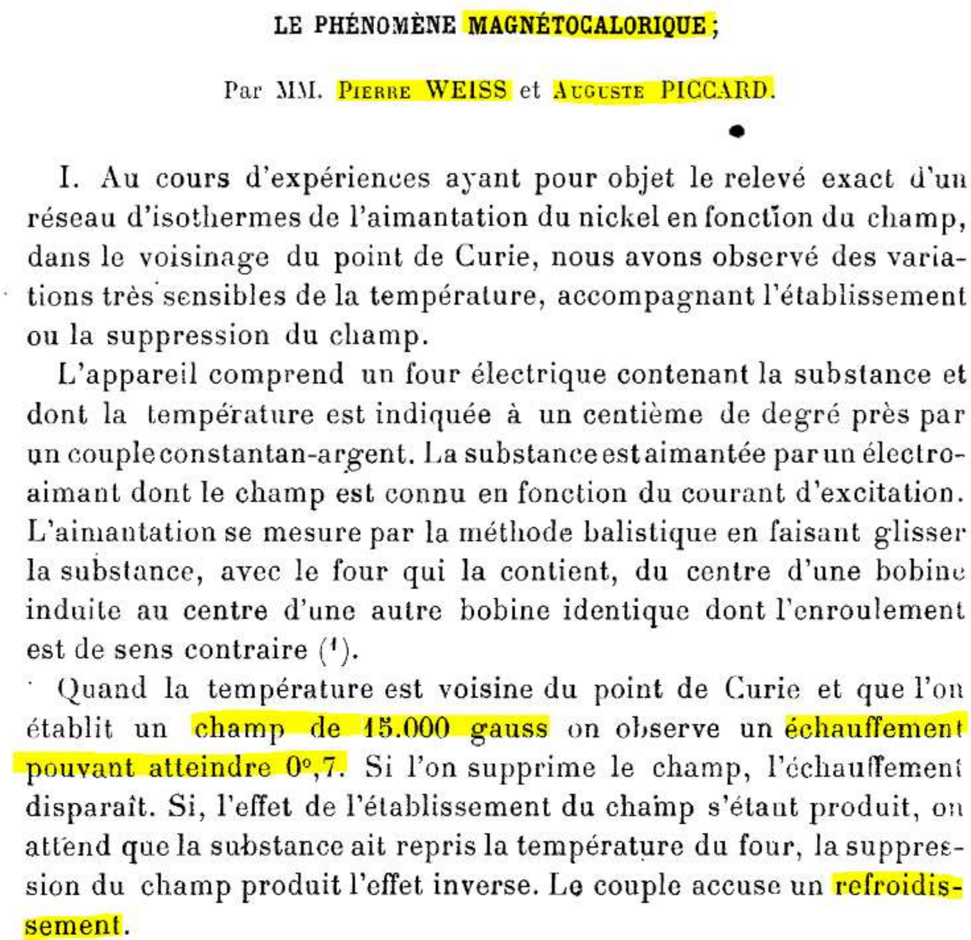
Magnetocaloric effects

Ekkes Brück

TU Delft

Magnetocaloric effect 1917 Weiss & Piccard (not Warburg as found on Wikipedia)


LE PHÉNOMÈNE MAGNÉTOCALORIQUE ;

Par MM. PIERRE WEISS et AUGUSTE PICCARD.

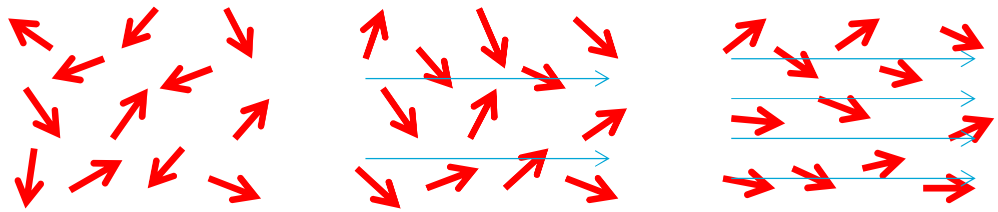
I. Au cours d'expériences ayant pour objet le relevé exact d'un réseau d'isothermes de l'aimantation du nickel en fonction du champ, dans le voisinage du point de Curie, nous avons observé des variations très sensibles de la température, accompagnant l'établissement ou la suppression du champ.

L'appareil comprend un four électrique contenant la substance et dont la température est indiquée à un centième de degré près par un couple constantan-argent. La substance est aimantée par un électro-aimant dont le champ est connu en fonction du courant d'excitation. L'aimantation se mesure par la méthode balistique en faisant glisser la substance, avec le four qui la contient, du centre d'une bobine induite au centre d'une autre bobine identique dont l'enroulement est de sens contraire ([1]).

