Materials for Eco-friendly Refrigeration

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(Egypt)
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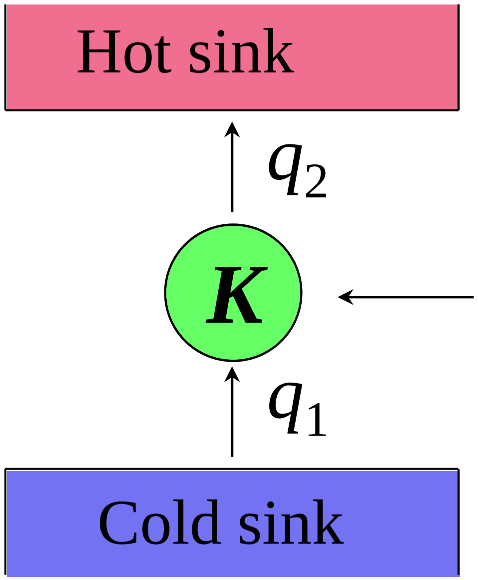
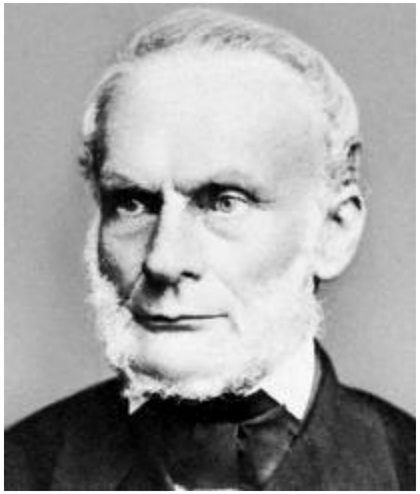
Mauritania
Mali
Niger
Chad
Sudan
Nigeria
Ethiopia
Kenya
DR Congo
Tanzania
Angola
Namibia
Botswana
Madagascar
South
Africa
(Thailand)
Indonesia
Venezuela
Colombia
Brasil
(Brazil)
Perú
Bolivia
Chile
South
Atlantic
Ocean

Modern society relies on the possibility of cooling below ambient

How to cool ?

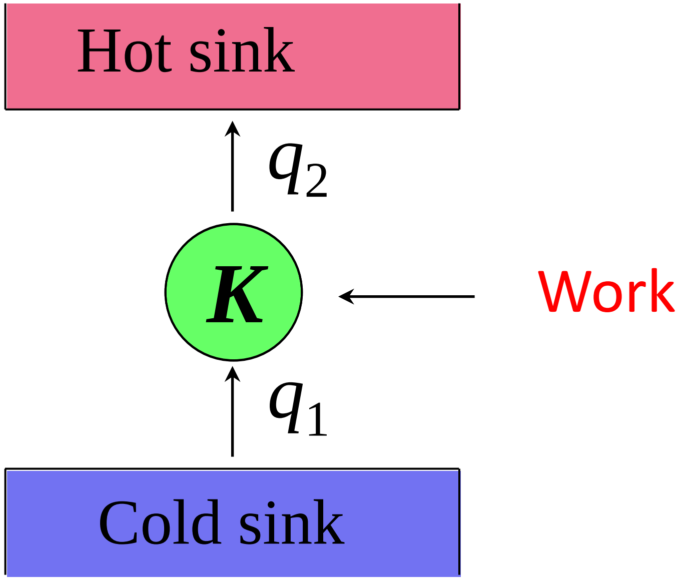


How to cool ?



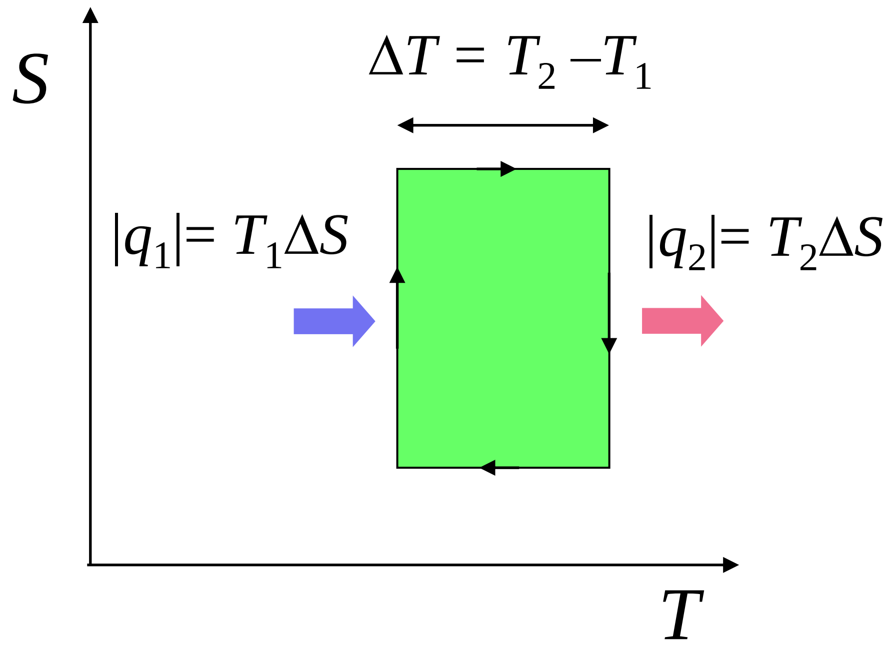
Rudolf Emmanuel Clausius (1822-1888)

Henri Poincaré (1854-1912)



NOT FOR FREE !!!!

The simplest cycle: The Carnot Cycle



Refrigerant capacity

$$R = \Delta S \Delta T$$

Need: Materials with large **changes in entropy and temperature**

Undergraduate Thermodynamics

$$dS = \frac{C}{T}dT + \sum_{i=1}^{n} \left(\frac{\partial x_i}{\partial T}\right)_{Y_j=1....n} dY_i$$

Generalized displacement

Generalized field

Caloric effects

$$\Delta S(0 \rightarrow Y_i) = \int_0^{Y_i} \left(\frac{\partial x_i}{\partial T}\right)_{Y_j=1....n} dY_i$$

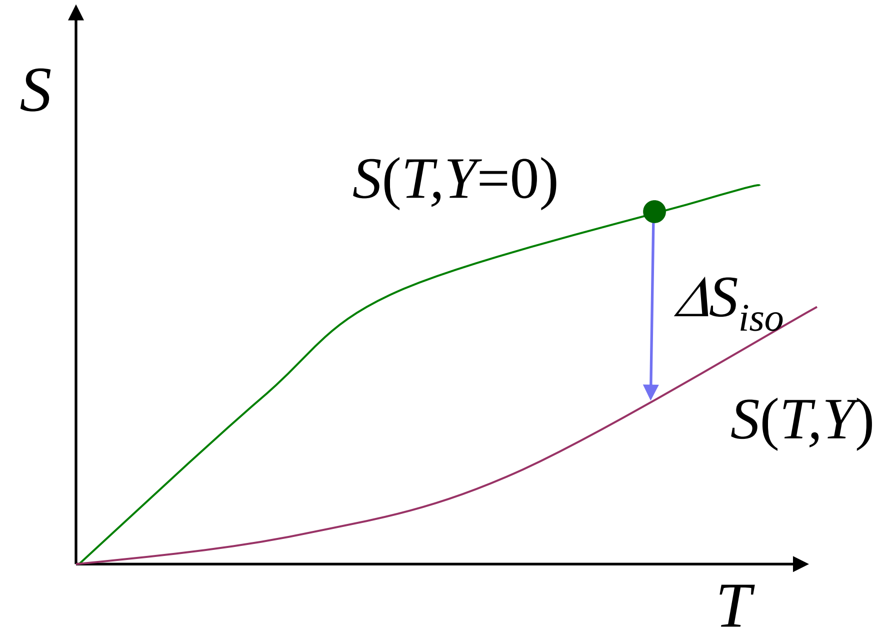
$$\Delta T(0 \rightarrow Y_i) = -\int_0^{Y_i} \frac{T}{C} \left(\frac{\partial x_i}{\partial T}\right)_{Y_j=1....n} dY_i$$

Large caloric effects when $\left(\frac{\partial x_i}{\partial T}\right)_{Y_j=1....n}$ is large

Isothermal entropy change

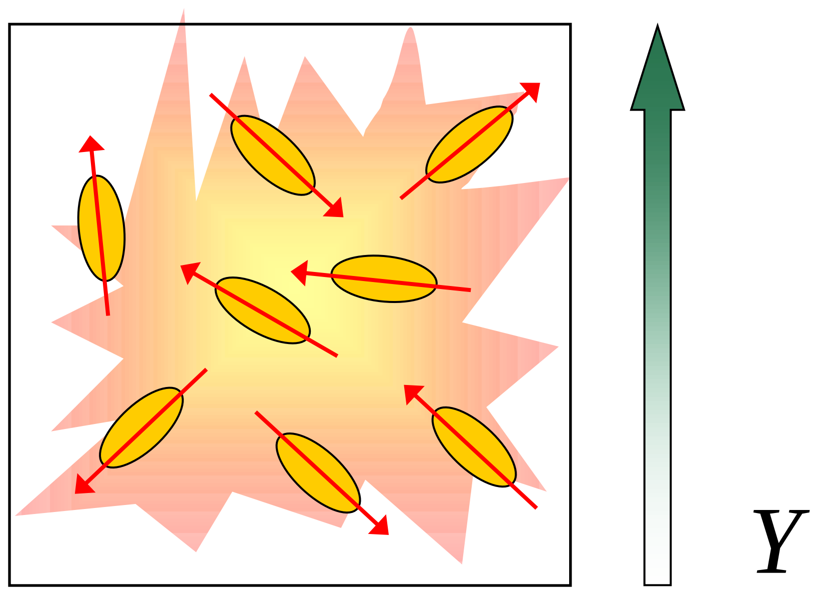
$$\Delta S_{iso} = \int_0^Y \left(\frac{\partial S}{\partial Y} \right)_T dY$$

$$\Delta T_{adi} = -\int_0^Y \frac{T}{C} \left(\frac{\partial S}{\partial Y} \right)_T dY$$



$$\Delta S_{iso} = S_f - S_i < 0$$

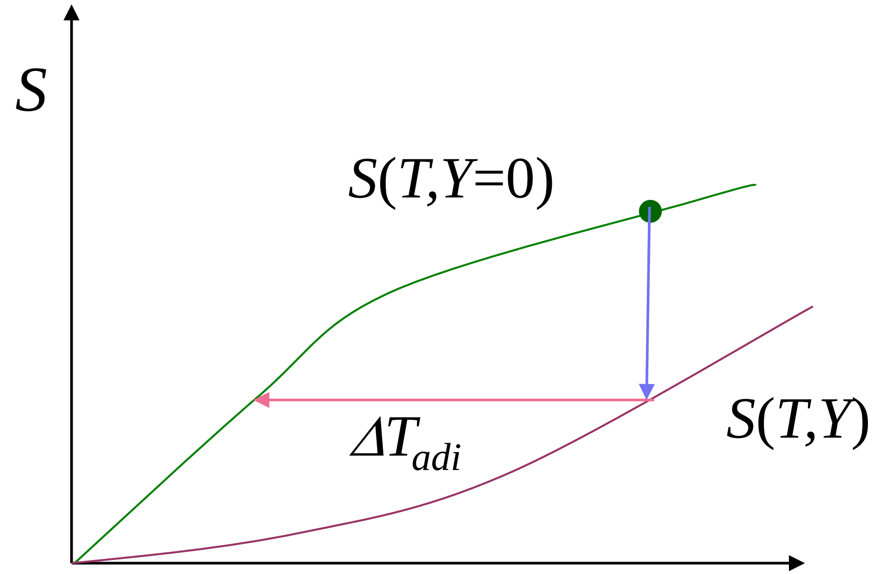
$$T_f = T_i$$



Adiabatic temperature change

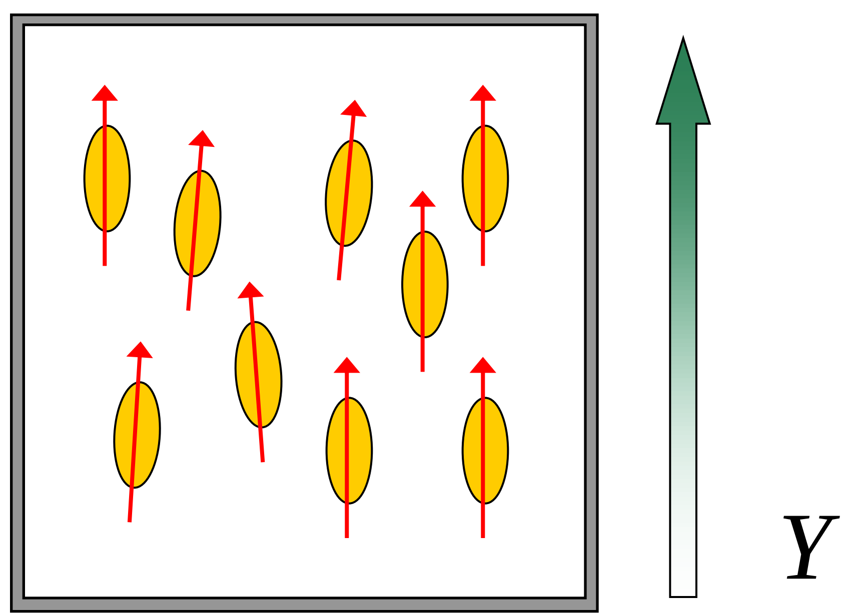
$$\Delta S_{iso} = \int_0^Y \left(\frac{\partial S}{\partial Y}\right)_T dY$$

