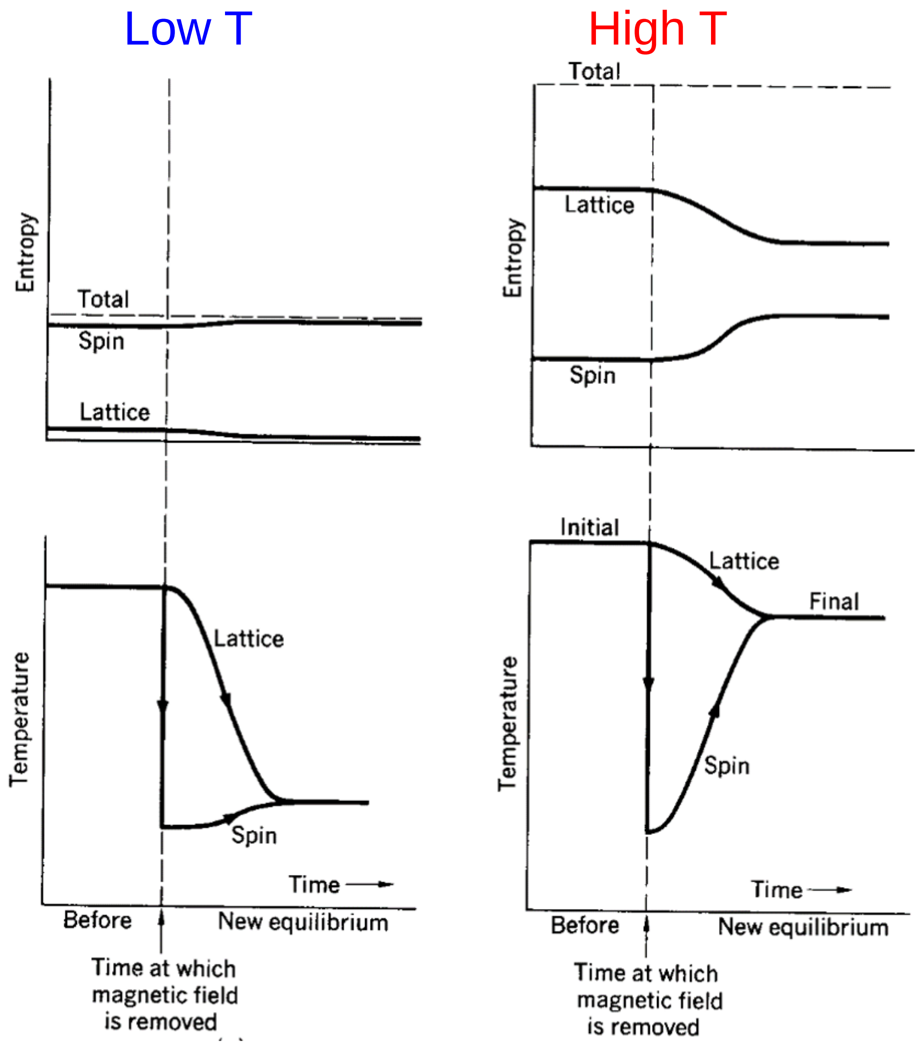


$$\Delta T_{ad} = T_2 - T_1$$

- Magnetic moments are aligned by the action of magnetic field
- The magnetic component of the entropy changes by $\Delta S_M$
- Adiabatic conditions
  - $S$ = const.
  - $B$=0: $S_1 = S_L + S_E + S_M$
  - $B$>0: $S_2 = (S_M - \Delta S_M) + (S_L + S_E + \Delta S_M)$

# ΔS and ΔT are related, but…

- Adiabatic conditions
  - $S$ = const.
  - $B$=0: $S_1 = S_L + S_E + S_M$
  - $B$>0: $S_2 = (S_M - \Delta S_M) + (S_L + S_E + \Delta S_M)$
- But
  - $S_L = \frac{1}{3}\beta T^3$
  - $S_E = \gamma T$
  - $S_M^{Max} = R ln(2J+1)$