Quand la température est voisine du point de Curie et que l'on établit un champ de 15.000 gauss on observe un échauffement pouvant atteindre 0°,7. Si l'on supprime le champ, l'échauffement disparaît. Si, l'effet de l'établissement du champ s'étant produit, on attend que la substance ait repris la température du four, la suppression du champ produit l'effet inverse. Le couple accuse un refroidissement.

Nickel metal $\Delta B = 1.5$ T $\Delta T = 0.7$K

Classical treatment of paramagnetism



- At *B* = 0, isolated (non-interacting) magnetic moments of a paramagnet point into random directions

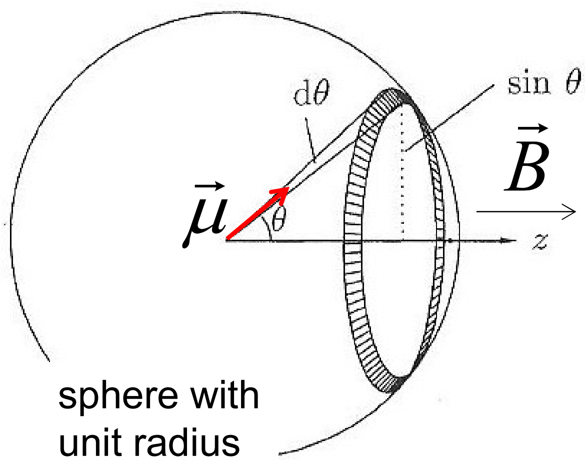
- At *B* ≠ 0, moments will be ligned up by the applied field *B*

- Degree of lining up (magnetization) will depend on *B* (lines up) and *T* (randomizes)

Find expression for $M(B,T)$

! We ignore that the moments can point only along certain directions because of quantization (Quantum Mechanics)

Probability of finding a moment in a particular direction:



Fraction of directions with angle between θ and $\theta + d\theta$ is proportional to shaded area, which is $2\pi \sin\theta d\theta$

Total surface area of unit sphere is 4π

Fraction is $\frac{1}{2}\sin\theta d\theta$

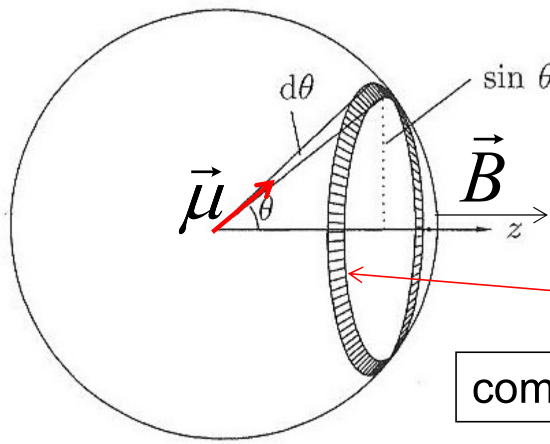
Moments in this direction have a component along $\vec{B}$ equal to $\mu \cos\theta$

and energy $E = -\mu B \cos\theta$

Probability of finding an atom in a state with energy E_i :

$$P_i = \frac{\exp\left(-E_i / kT\right)}{\sum_i \exp\left(-E_i / kT\right)}$$

(Boltzman distribution)



fraction of total sphere

component along $\vec{B}$

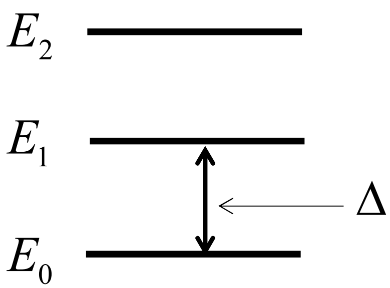
$-E$

Average moment along $\vec{B}$ at temperature *T*:

$$\langle \mu_z \rangle = \frac{\int_0^{\pi} \mu \cos\theta \exp\left(\mu B \cos\theta / kT\right) \tfrac{1}{2} \sin\theta d\theta}{\int_0^{\pi} \exp\left(\mu B \cos\theta / kT\right) \tfrac{1}{2} \sin\theta d\theta} = \mu \frac{\int_{-1}^{1} x e^{yx} dx}{\int_{-1}^{1} e^{yx} dx}$$