$$\Delta T_{adi} = -\int_0^Y \frac{T}{C}\left(\frac{\partial S}{\partial Y}\right)_T dY$$



$$\Delta T_{adi} = T_f - T_i < 0$$

$$S_f = S_i$$



Caloric effect

Conventional caloric effect

- In general $\left(\frac{\partial x}{\partial T}\right)_H < 0 \quad \Rightarrow \Delta S_{iso}<0$ when $\Delta Y > 0$

$$\Downarrow$$

Sample heats up when applying field adiabatically

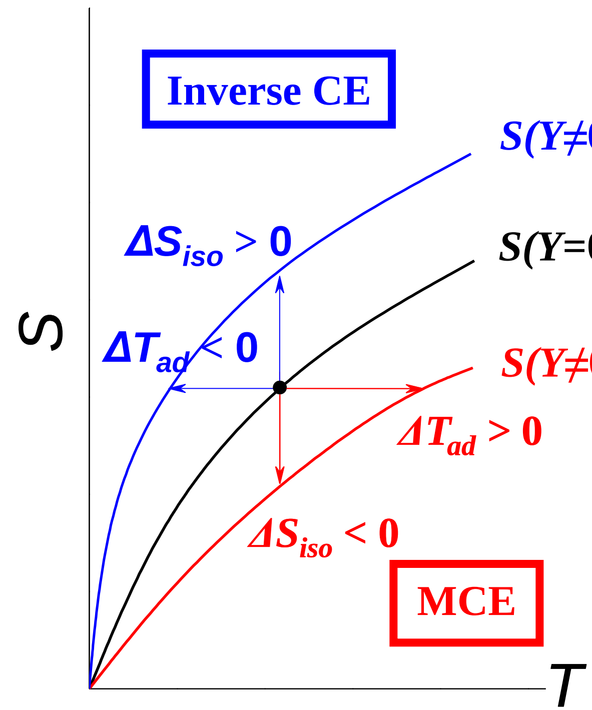
But.....

$$\left(\frac{\partial x}{\partial T}\right)_H > 0 \quad \Rightarrow \quad \Delta S_{iso} > 0 \text{ when } \Delta Y > 0$$

$$\Downarrow$$

Sample cools down when applying field adiabatically

Inverse caloric effect



Computation of caloric effects

$$dS = \frac{C}{T}dT + \sum_{i=1}^{n} \left(\frac{\partial x_i}{\partial T}\right)_{Y_j=1\dots n} dY_i$$

Calorimetric (adiabatic, relaxational, ac,..) measurement of *C* under field

$$S(T,Y) = \int_{T_i}^{T} \frac{C}{T} dT$$

From Maxwell relation:
Isothermal measurements *x* vs *Y*

$$\Delta S(0 \rightarrow Y_i) = \int_0^{Y_i} \left(\frac{\partial x_i}{\partial T}\right)_{Y_j=1\dots n} dY_i$$

Direct methods: adiabatic measurement of temperature

Other methods: pulsed fields, Clausius-Clapeyron, etc…

Undergraduate Thermodynamics

$$dS = \frac{C}{T}dT + \sum_{i=1}^{n} \left(\frac{\partial x_i}{\partial T}\right)_{Y_j=1\ldots n} dY_i$$

Generalized displacement

Generalized field

Caloric effects

$$\Delta S(0 \to Y_i) = \int_0^{Y_i} \left(\frac{\partial x_i}{\partial T}\right)_{Y_j=1\ldots n} dY_i$$

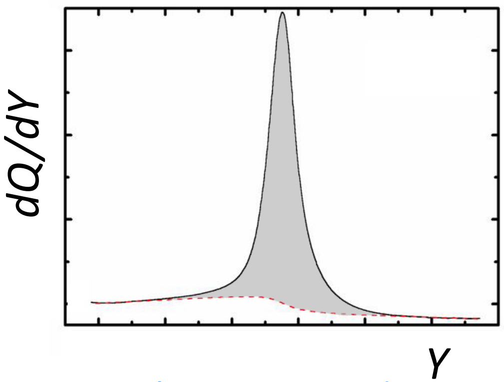
$$\Delta T(0 \to Y_i) = -\int_0^{Y_i} \frac{T}{C} \left(\frac{\partial x_i}{\partial T}\right)_{Y_j=1\ldots n} dY_i$$

At a first order phase transition !!

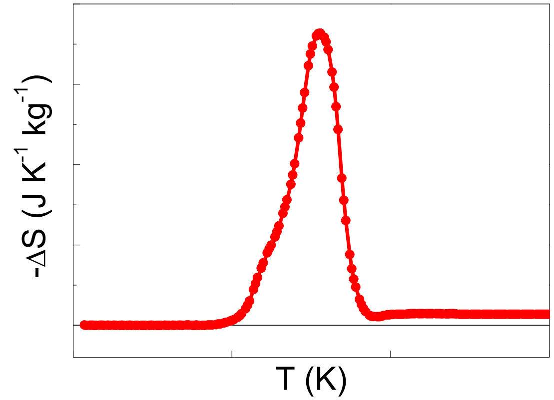
Large caloric effects when $\left(\frac{\partial x_i}{\partial T}\right)_{Y_j=1\ldots n}$ is large

Measurements of entropy changes at a first order phase transition:

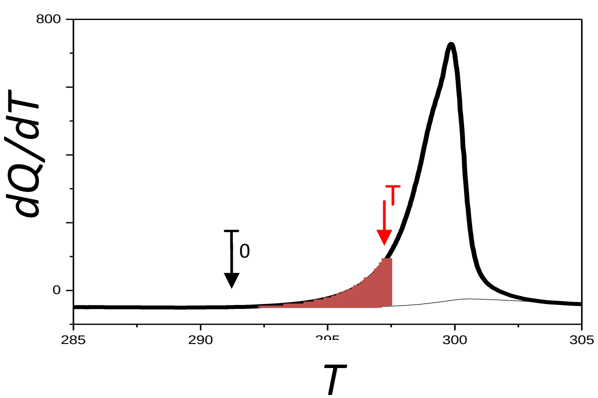
DSC Calorimetry under constant temperature (*T*): sweeping field (Y)

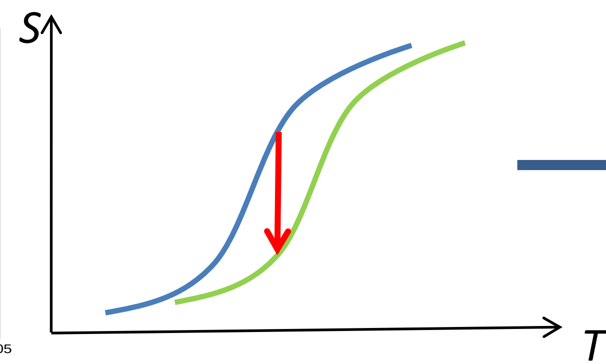


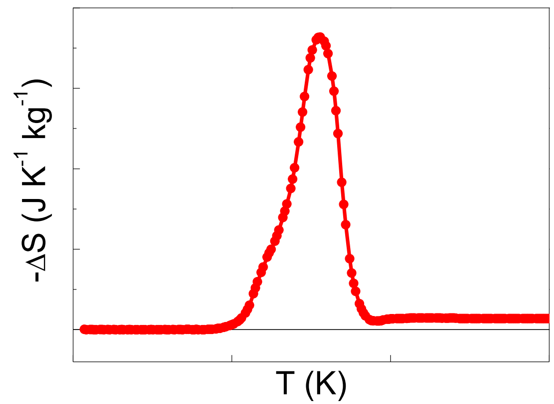
$$\Delta S_Y = \frac{1}{T}\int_0^Y \frac{dQ}{dY}dY$$



DSC Calorimetry under constant field (Y): sweeping temperature (*T*)

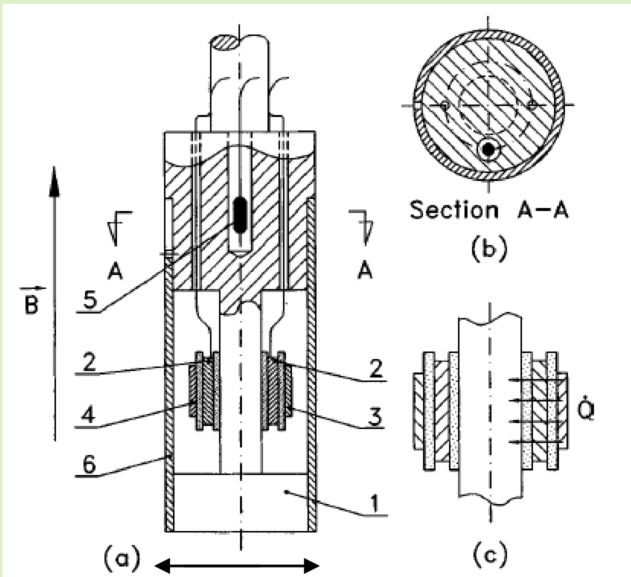






$$S(T,Y) - S(T_0,Y) = \int_{T_0}^{T} \frac{1}{T}\frac{dQ}{dT}dT$$

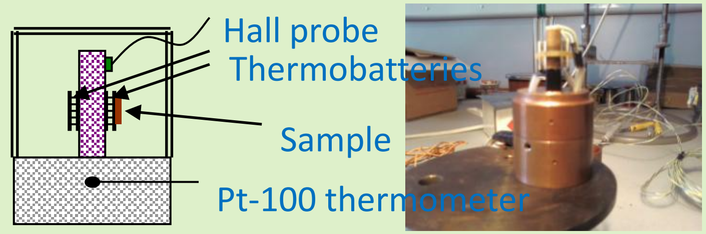
$$\Delta S_Y = S(T,Y) - S(T,0)$$

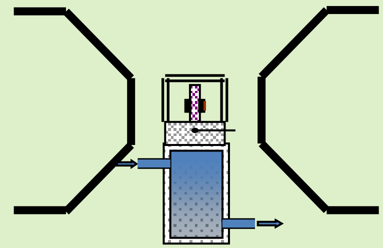


16 mm

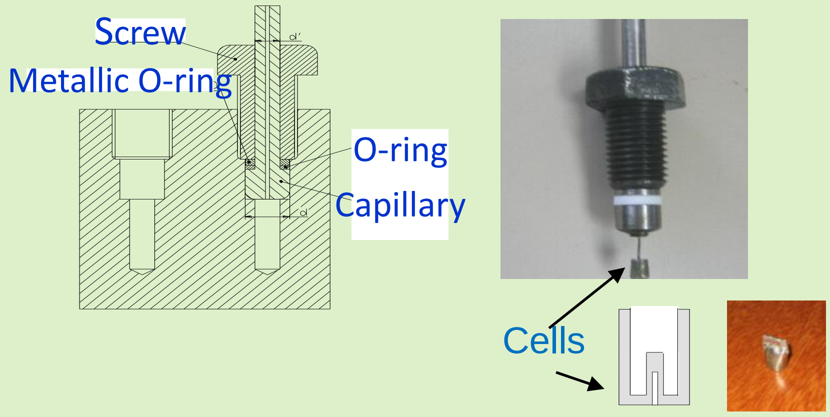
1 Cu block
2 Sensors (thermobatteries)
3 Sample
4 Reference
5 Carbon-glass resistor (T)

Marcos et al., Rev. Sci.Ints., 74, 4768 (2003)

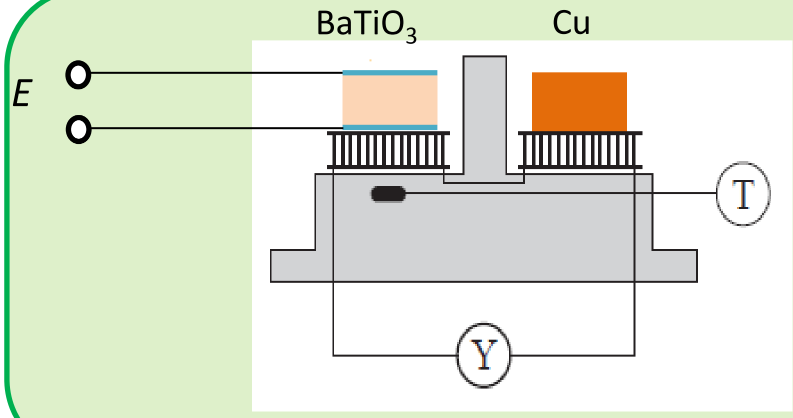




Calorimeters under magnetic field.



Calorimeter under hydrostatic pressure.



Calorimeters under electric field.