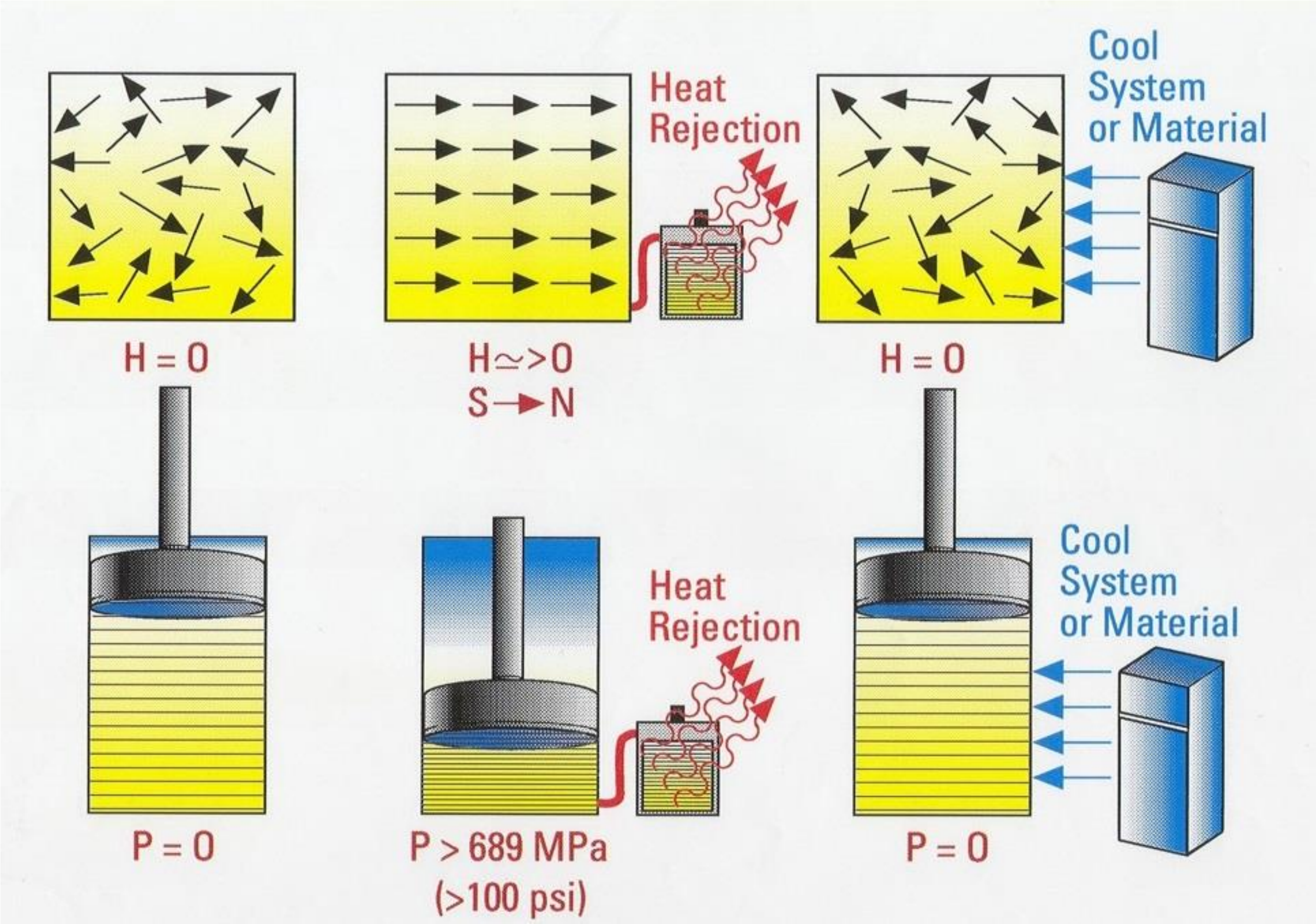



C. Kittel, Intro to Solid State Physics, Wiley (1971)

# How does this work?

Magnetic material near its $T_C$

A gas or a volatile liquid (vapor compression, VC)



# Calorics in general

- Reversible ΔT and ΔS as a result of ΔΦ
- Field, Φ
  - Magnetic – magnetocaloric effect
  - Stress – elastocaloric effect
  - Electric – electrocaloric effect
- Applications of magnetocaloric effect are most mature

# First application of the magnetocaloric effect

768 LETTERS TO THE EDITOR

**Attainment of Temperatures Below 1° Absolute by Demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$**

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$ at the temperatures of liquid helium. As previously predicted by one of us, a large fractional lowering of the absolute temperature was obtained.

An iron-free solenoid producing a field of about 8000 gauss was used for all the measurements. The amount of $Gd_2(SO_4)_3 \cdot 8H_2O$ was 61 g. The observations were checked by many repetitions of the cooling. The temperatures were measured by means of the inductance of a coil surrounding the gadolinium sulfate. The coil was immersed in liquid helium and isolated from the gadolinium by means of an evacuated space. The thermometer was in excellent agreement with the temperature of liquid helium as indicated by its vapor pressure down to 1.5°K.

On March 19, starting at a temperature of about 3.4°K, the material cooled to 0.53°K. On April 8, starting at about 2°, a temperature of 0.34°K was reached. On April 9, starting at about 1.5°, a temperature of 0.25°K was attained.

It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

W. F. Giauque
D. P. MacDougall

Department of Chemistry,
University of California,
Berkeley, California,
April 12, 1933.