with $y = \frac{\mu B}{kT}$ and $x = \cos\theta$

Boltzman distribution for three equidistant levels



$$P_i = \frac{\exp\left(-E_i / kT\right)}{\sum_i \exp\left(-E_i / kT\right)}$$

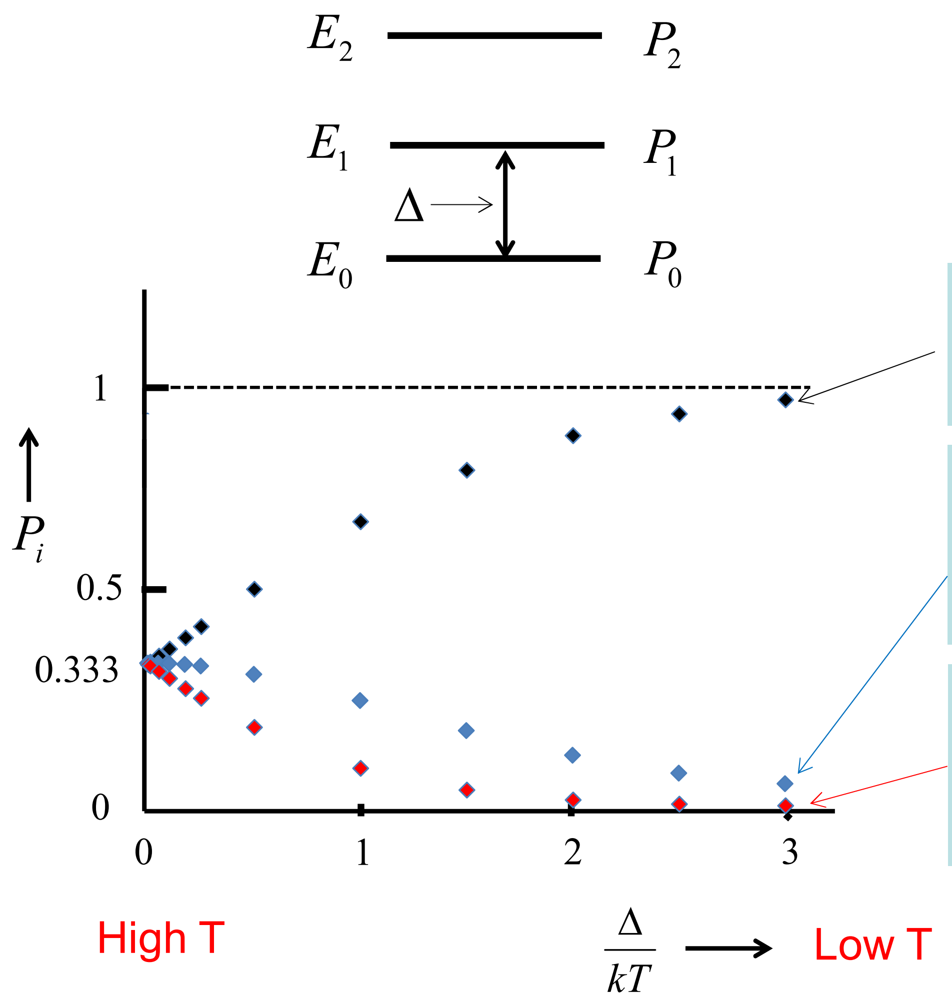
$$\times e^{+\frac{E_0}{kT}}$$

$$P_i = \frac{e^{-\frac{E_i}{kT}}}{e^{-\frac{E_0}{kT}} + e^{-\frac{E_1}{kT}} + e^{-\frac{E_2}{kT}}} = \frac{e^{-\frac{E_i - E_0}{kT}}}{1 + e^{-\frac{E_1 - E_0}{kT}} + e^{-\frac{E_2 - E_0}{kT}}}$$

$$P_0 = \frac{1}{1 + e^{-\frac{\Delta}{kT}} + e^{-\frac{2\Delta}{kT}}}$$

$$P_1 = \frac{e^{-\frac{\Delta}{kT}}}{1 + e^{-\frac{\Delta}{kT}} + e^{-\frac{2\Delta}{kT}}}$$

$$P_2 = \frac{e^{-\frac{2\Delta}{kT}}}{1 + e^{-\frac{\Delta}{kT}} + e^{-\frac{2\Delta}{kT}}}$$



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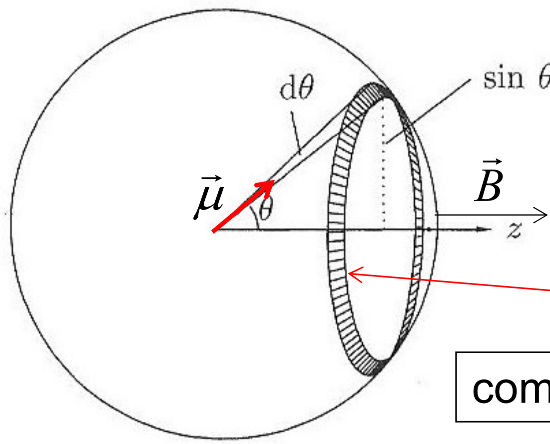