A FEW EXPERIMENTAL RESULTS

Magneto caloric effect: Ni-Mn-Sn; Ni-Mn-In

T. Krenke et al. Nature Mater. 4 (2005) 450

Barocaloric effect: Ni-Mn-In, La-Fe-Co-Si

L. Mañosa et al. Nature Mater. 9 (2010) 478.

L. Mañosa et al. Nature Comm. 2(2011) 595.

Elastocaloric effect: Cu-Zn-Al

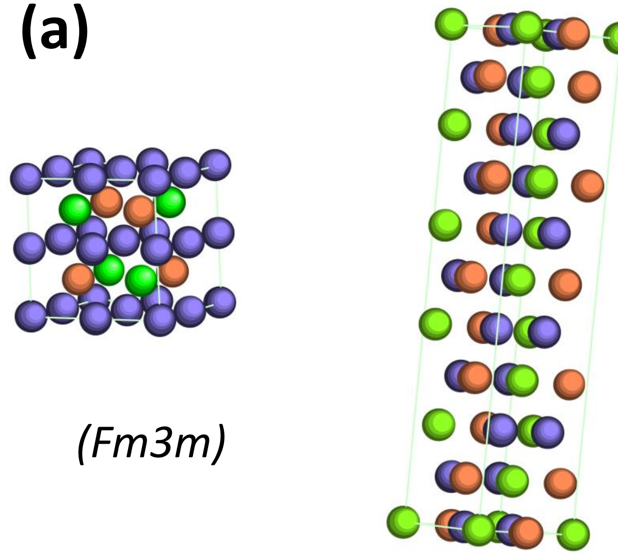
E. Bonnot et al. Phys. Rev. Lett. 100 (2008) 125901.

Electrocaloric effect: $BaTiO_3$

Magnetic shape memory alloys

Martensitic transition

(a)



(b)

(Fm3m)

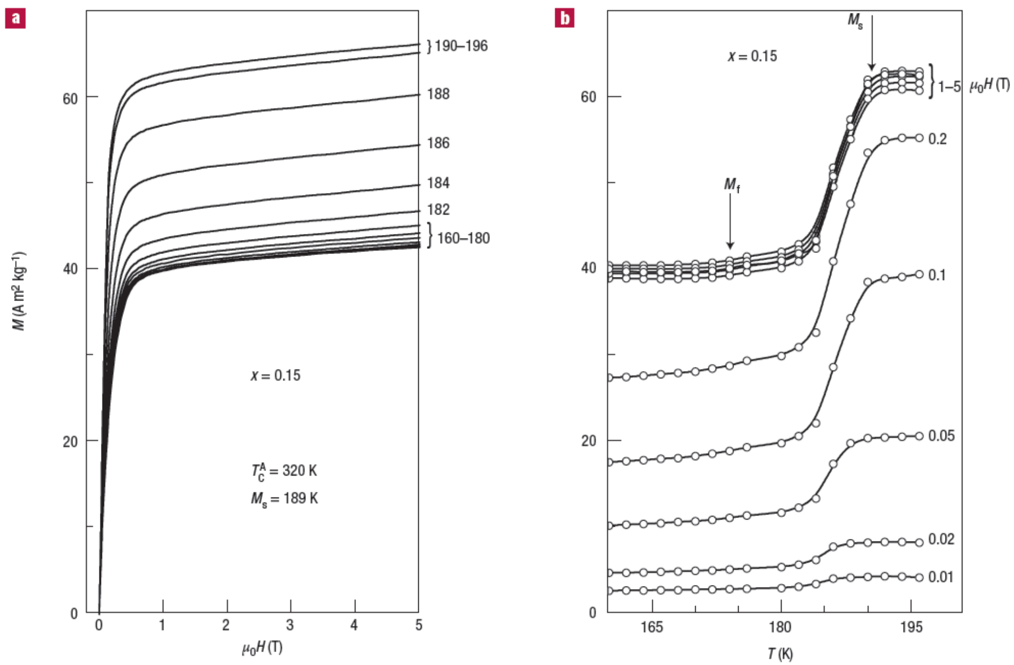
Heusler X_2YZ

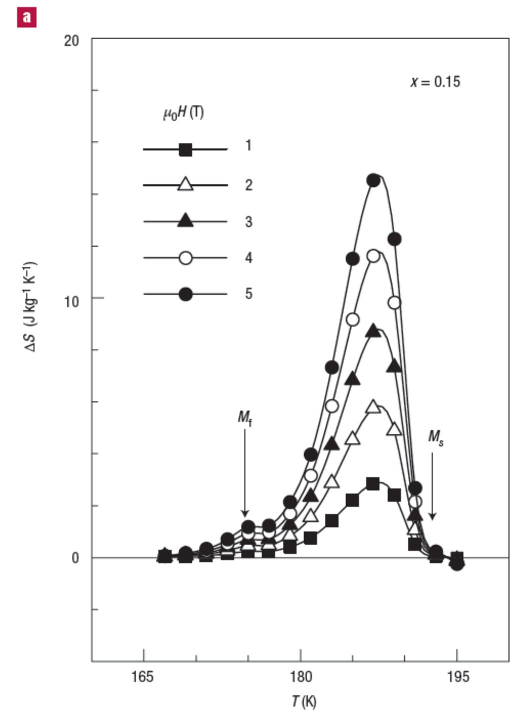
Change in symmetry + Change in magnetization + Change in volume + Change in strain

Magnetocaloric effect

Ni-Mn-X (X=Sn,In,Sb,Ga)

Ni-Mn-Sn



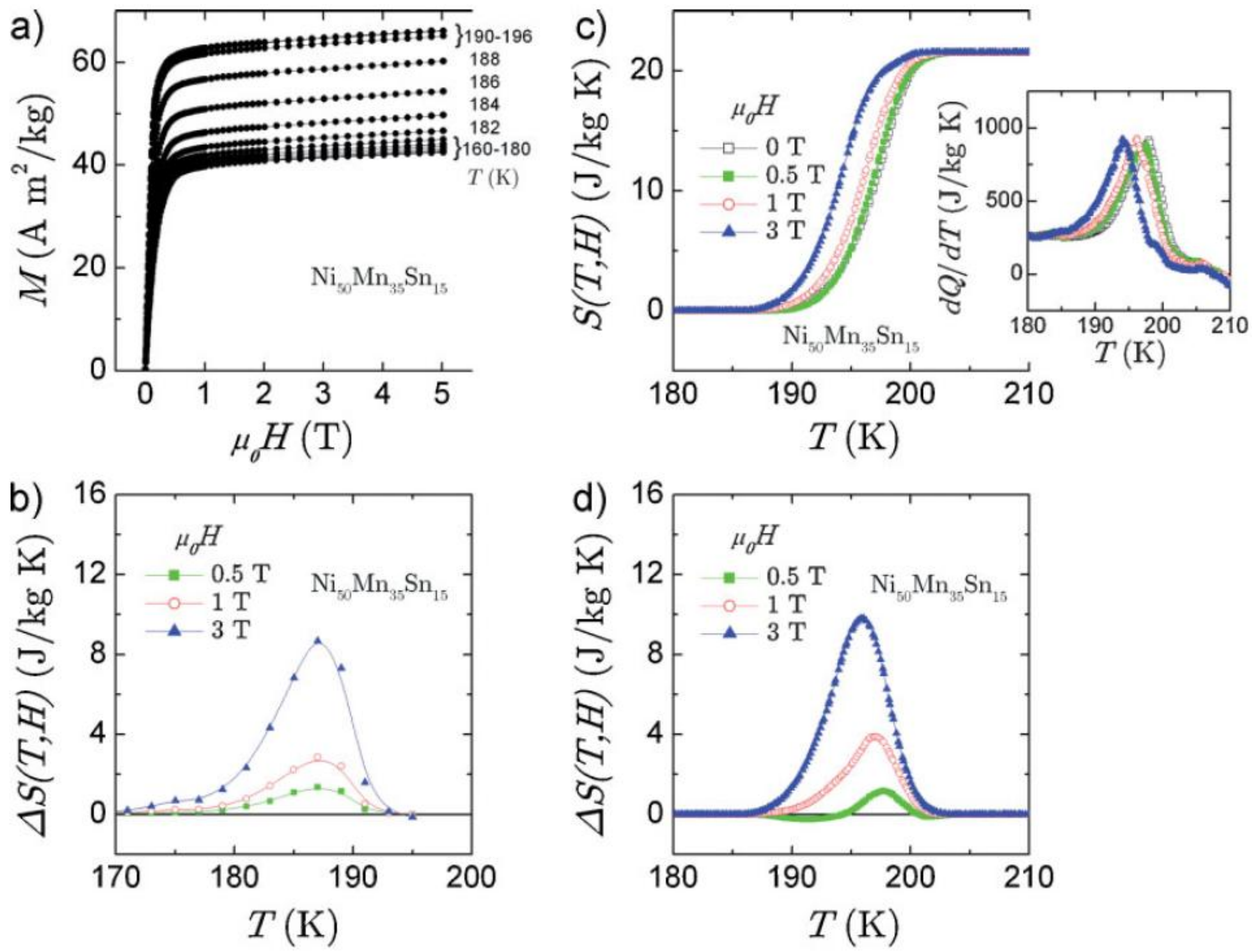


T. Krenke et al. Nature Mater. 4 (2005) 450

Magnetocaloric effect is inverse: entropy increases on applying field

Magnetocaloric effect

Ni-Mn-X (X=Sn,In,Sb,Ga)



T. Krenke et al. Nature Mater. 4 (2005) 450

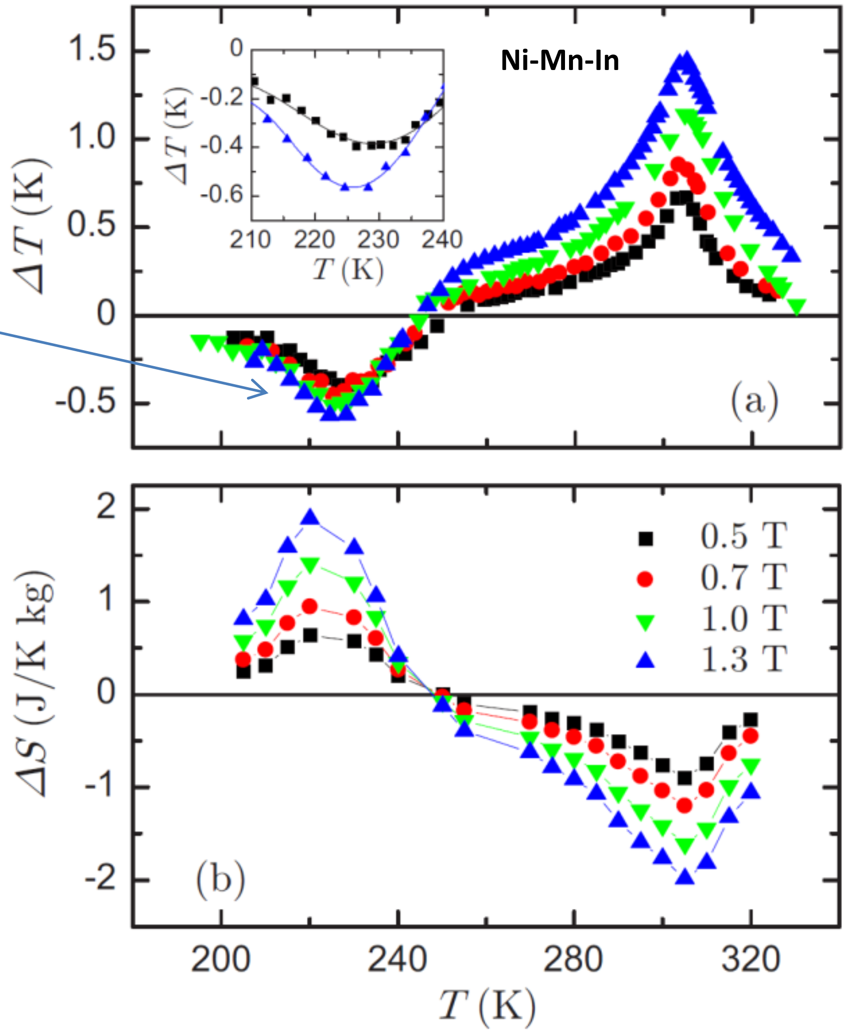
L. Mañosa et al., Adv. Mater. 21 (2009) 3725.

Magnetocaloric effect

Ni-Mn-X (X=Sn,In,Sb,Ga)

Inverse magnetocaloric:

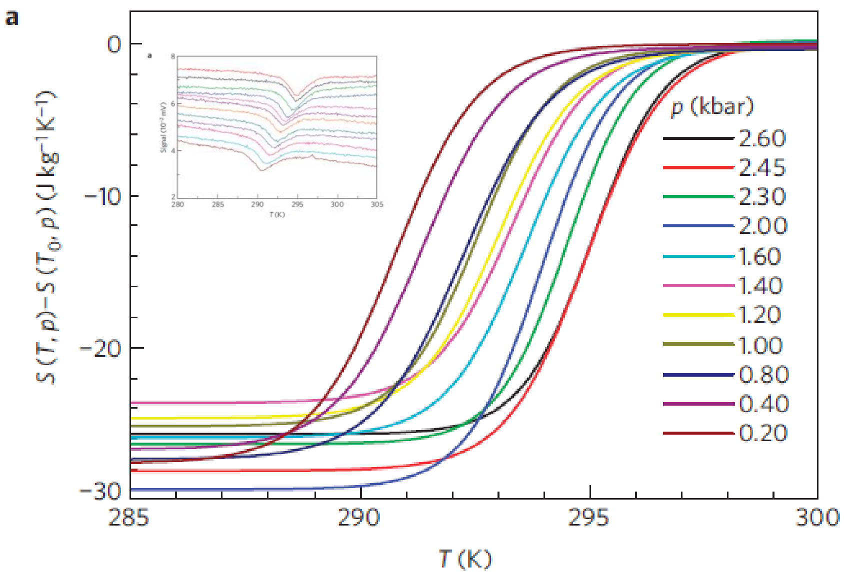
Sample **cools** on applying Magnetic field.