Phys. Rev., **43** 768 (1933)

# Adiabatic demagnetization today

**"…[W.F. Giauque's] magnetic cooling method deserves special mention. This method has made it possible to reach temperatures nearer to absolute zero than was possible by any earlier technique."**

Arne Tiselius, 1949 Nobel committee presentation


Janis

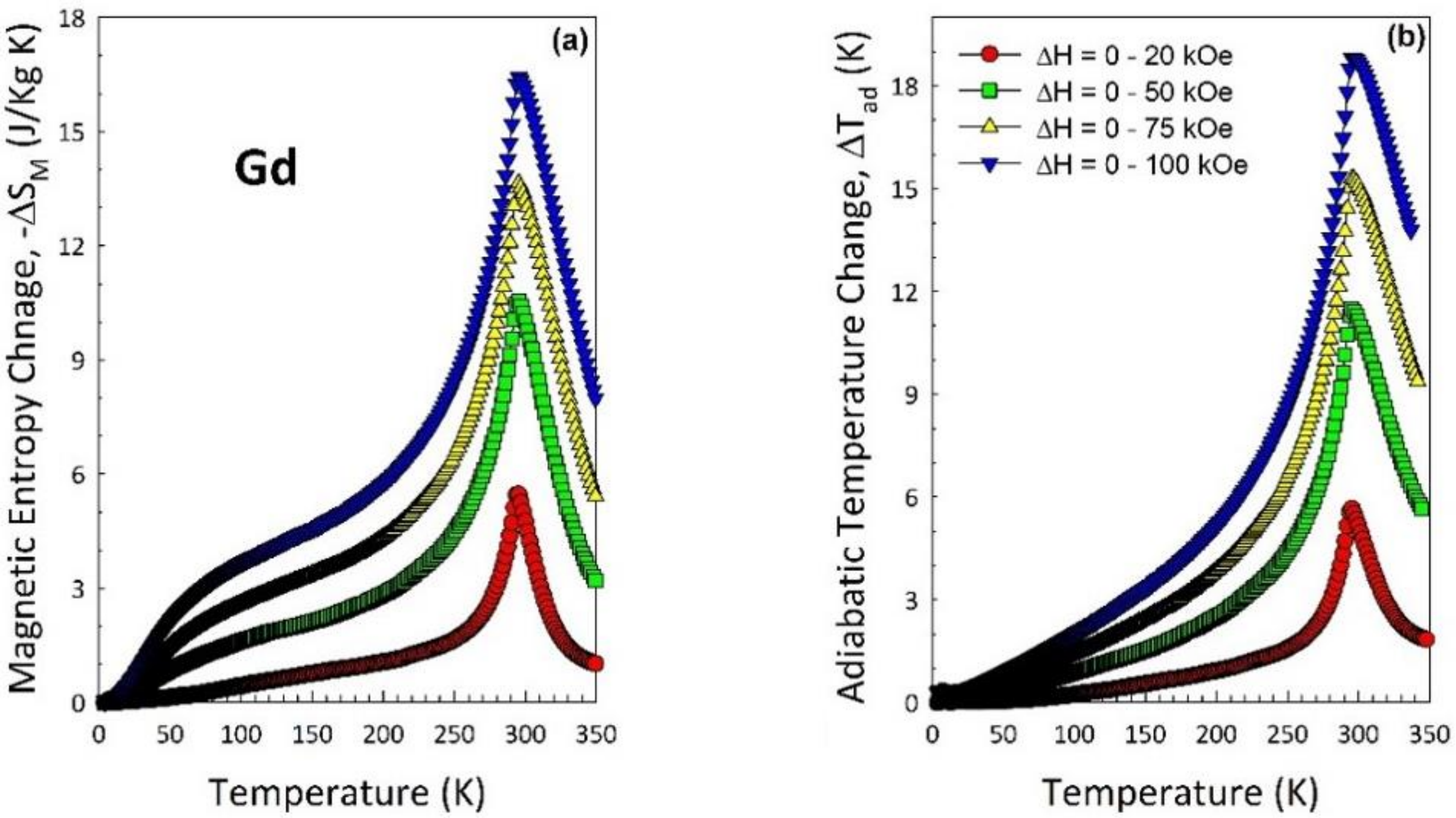
Many others… GGG is a typical coolant

4T magnet; Low T of 50 mK

No-load hold time: 2 days

Regeneration: a few hours