fraction of total sphere

component along $\vec{B}$

$-E$

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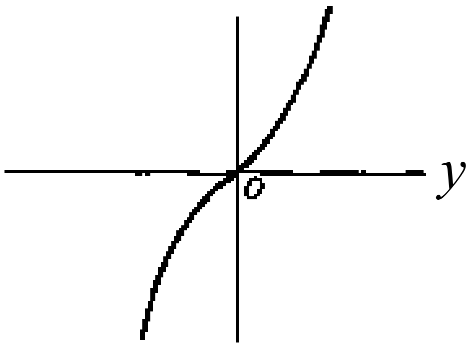
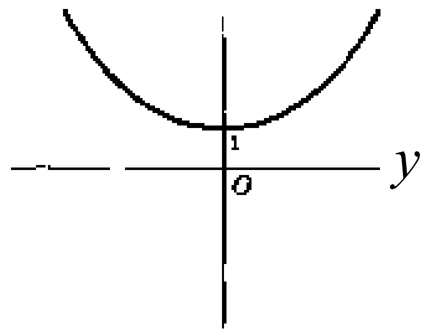
with $y = \dfrac{\mu B}{kT}$ and $x = \cos\theta$

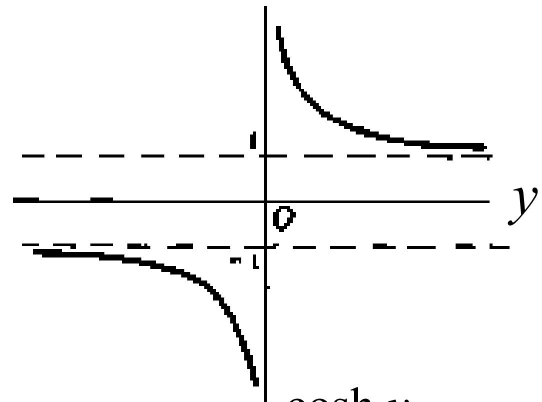
Coth y for y << 1



$\sinh y = (e^{y} - e^{-y})/2$



$\cosh y = (e^{y} + e^{-y})/2$



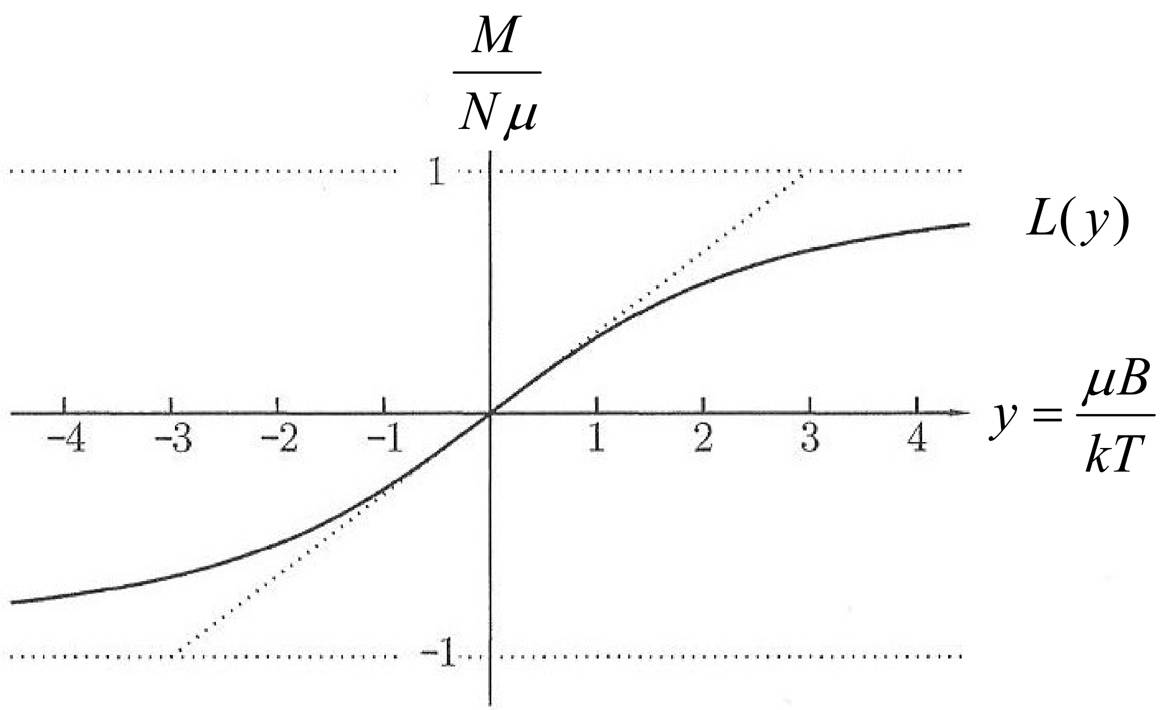
$\coth y = \dfrac{\cosh y}{\sinh y}$

$y << 1$

$$\coth y = \frac{e^{y} + e^{-y}}{e^{y} - e^{-y}} = \frac{1 + y + \frac{1}{2}y^2 + \frac{1}{6}y^3 + 1 - y + \frac{1}{2}y^2 - \frac{1}{6}y^3}{1 + y + \frac{1}{2}y^2 + \frac{1}{6}y^3 - 1 + y - \frac{1}{2}y^2 + \frac{1}{6}y^3} =$$

$$= \frac{2 + y^2}{2y + \frac{1}{3}y^3} = \frac{2(1 + \frac{1}{2}y^2)}{2y(1 + \frac{1}{6}y^2)} = \frac{1}{y}(1 + (\tfrac{1}{2} - \tfrac{1}{6})y^2) = \frac{1}{y} - \frac{y}{3}$$