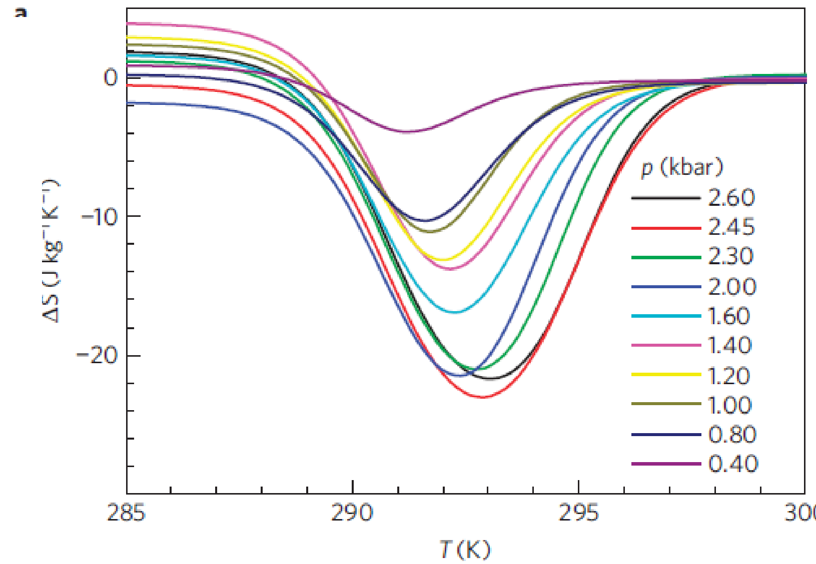


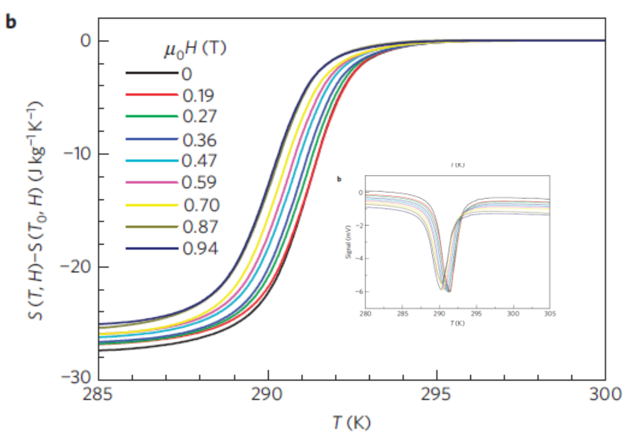
X. Moya et al. Phys. Rev. B 75 (2007) 184412

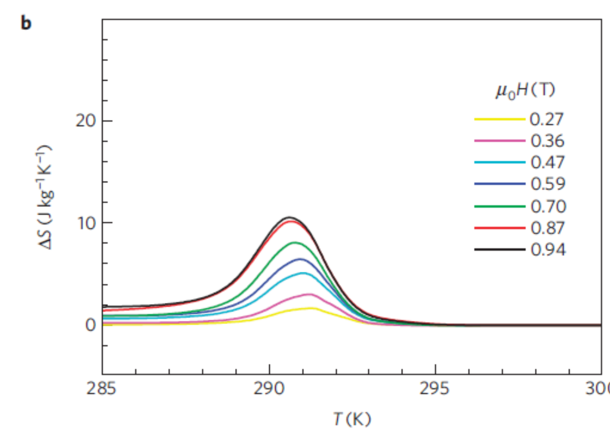
Barocaloric effect

Ni-Mn-In





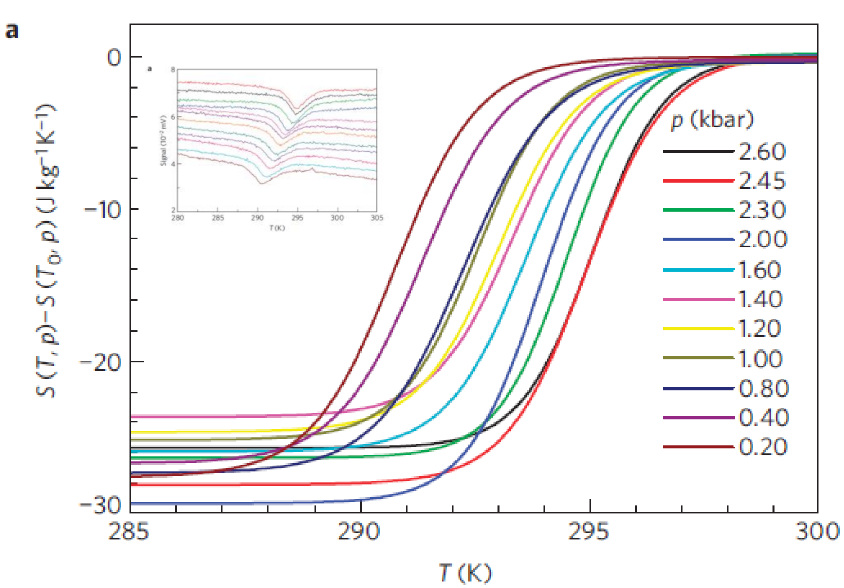


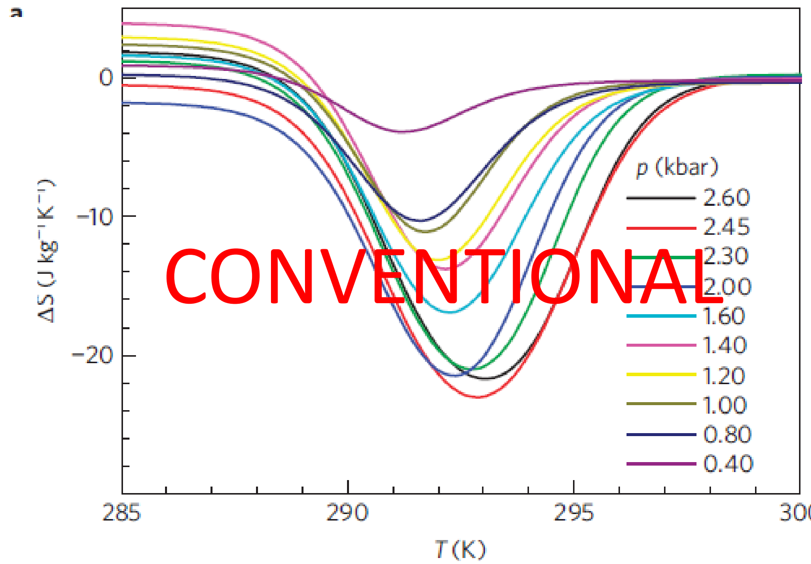


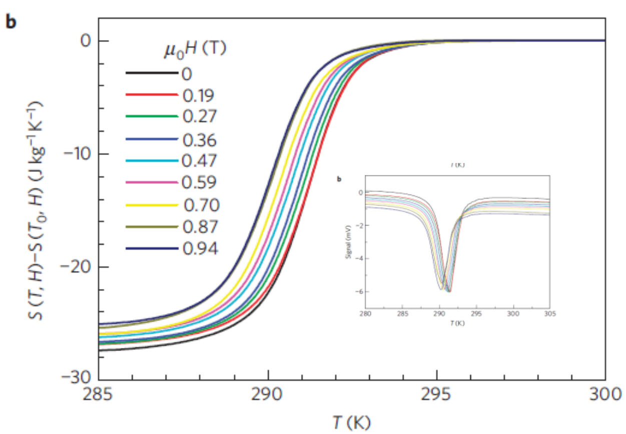
L. Mañosa et al Nature Mater. 9 (2010) 478

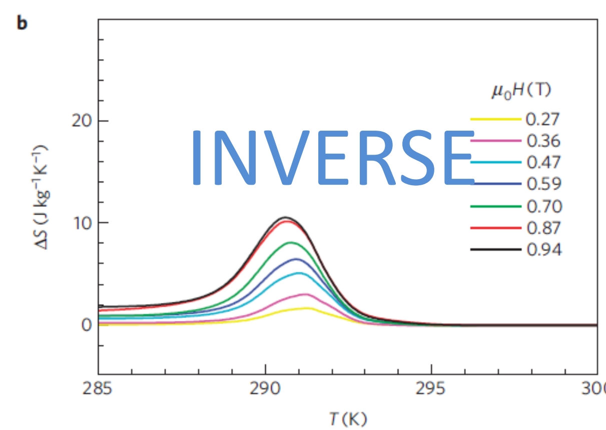
Barocaloric effect

Ni-Mn-In



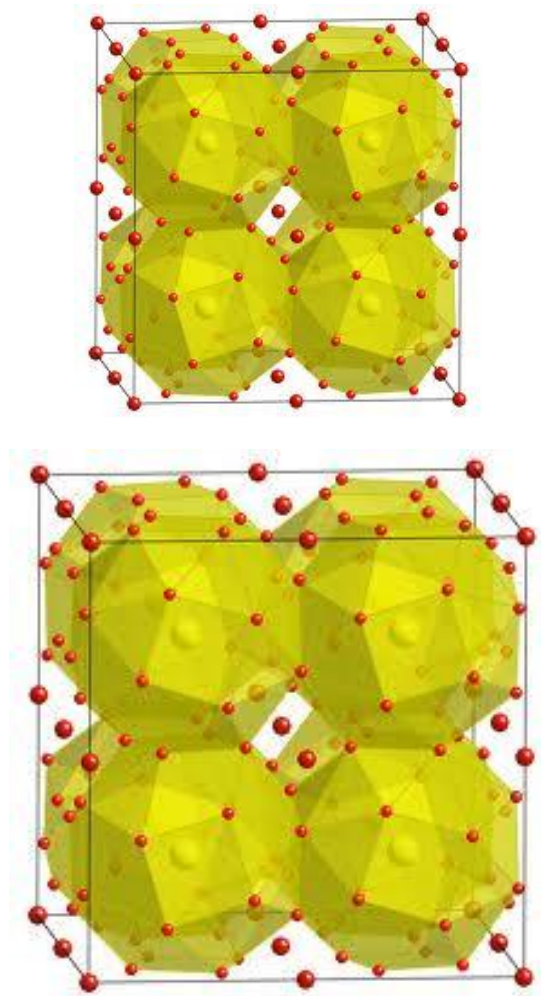






L. Mañosa et al Nature Mater. 9 (2010) 478

La-Fe-Si

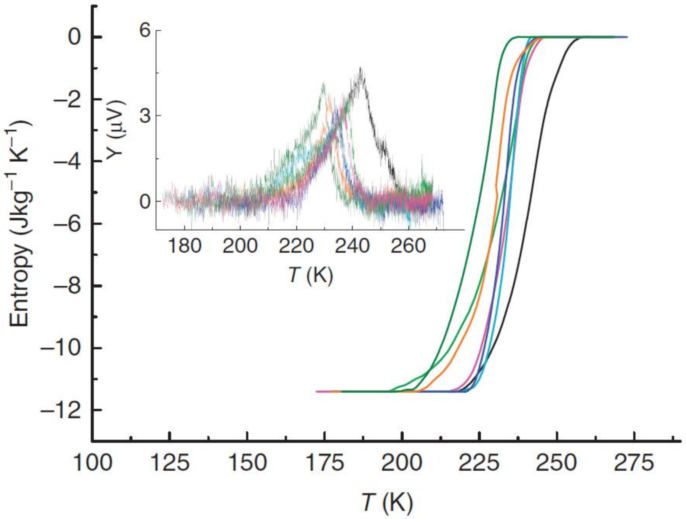


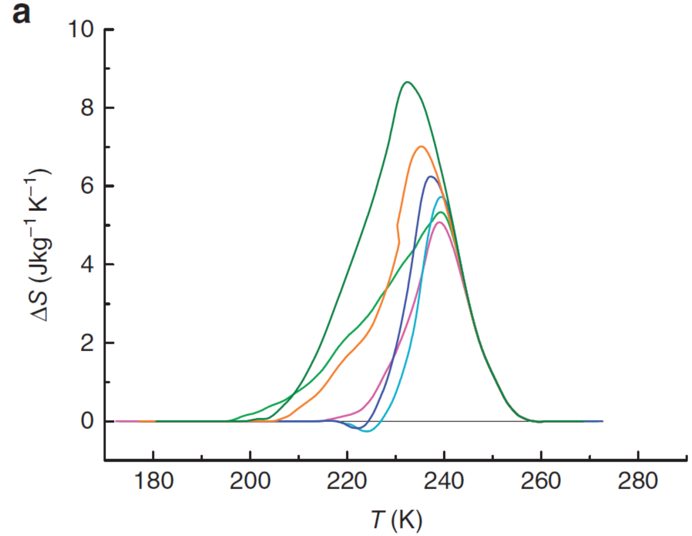
$NaZn_{13}$ structure

(Fm-3c)