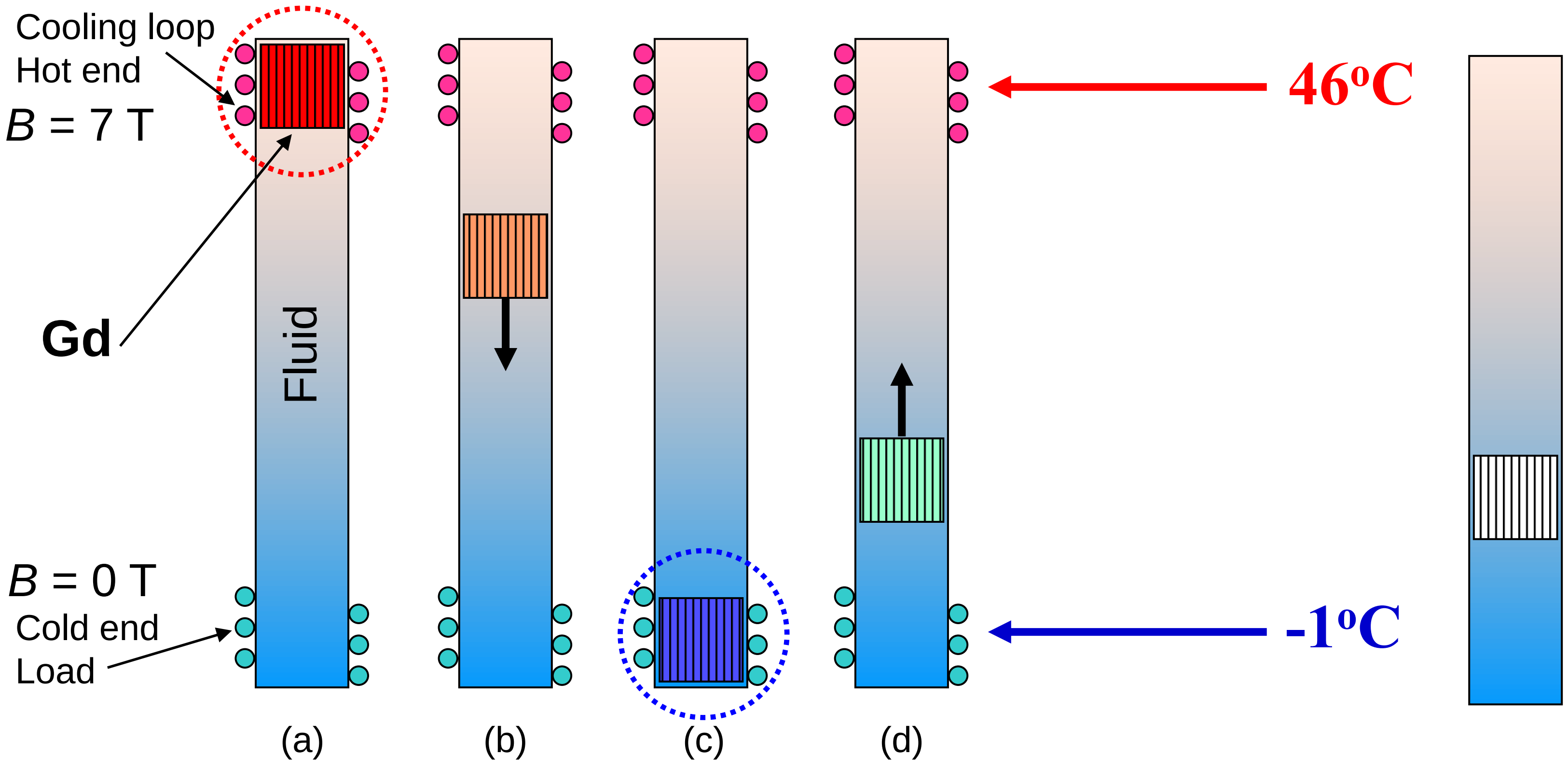
# Magnetocaloric effect near room temperature




Y. Mudryk, V.K. Pecharsky, Materials for solid state cooling, in: Rare Earth Chemistry, De Gruyter (Berlin), 2020

# First application near room temperature

- **1976 Gerald Brown (NASA)**
  - Temperature span of 47°C using Gd plates to regenerate a column of a water-alcohol mixture; 7 T, cycle time – several min; ~50 cycles to get there.  Later reached 80°C span, but never published.