Langevin function 1905



$$\frac{M}{N\mu} = \frac{\langle \mu_z \rangle}{\mu} = \coth y - \frac{1}{y} \equiv L(y)$$

number of atoms

saturation magnetization

Langevin function

At high temperatures or low fields $y = \frac{\mu B}{kT} \ll 1$

For small *y*: $\coth y = \frac{1}{y} + \frac{y}{3} + O(y^3)$ so that

$$L(y) = \coth y - \frac{1}{y}$$

↓

$$L(y) = \frac{y}{3}$$

$$\frac{M}{M_s} = L(y) \simeq \frac{y}{3} = \frac{\mu B}{3kT} = \frac{\mu_0 \mu H}{3kT}$$

→

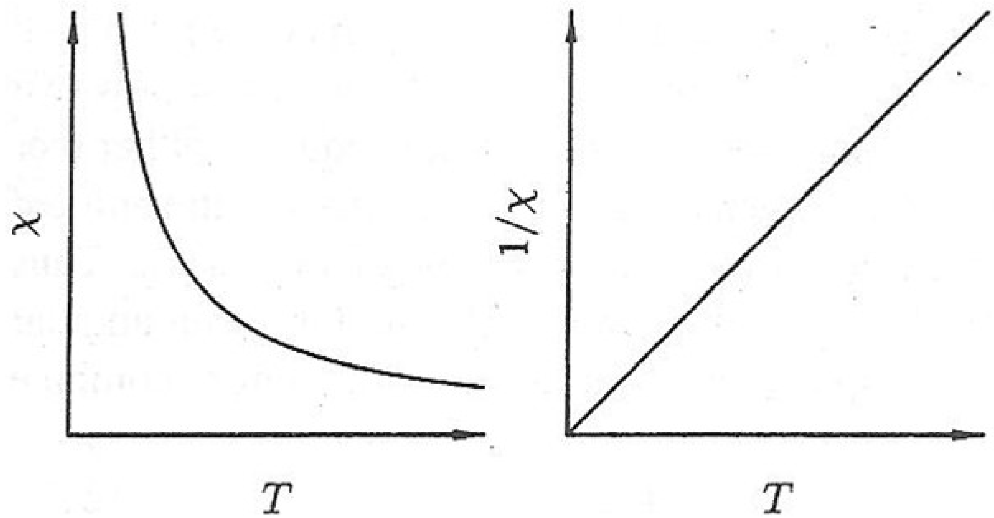
$$\chi = \frac{M}{H} = \frac{N \mu_0 \mu^2}{3kT}$$

$M_s = N\mu$

magnetic susceptibility

Curie law

Curie law



magnetic susceptibility

$$\chi = \frac{N\mu_0\mu^2}{3kT} = \frac{C}{T}$$

Curie constant

Magnetic cooling: Debye and Giauque 1926

Es ist eine bekannte Tatsache, daß die Langevinsche Formel imstande ist die paramagnetische Sättigung wiederzugeben, wie das von Kamerling-Onnes am Falle des Gadoliniumsulfats experimentell gezeigt wurde. Daß dieses möglich ist, obwohl die Voraussetzungen, die Langevin bei seiner Ableitung der Formel gemacht hat, nicht im mindesten zutreffen, gibt Anlaß zu einem reizvollen Problem, das erst eine teilweise Bearbeitung erfahren hat. Es soll im folgenden einerseits gezeigt werden, daß die Langevinsche Formel, trotz ihrer experimentellen Bestätigung nicht genau richtig sein kann, da sie zu Folgerungen Anlaß gibt, die mit dem Nernstschen Wärmesatz in Widerspruch stehen. Andererseits soll aus derselben Formel ein quantitativer Schluß auf die Temperaturänderung bei einem adiabatischen magnetischen Prozeß versucht werden. Dieselbe scheint sich als relativ beträchtlich zu ergeben und veranlaßt deshalb die Frage, ob man nicht versuchen sollte, sich dem absoluten Nullpunkt mit Hilfe eines solchen Prozesses zu nähern.

Nobel prize 19

Langevin equation in conflict with 3rd law of Thermodynamics.
But we may see a large cooling effect to approach 0K

Magnetic cooling: Debye and Giauque 1926

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.