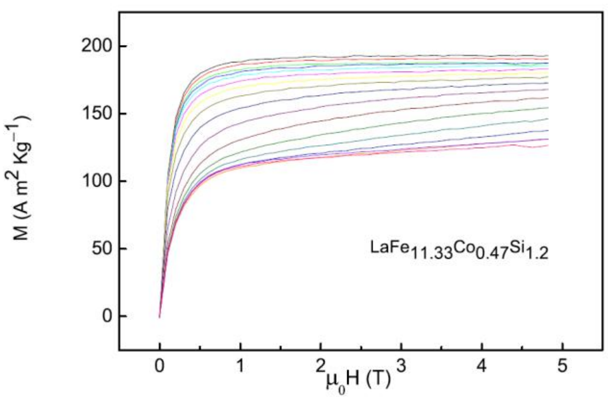
No change in symmetry + Change in magnetization + Change in volume

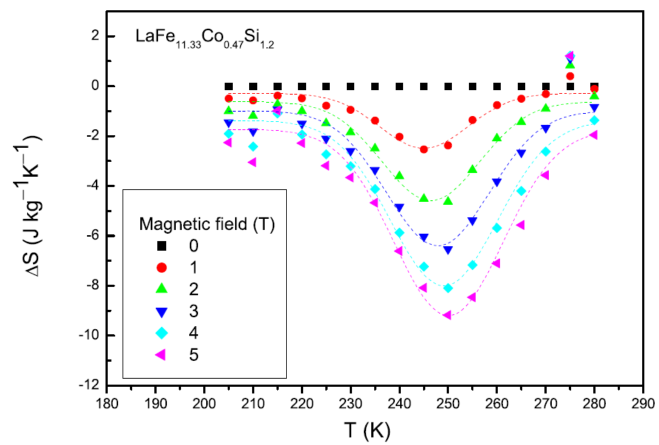
Barocaloric effect





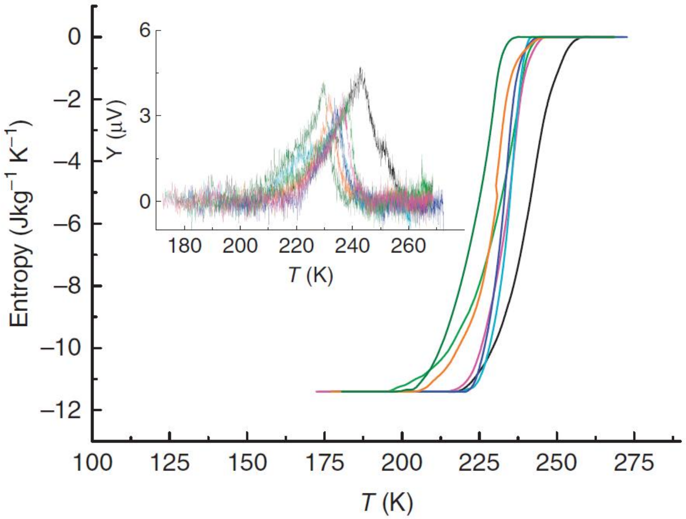
Magnetocaloric effect

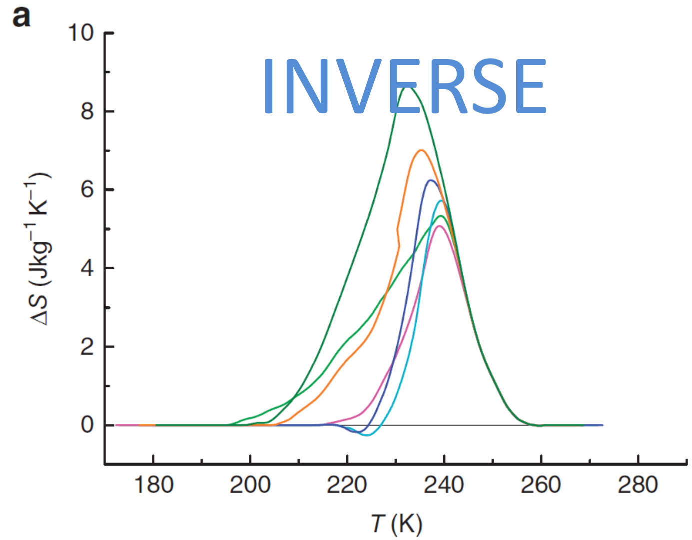




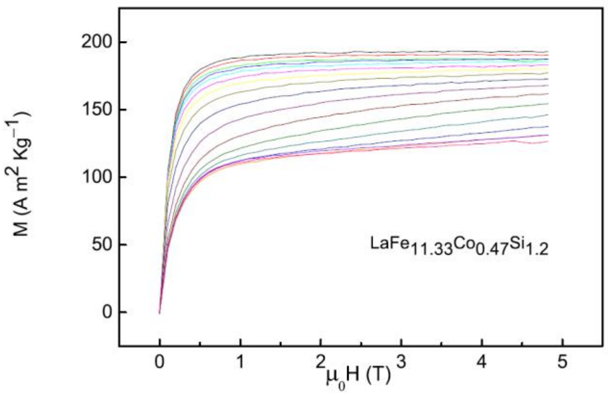
L. Mañosa et al Nature Commun. 2 (2011) 595

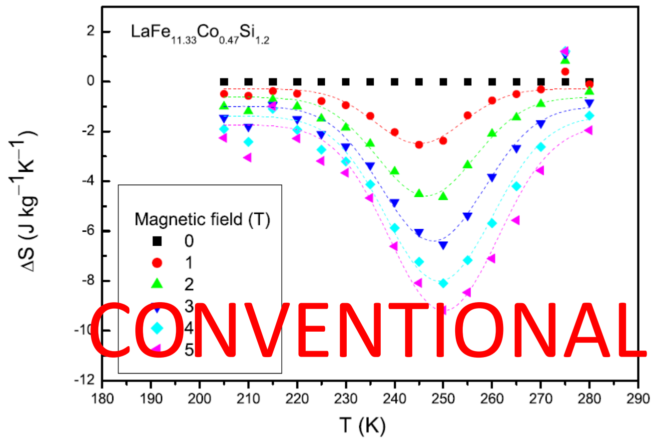
Barocaloric effect



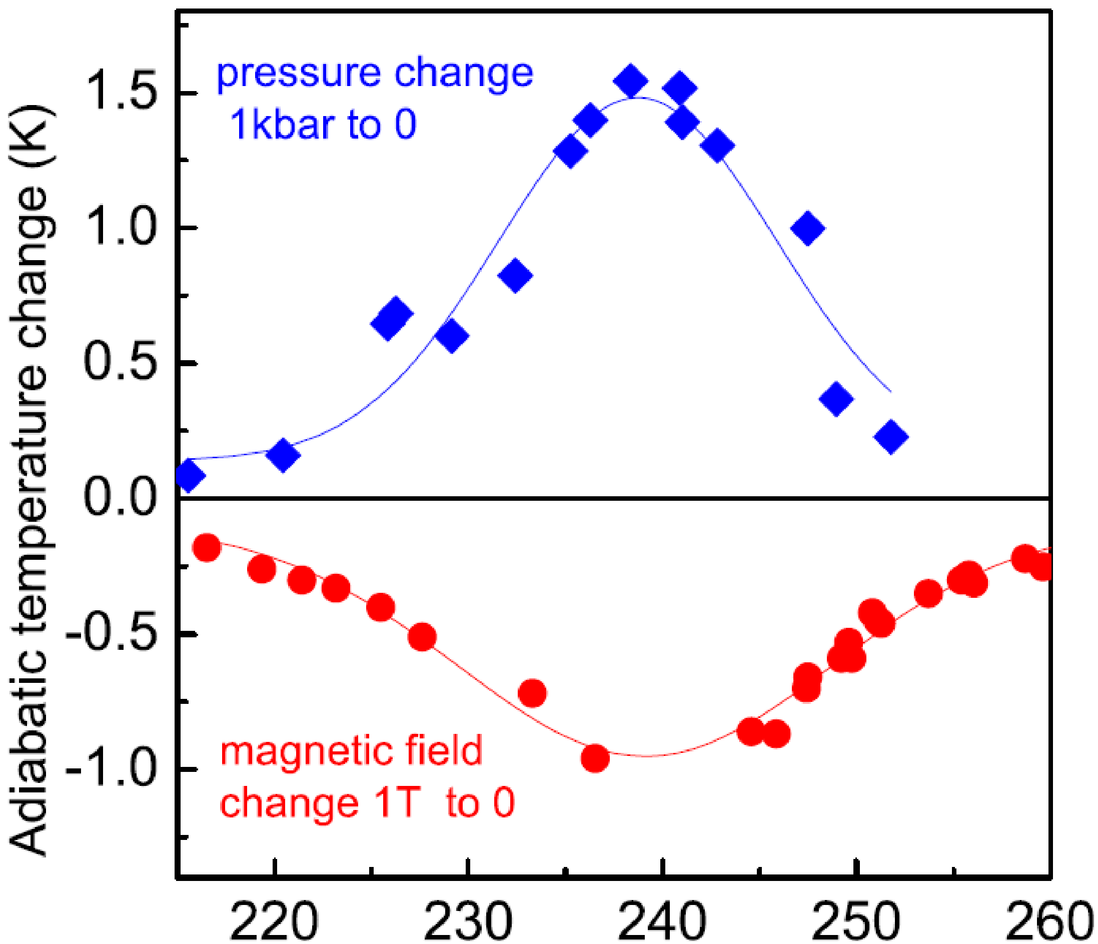


Magnetocaloric effect





L. Mañosa et al Nature Commun. 2 (2011) 595



Inverse caloric effect

Sample warms up on releasing pressure.

Conventional caloric effect

Sample cools down on removing field.

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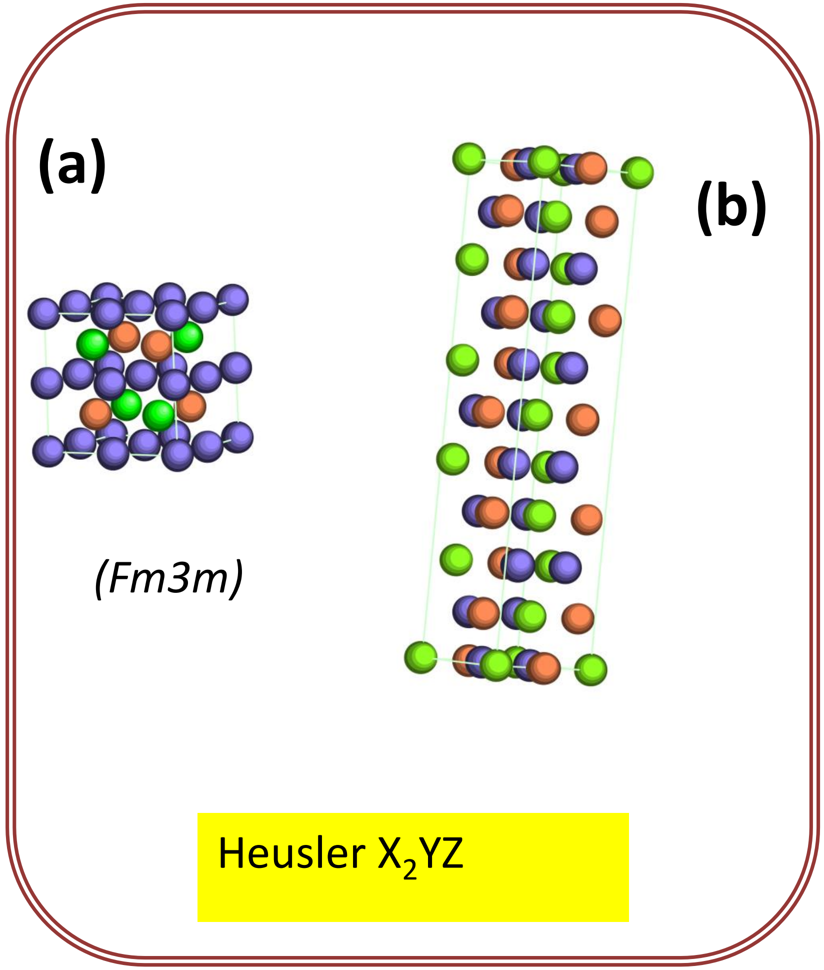
Shape memory alloys (the classic ones)