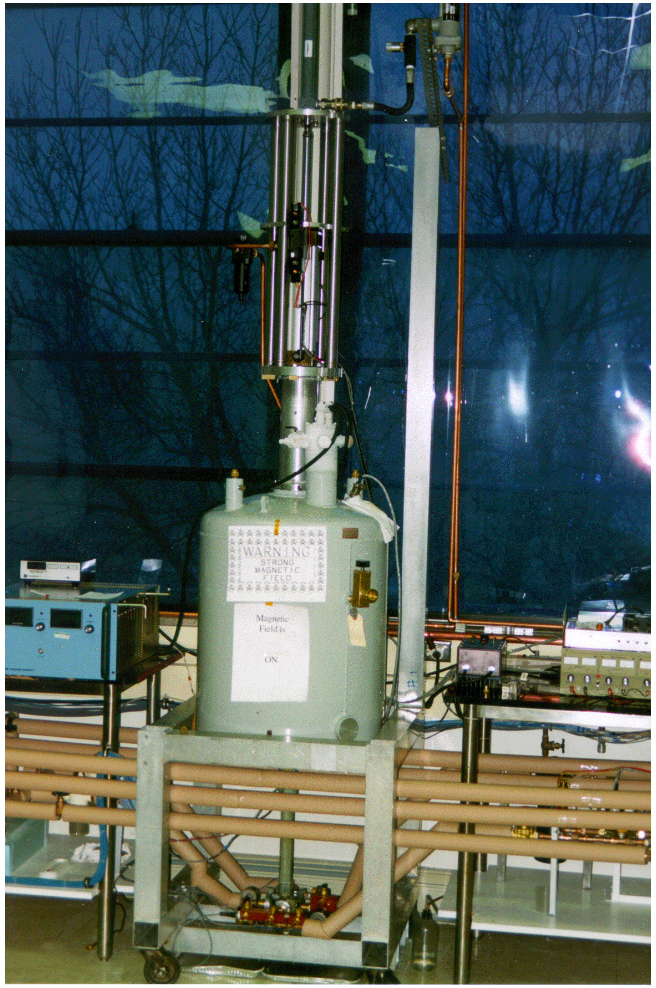

G.V. Brown, Magnetic heat pumping near room temperature, J. Appl. Phys. **47**, 3673 (1976)

# Why magnetocaloric effect is important?

- Cooling today: nearly exclusively VC; $^{1}/_{3}$ of 4,000,000,000,000,000 (4QWh) of the electricity generated in the U.S. (2016 data)
- Magnetocaloric heat pumping/refrigeration
  - Efficiency
    - Magnetocaloric effects can be generated with 99+% efficiency
    - Magnetocaloric cooling can be 1/4 to 1/3 more efficient than VC
    - U.S.: 300 TWh ($30B, assuming $0.1/kWh) saved annually
  - Safety and environment
    - No CFC's, HFC's, $NH_3$, flammable(s)
    - Solid refrigerant
    - Benign (water-based) heat exchange fluid, low pressure

# Past 23 years…

~9ft (~2.7 m)




February, 1997

http://www.astronautics.com/premiere-of-cutting-edge-cooling-appliance-at-ces-2015/

January, 2015

# Giant magnetocaloric effect

## Giant Magnetocaloric Effect in $Gd_5(Si_2Ge_2)$

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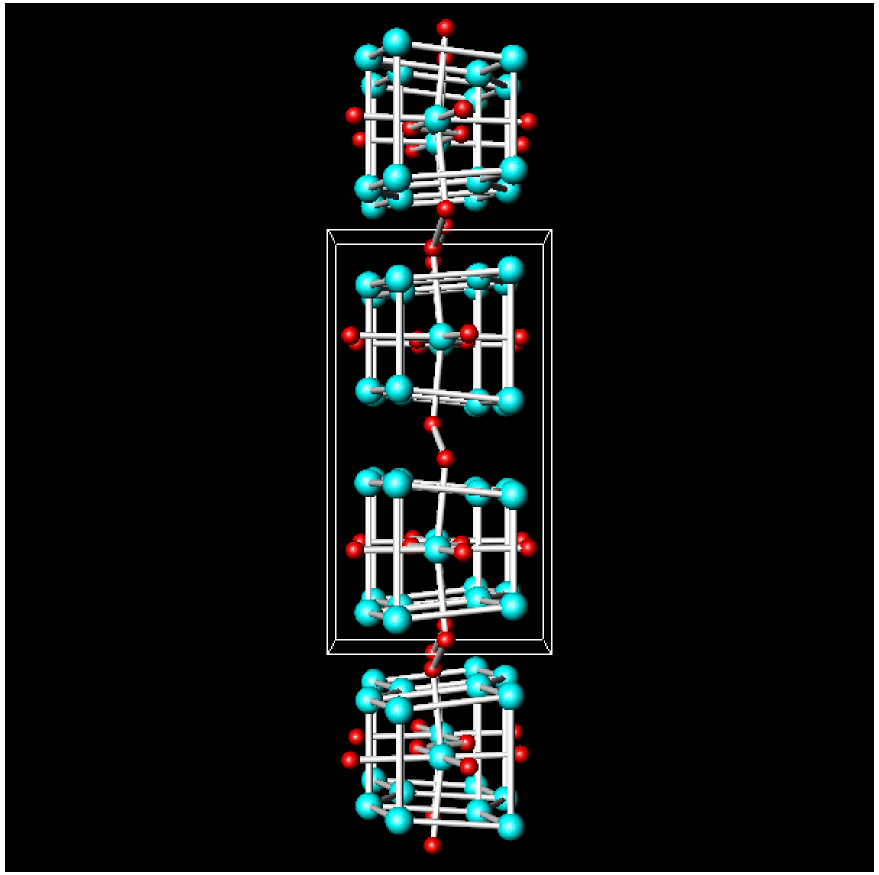
(Received 22 November 1996)