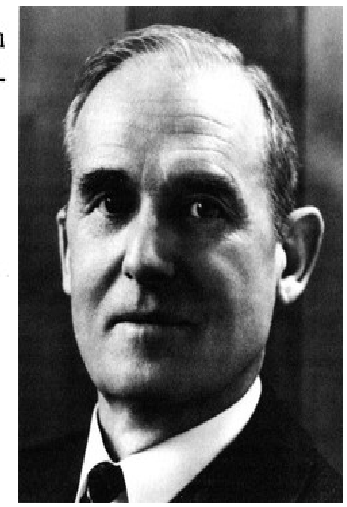
On March 19, starting at a temperature of about 3.4°K, the material cooled to 0.53°K. On April 8, starting at about 2°, a temperature of 0.34°K was reached. On April 9, starting at about 1.5°, a temperature of 0.25°K was attained.

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.

61g $Gd_2(SO_4)_3 \cdot 8H_2O$, ΔB=0.8T, 1.5K →0.25K

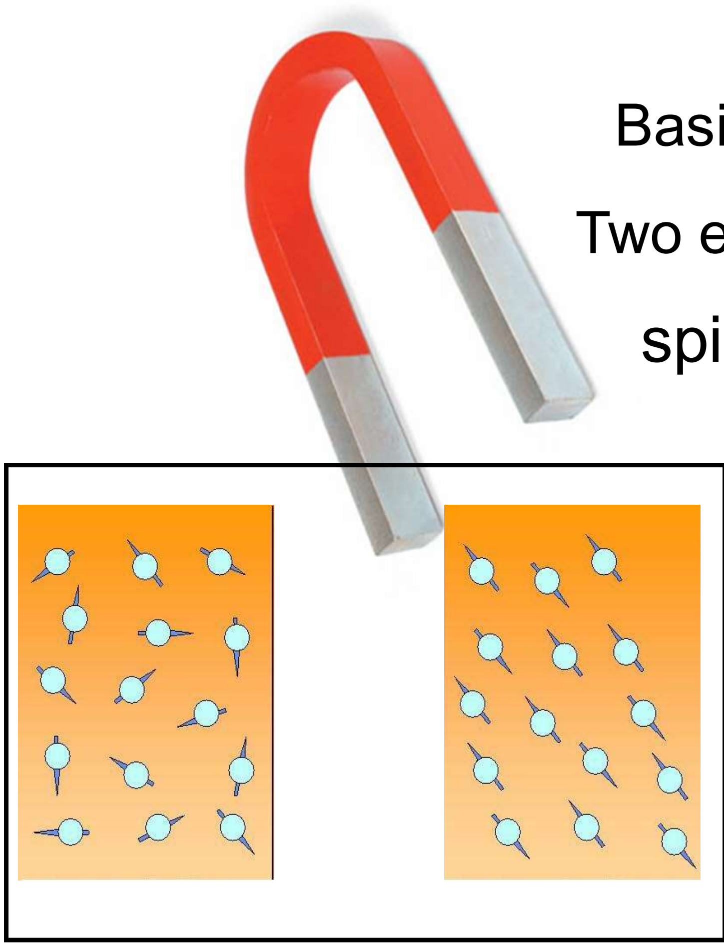


Nobel prize 1949

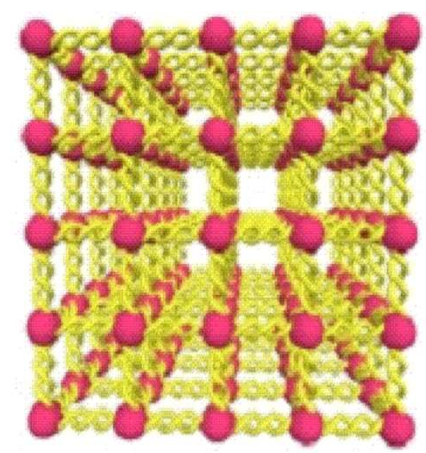
Basic magnetocalorics

Two energy reservoirs

spins → lattice

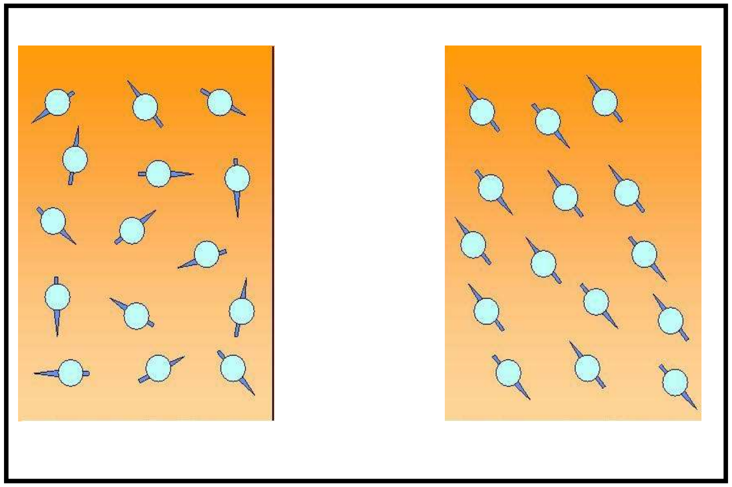


E →

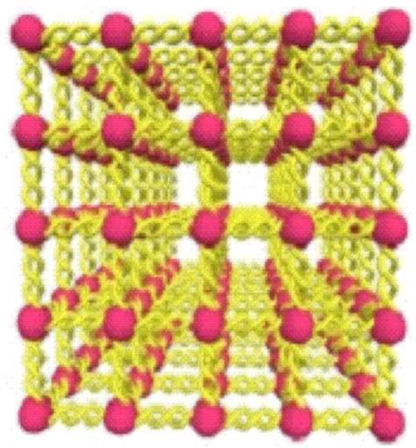


Basic magnetocalorics

spins ⟵ lattice



E ⟵



CES

Magnetic heat pump

https://www.youtube.com/watch?v=jnl9m0rSE7U

Thermodynamics:

Magnetic material Gibs free energy $G(T, B, p)$