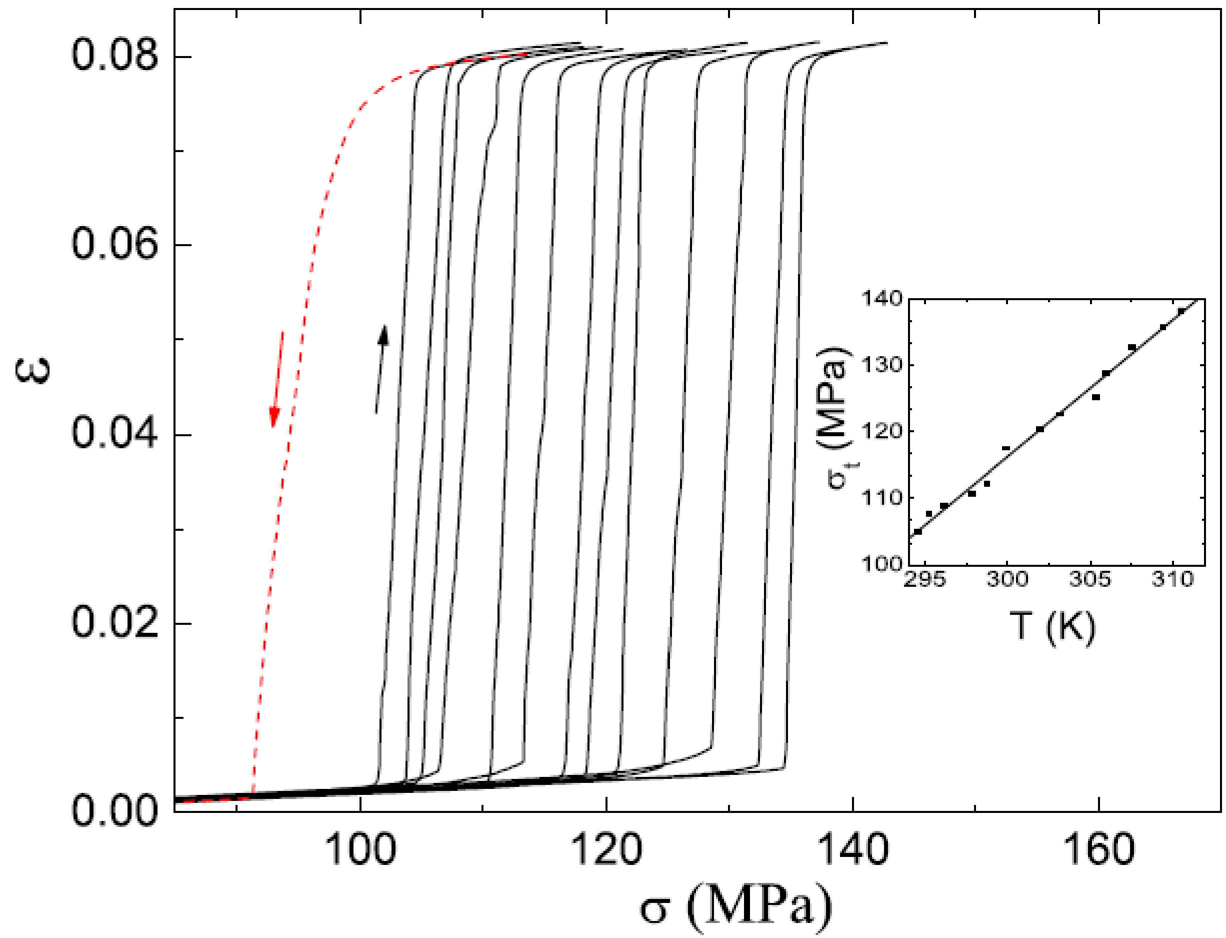
Martensitic transition



Change in symmetry + NO Change in volume + Change in strain

Elastocaloric effect

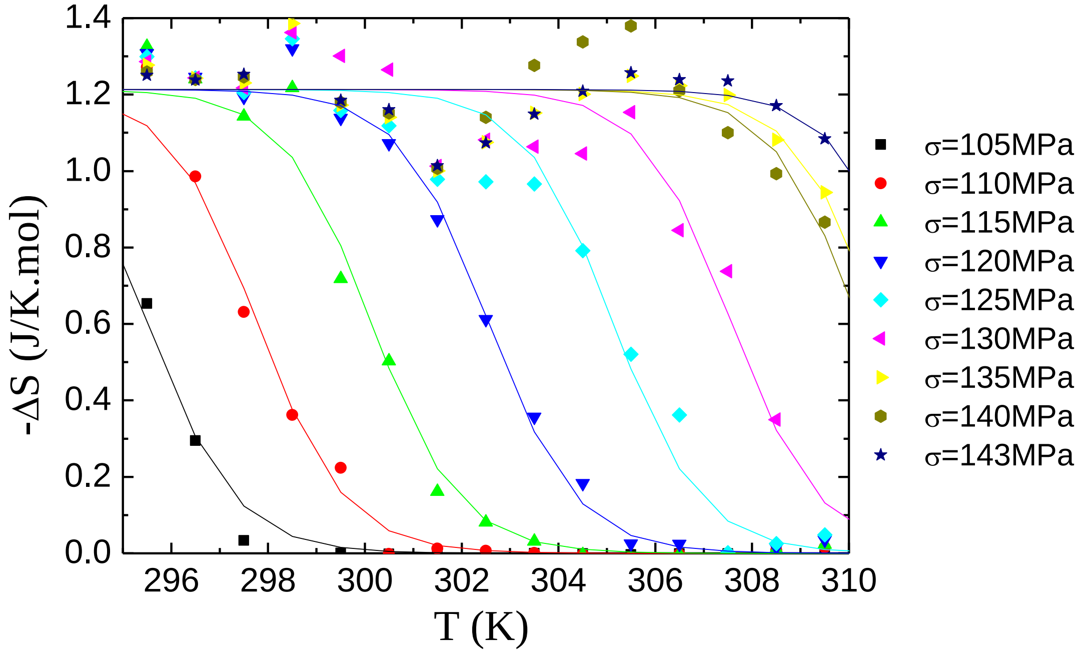
$Cu_{0.6813}Zn_{0.1574}Al_{0.1613}$



$$\Delta S(0 \to \sigma) = \int_0^{\sigma} \left(\frac{\partial S}{\partial \sigma} \right)_T d\sigma = \int_0^{\sigma} \left(\frac{\partial \varepsilon}{\partial T} \right)_{\sigma} d\sigma$$

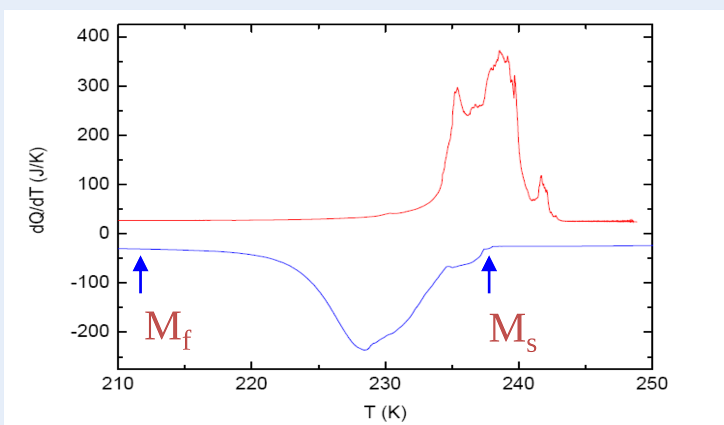
E. Bonnot et al.
Phys. Rev. Lett 100 (2008) 125901

Elastocaloric effect



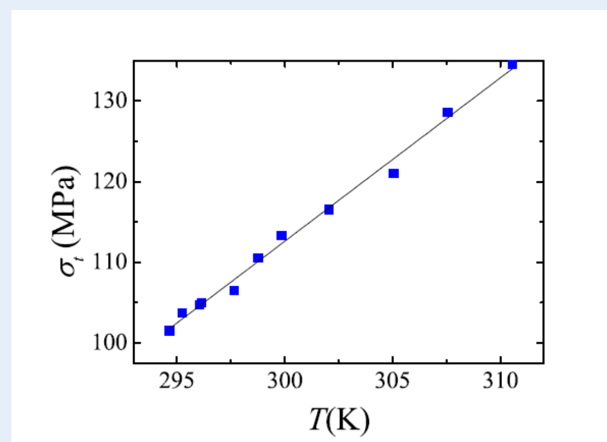
$\Delta S_{max} = \Delta S_t$ = -1.2 J/mol K
= - 20 J/kg K