An extremely large magnetic entropy change has been discovered in $Gd_5(Si_2Ge_2)$ when subjected to a change in the magnetic field. It exceeds the *reversible* (with respect to an alternating magnetic field) magnetocaloric effect in any known magnetic material by at least a factor of 2, and it is due to a first order [ferromagnetic (I) ↔ ferromagnetic (II)] phase transition at 276 K and its unique magnetic field dependence. [S0031-9007(97)03321-8]



Phys. Rev. Lett. **78**, 4494 (1997)

# Nature of the giant magnetocaloric effect



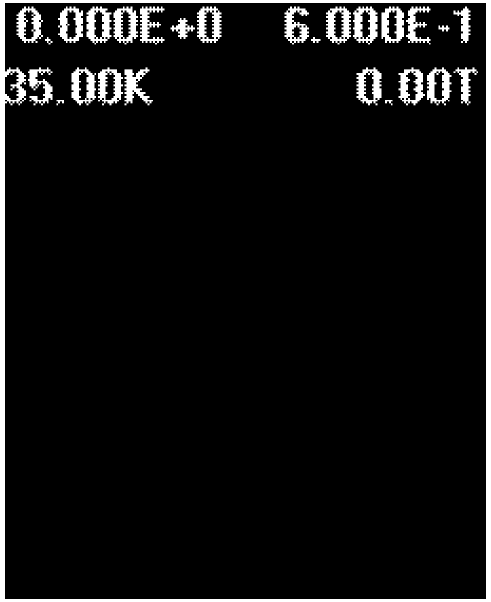
0.23 Å

0.23 Å

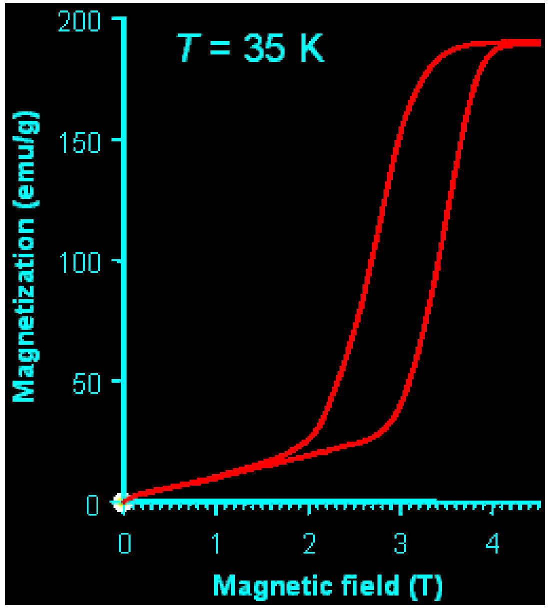
0.23 Å

0.23 Å

1000 μm




500 μm




■ -AFM

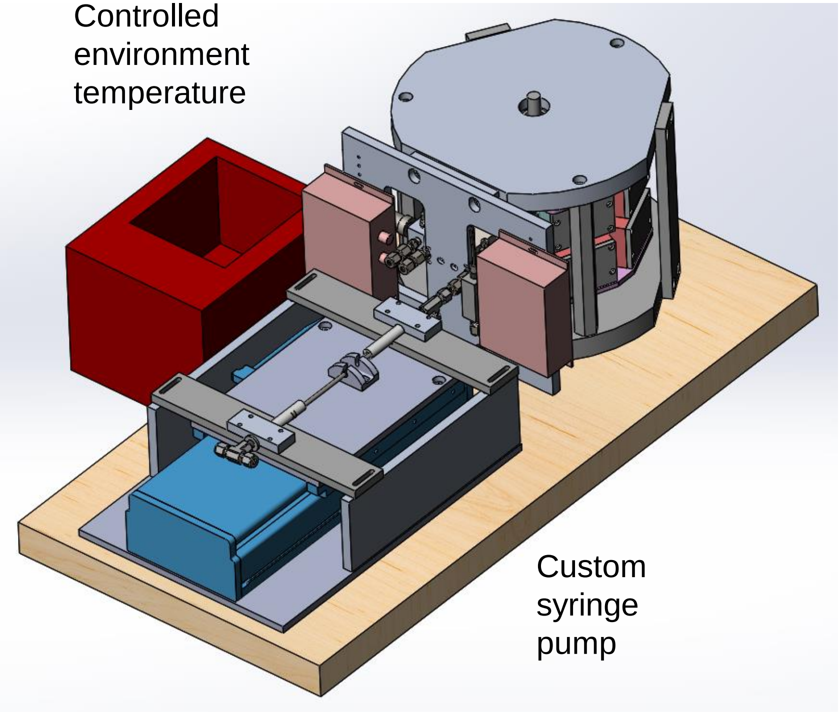
□ -FM

# Why aren't we there yet?

- ΔS reported for hundreds if not thousands of materials
  - A few "new and promising" materials are reported every week
- Only three, far from ideal, materials families have been proved "practical" and are (?) available