Differential of Gibbs free energy

$$S(T,B,p) = -\left(\frac{\partial G}{\partial T}\right)_{B,p}, M(T,B,p) = -\left(\frac{\partial G}{\partial B}\right)_{T,p}, V(T,B,p) = -\left(\frac{\partial G}{\partial p}\right)_{T,B}$$

Entropy Magnetization Volume

Differential of entropy

$$dS = \left(\frac{\partial S}{\partial T}\right)_{B,p} dT + \left(\frac{\partial S}{\partial B}\right)_{T,p} dB + \left(\frac{\partial S}{\partial p}\right)_{T,B} dp$$

Identification of terms

$$dS = \frac{C_{B,p}}{T} dT + \left(\frac{\partial S}{\partial B}\right)_{T,p} dB - \alpha V dp$$

Adiabatic process at constant pressure

$$dT = -\frac{T}{C_{B,p}} \left(\frac{\partial S}{\partial B}\right)_{T,p} dB$$

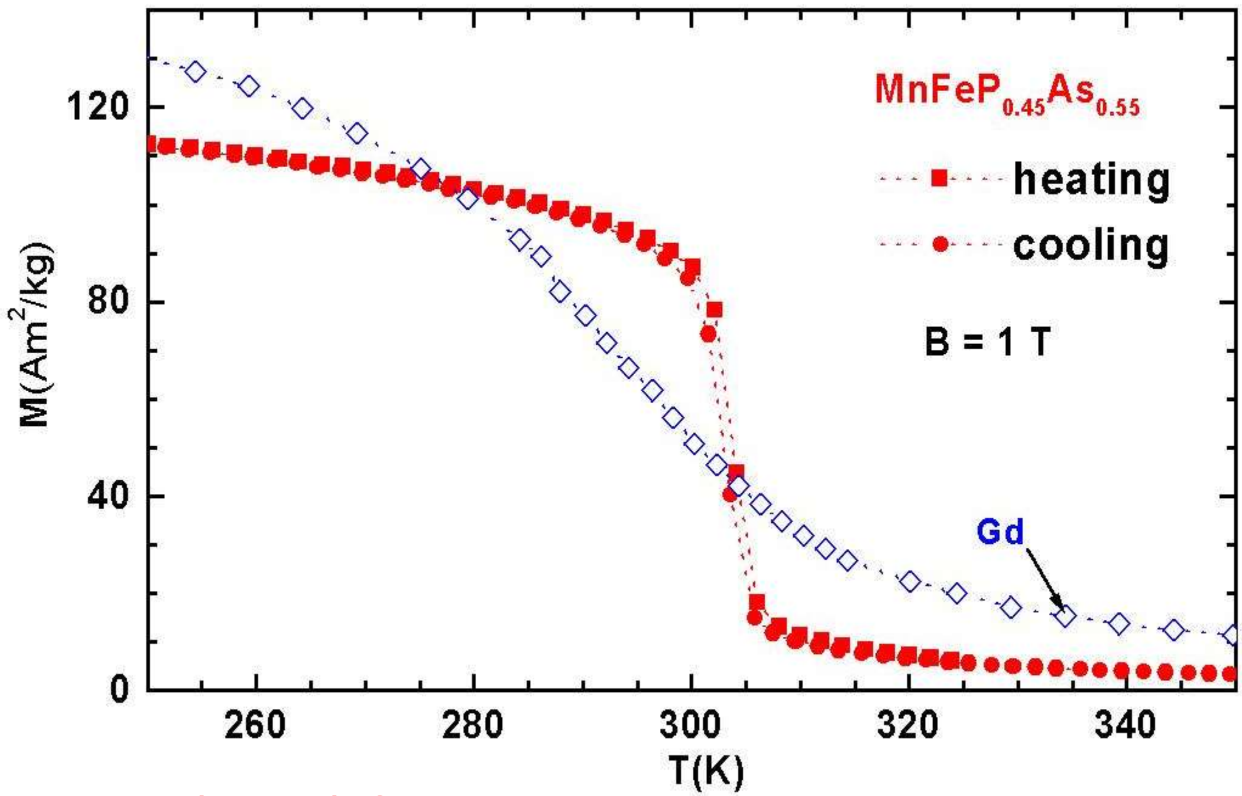
Maxwell relations $\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$