calorimetry



$$\Delta S = \int_{M_s}^{M_f} \frac{1}{T}\frac{dQ}{dT}dT = -1.3 J/molK$$

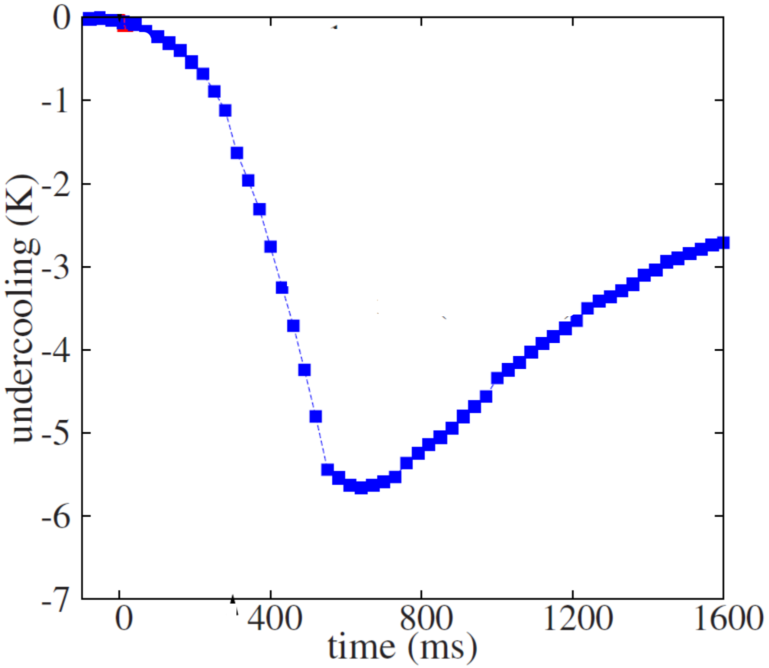
Clausius-Clapeyron

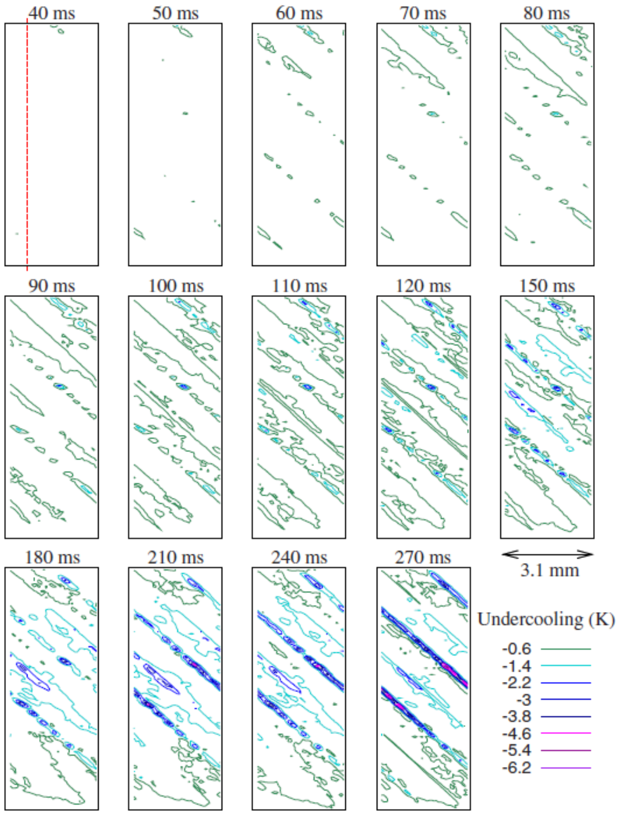


$$\Delta S_t = V\Delta\varepsilon \frac{d\sigma_t}{dT} = -1.2 J/molK$$

Elastocaloric effect

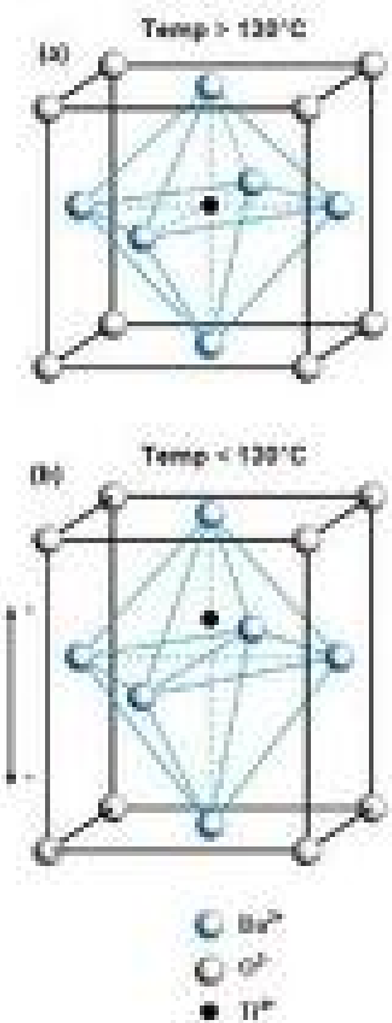
Adiabatic temperature change





E. Vives et al. Appl. Phys. Lett. 98 (2011) 011902

$BaTiO_3$



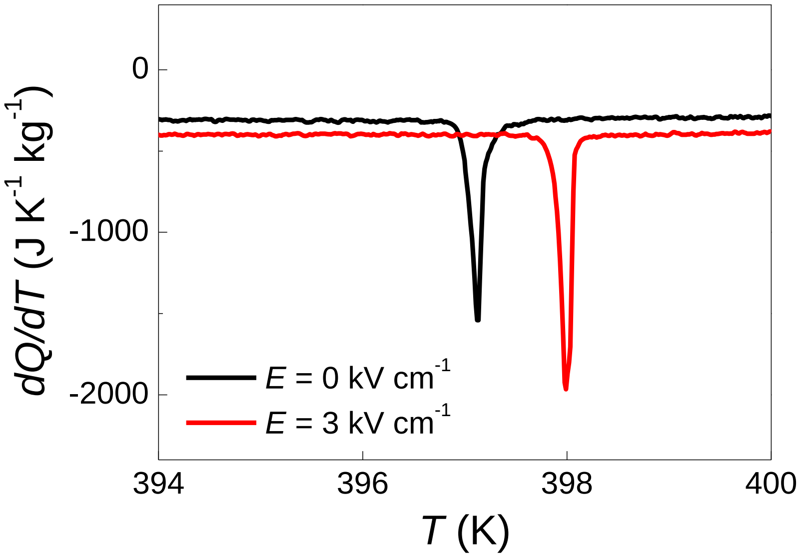
Pm3m

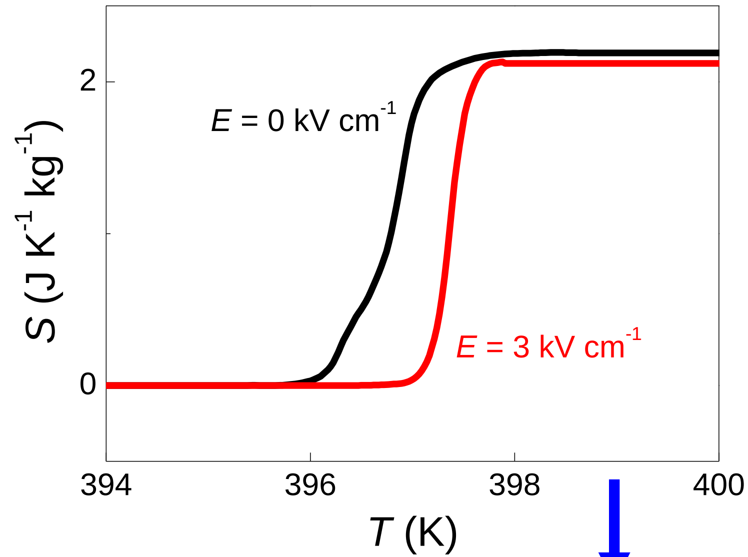
P4/mmm

Change in symmetry + Change in volume + Change in polarization

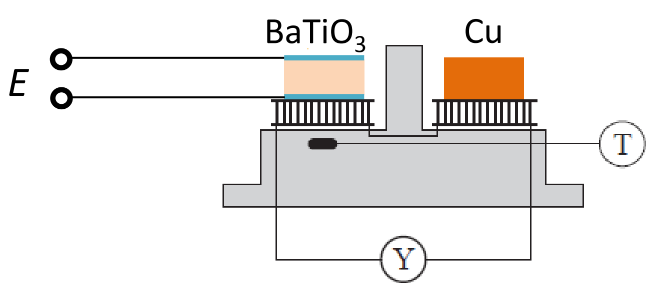
Electrocaloric effect

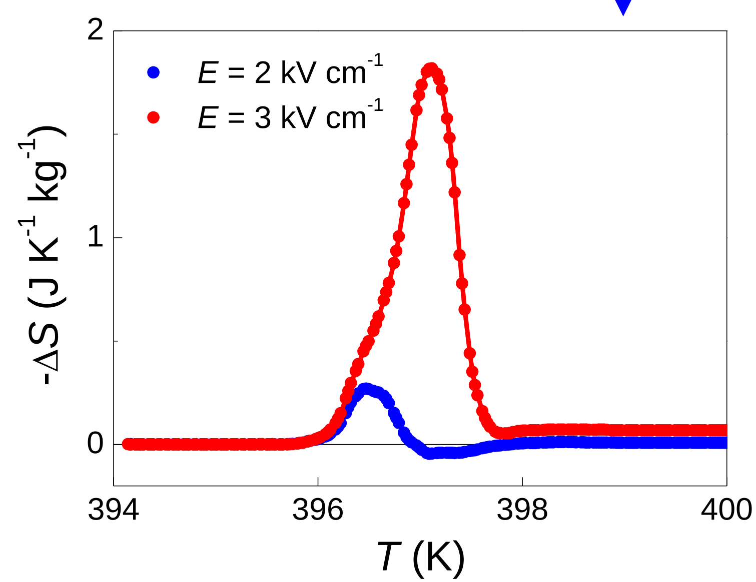
Sweeping temperature





T - C phase transition (cooling)

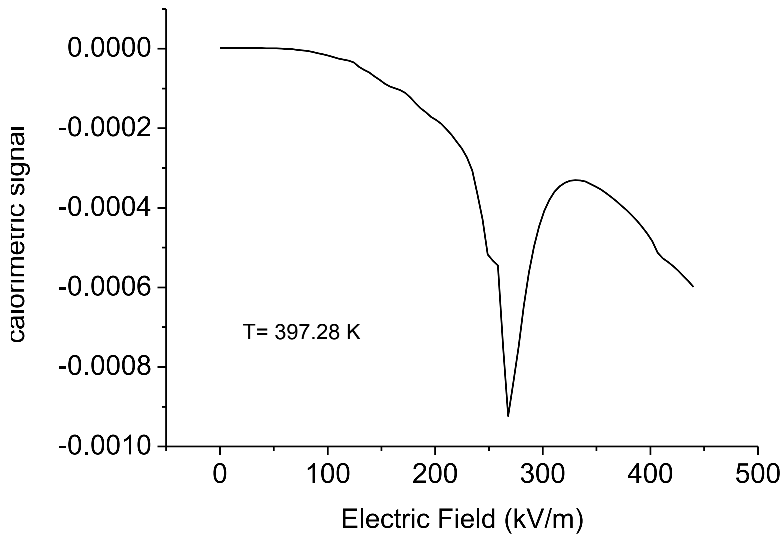


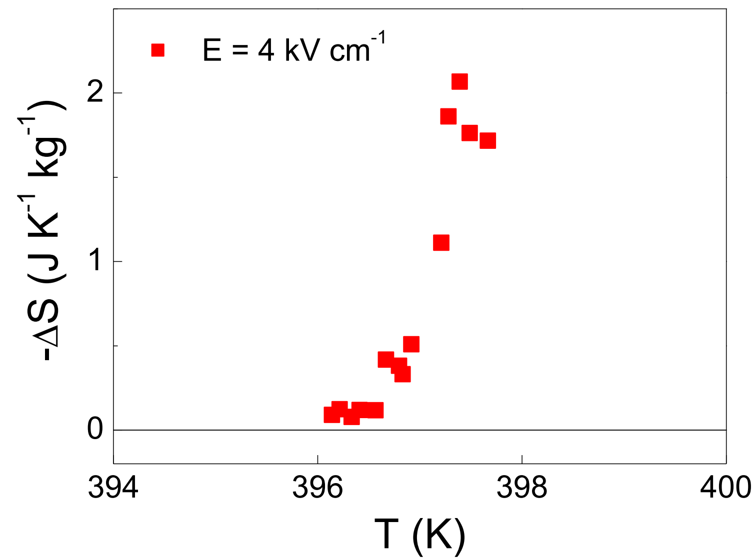


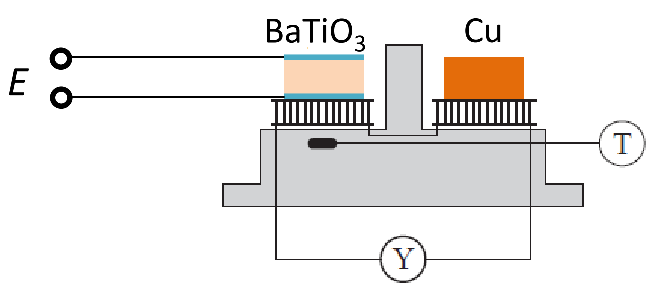
Electrocaloric effect

Sweeping electric field

Field-induced transition





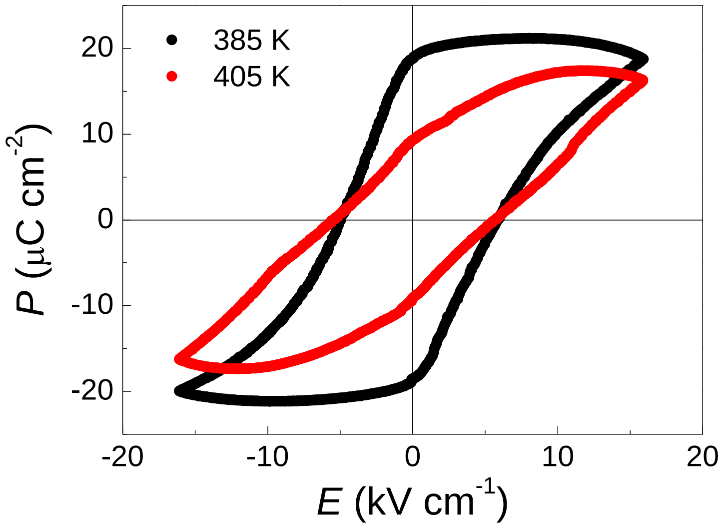


$$\Delta S = \int_{E_i}^{E_f} \frac{1}{T} \left(\frac{dQ}{dE} \right) dE$$

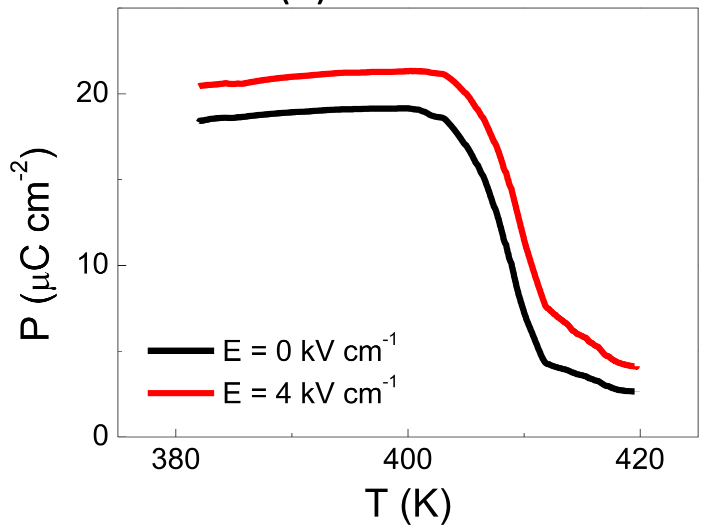
Electrocaloric effect

Indirect method: *P*(*T*,*E*)

P(*E*) different *T* (cooling)

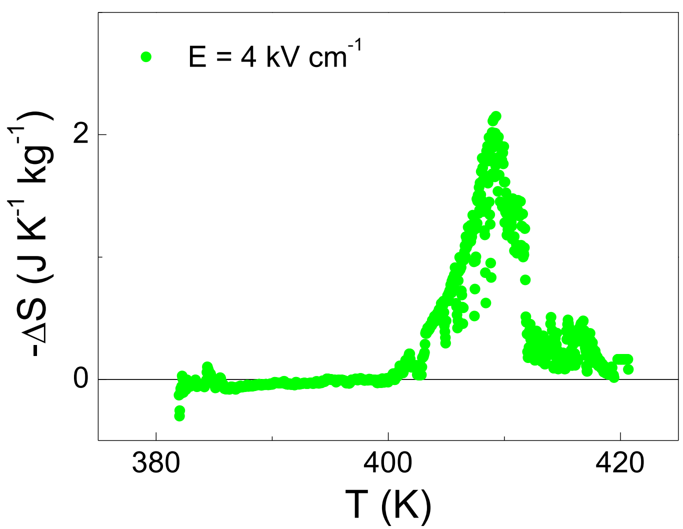


P(*T*) different *E*



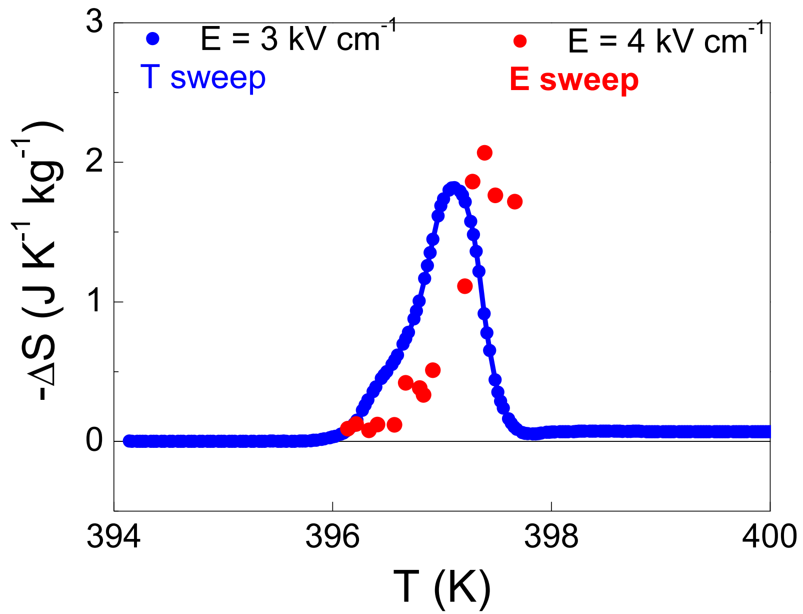
$$\Delta S_{iso} = \int_{E_i}^{E_f} \left(\frac{\partial P}{\partial T}\right)_E dE$$