  - "Gd-based (Gd, $Gd_{1-x}R_x$)," "La-Fe-Si (1:13)," "Mn-Fe-P-Si ($Fe_2P$)"
- Majority of "new and promising" materials are shelved
  - No proven methodology to predict performance – caloric "zT"?
  - Scale-up (from grams to kilograms) for testing is cost-prohibitive

# Rapid testing and validations of materials is key!

- CaloriSMART (Small-scale Modular Advanced Research Test-station) for rapid evaluation of *small quantities* of caloric materials
- Evaluate new caloric materials under a wide range of operating conditions quickly and cost-effectively






L.G. Griffith et al, CaloriSMART: Small-scale test-stand for rapid evaluation of active magnetic regenerator performance, Energy Conversion and Management **199**, 111948 (2019).

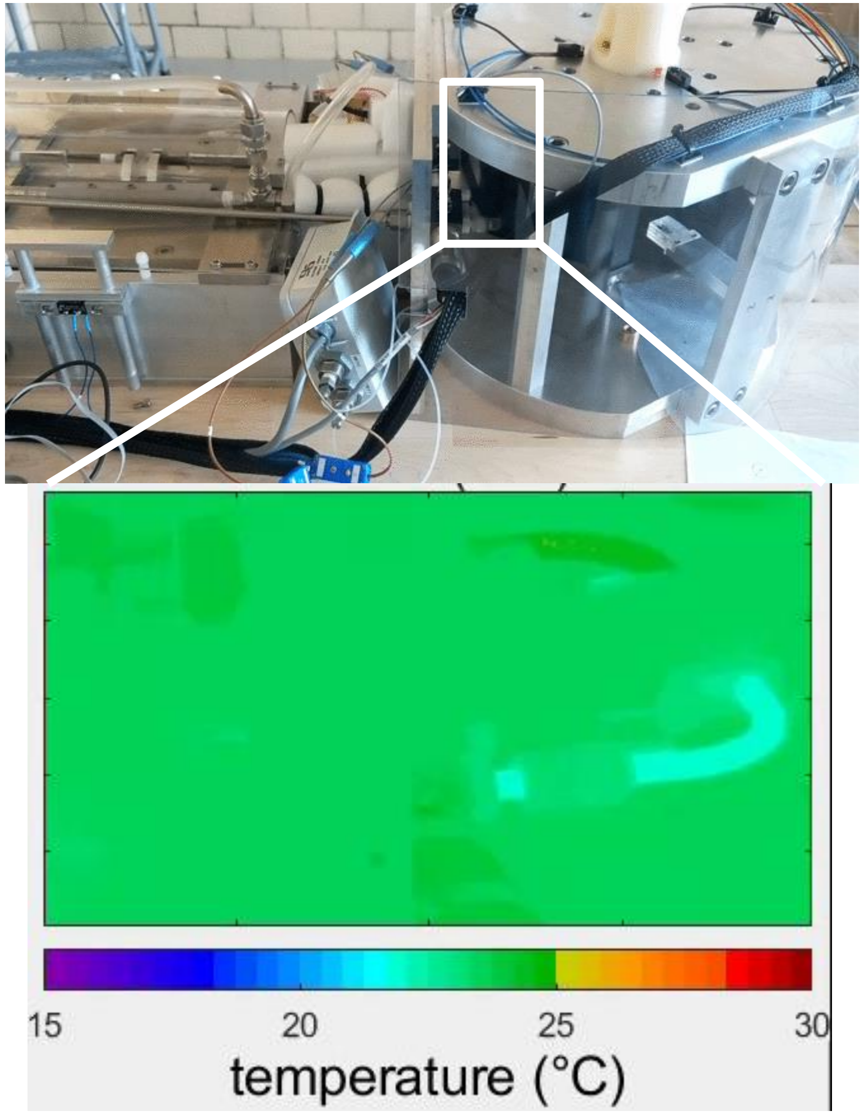
# CaloriSMART

## Control

- Regenerator volume 2-7 $cm^3$, typical 5 $cm^3$
- Demonstrated frequency up to 4 Hz
- Max field of 1.45 T or 1.13 T
- Hot-side exhaust temperature 0 to 80 °C
- Applied cooling load up to 20 W