ECE

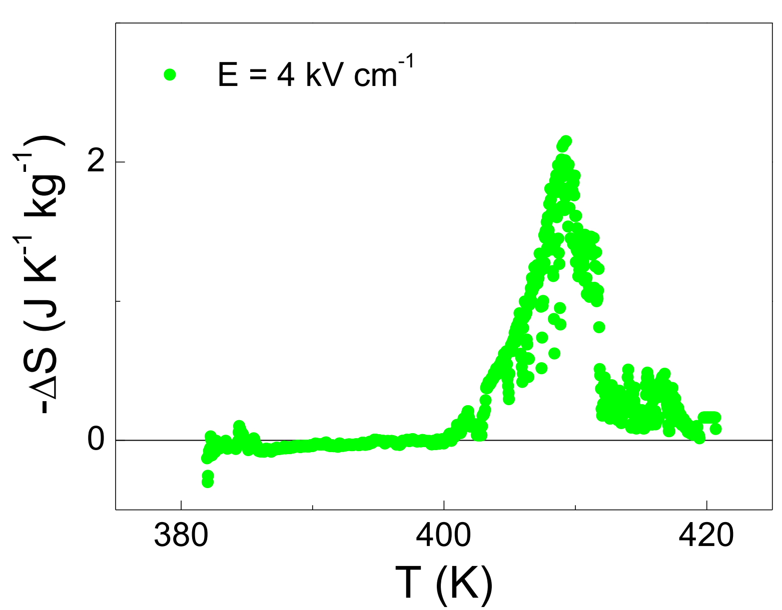


Electrocaloric effect

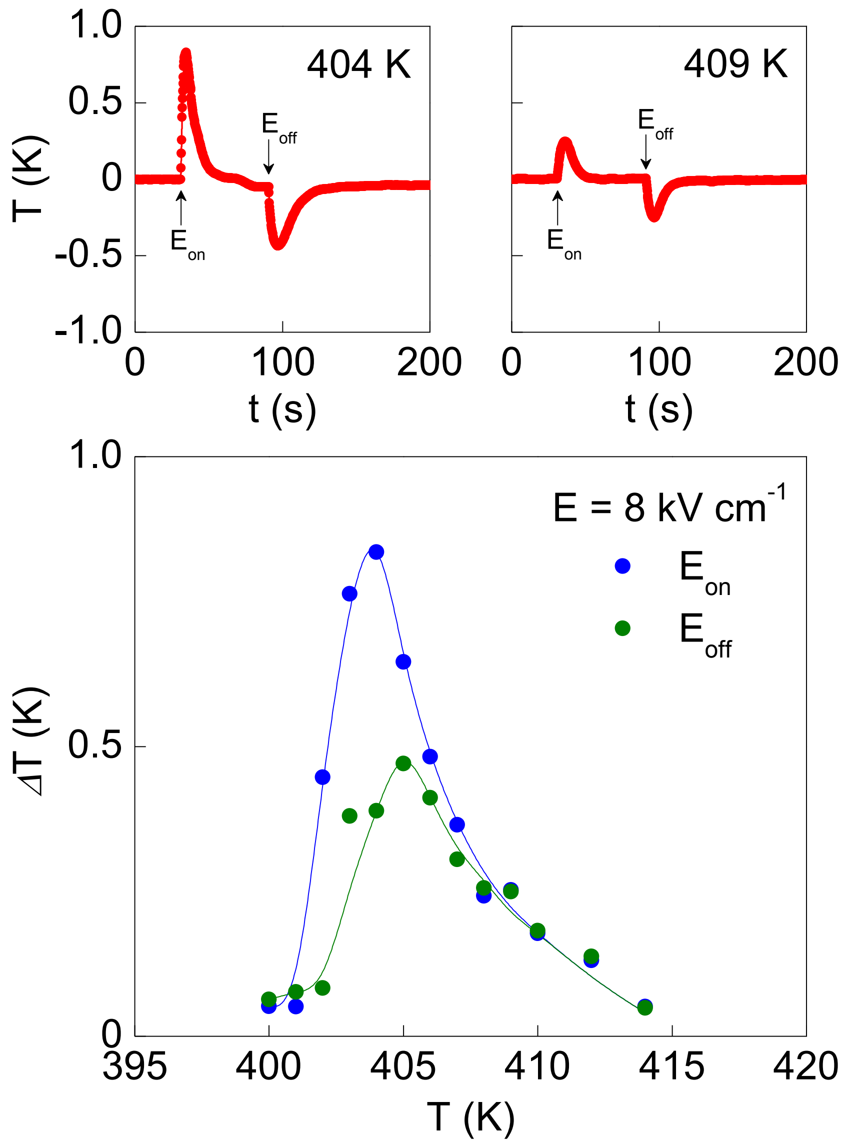
Direct



Indirect



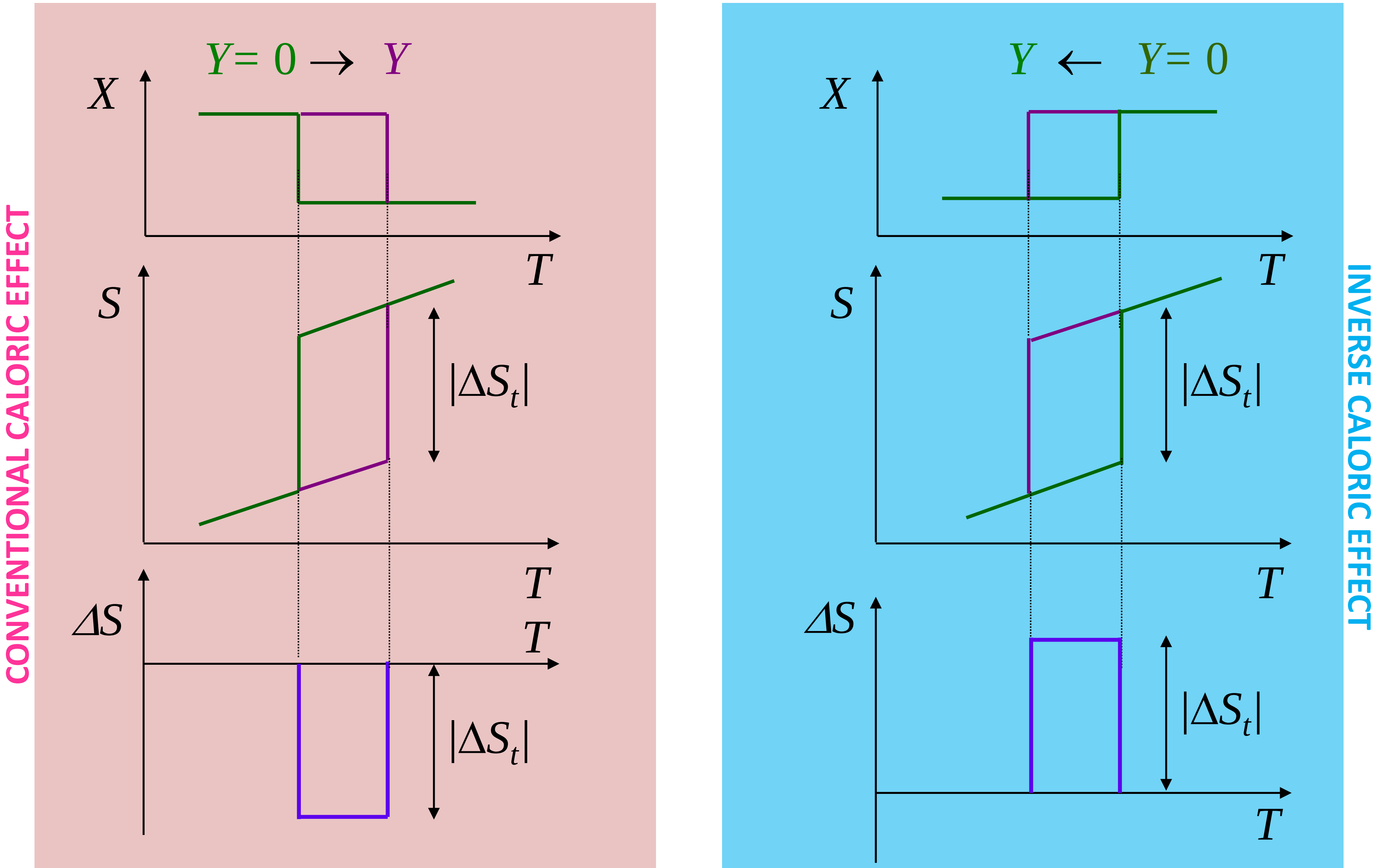
Electrocaloric effect



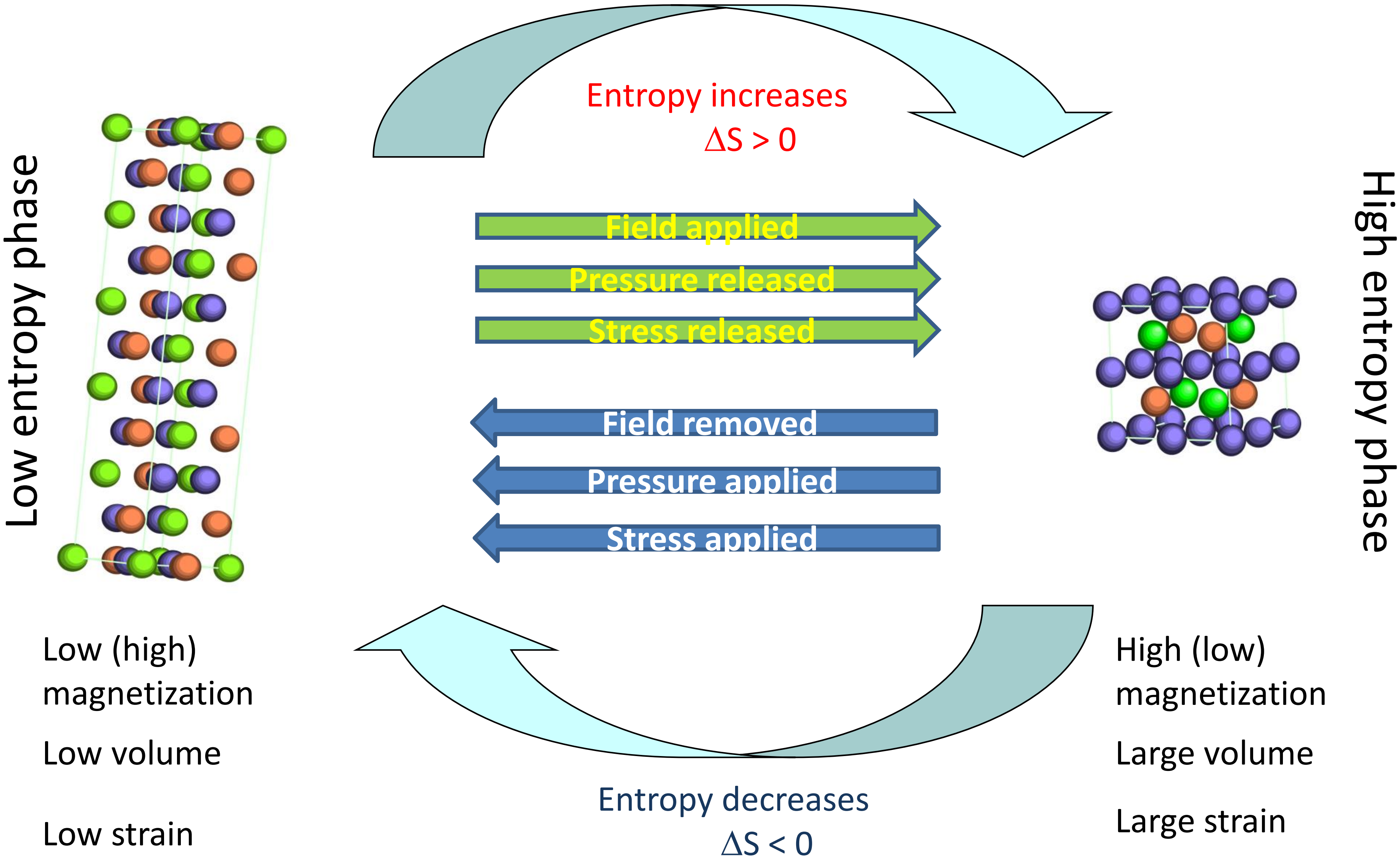
$$\Delta S = \Delta S_{mag} + \Delta S_{str} + \Delta S_{el}$$

$$S_{\text{low } T} < S_{\text{high } T}$$

$$\frac{dT}{dY} = -\frac{\Delta X}{\Delta S}$$



Caloric effect ⟺ latent heat of the transition



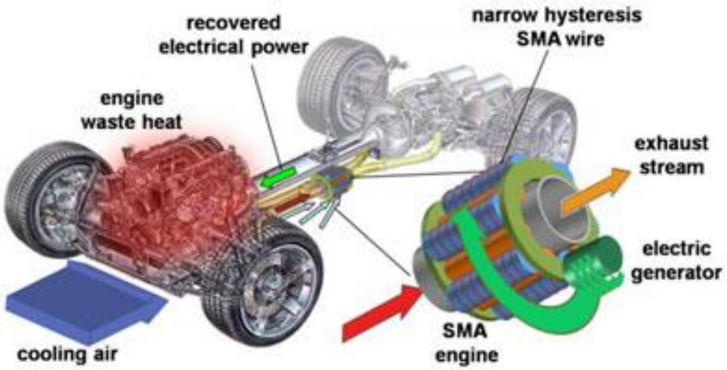
In summary

Materials with structural transitions + LARGE changes in extensive properties (Cross-response to external stimuli)

GIANT caloric effects

Eco-friendly refrigeration

Energy Harvesting




THANKS FOR YOUR ATTENTION