## Operation

- Fast, automatic measurements (0.1 to 2.3 h)
- Couple hours for setup

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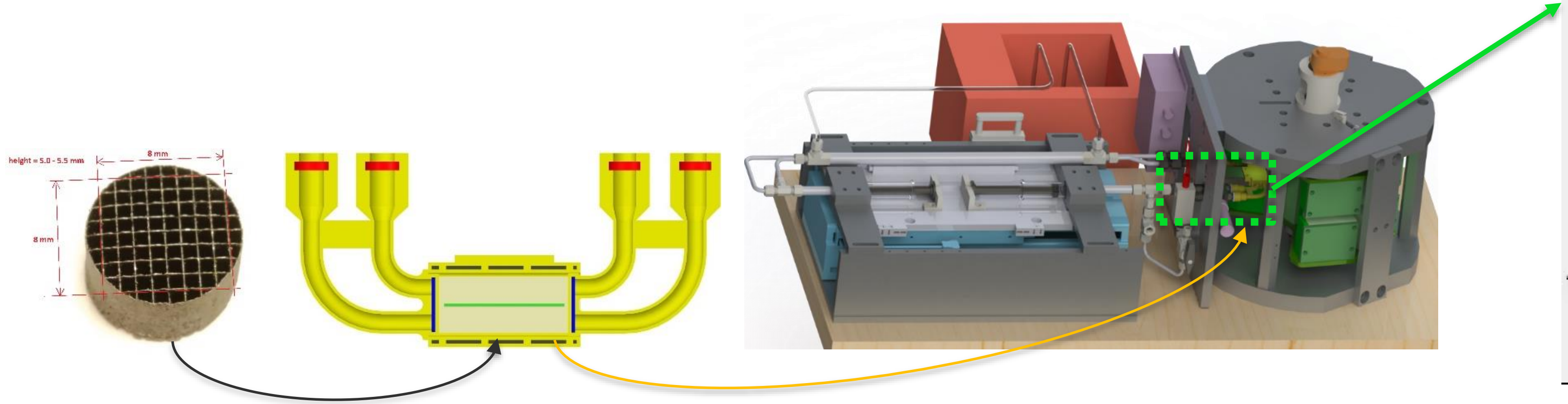
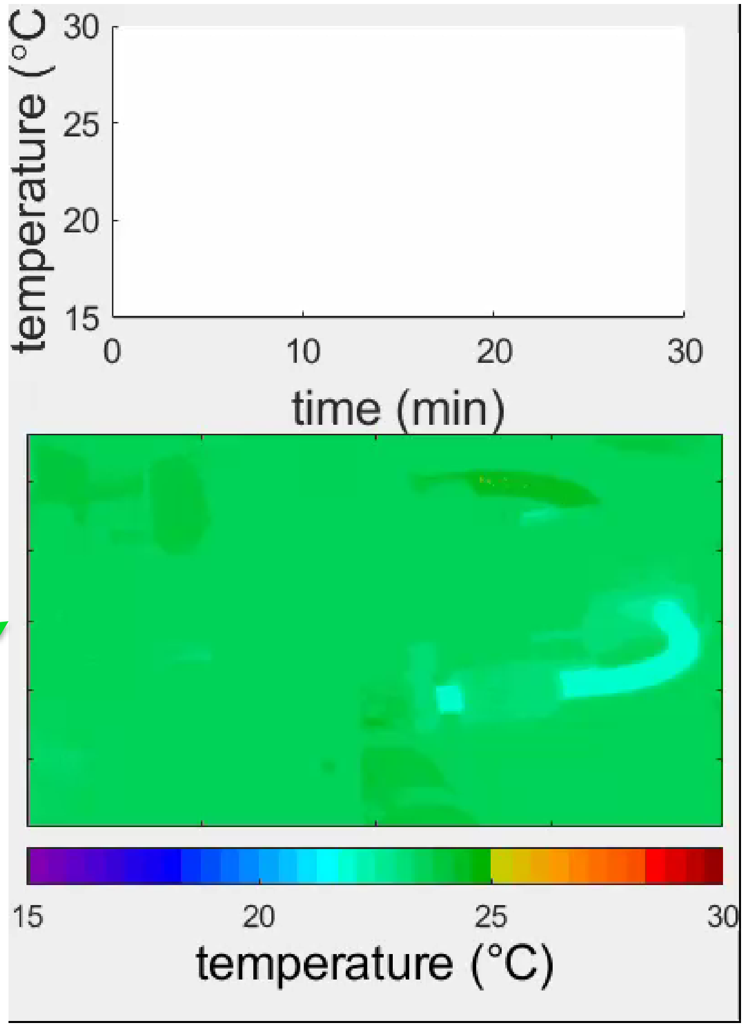
# The future

- Innovations in energy efficient materials and systems can and must be accelerated
- Close the gap between discovery, synthesis, and characterization of materials and their performance as critical system components





# Thank you very much for your attention!