Magnetic entropy

$$\Delta S_m = \int_0^B \left(\frac{\partial M}{\partial T}\right)_B dB$$

Steep change of magnetization → large ΔS_m

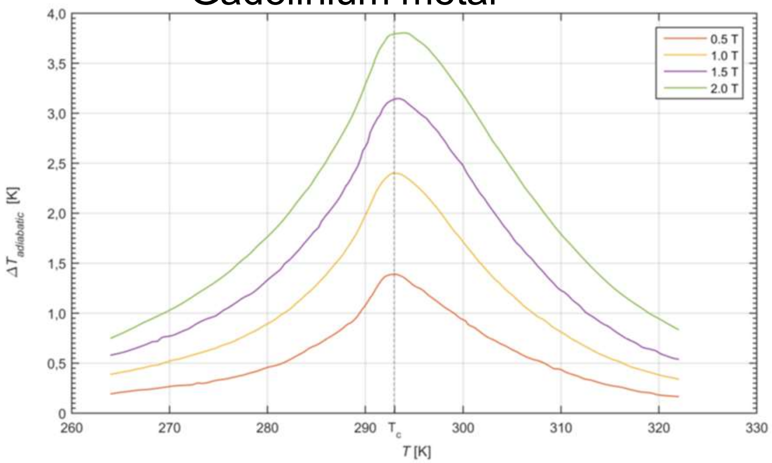
Magnetization vs temperature of Gadolinium and MnFe(P,As)

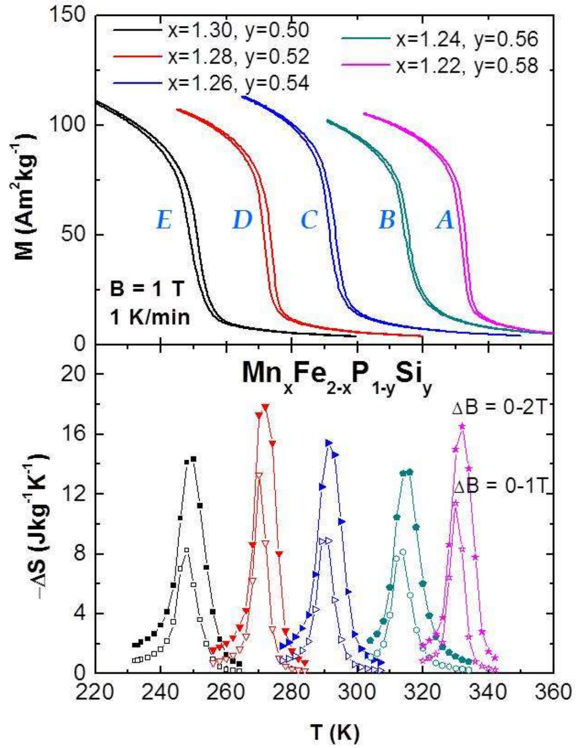


For MnFe(P,As) first order phase transition, much steeper near Curie temperature!

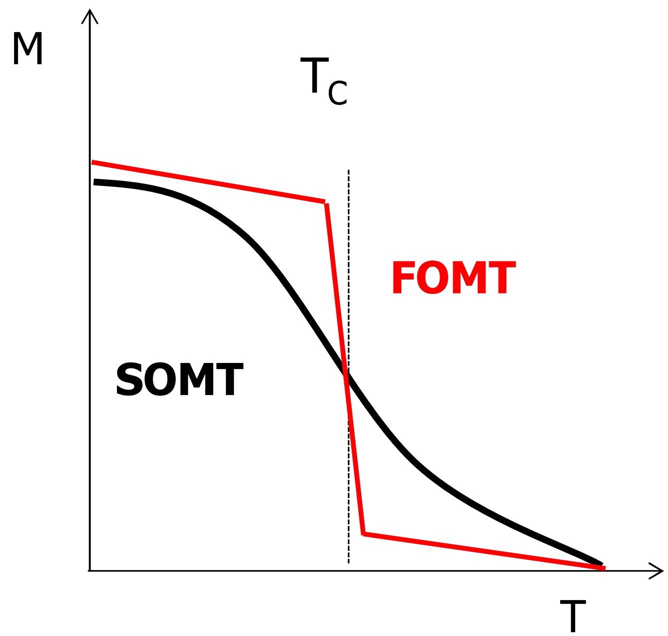
Second order versus first order materials

Gadolinium metal

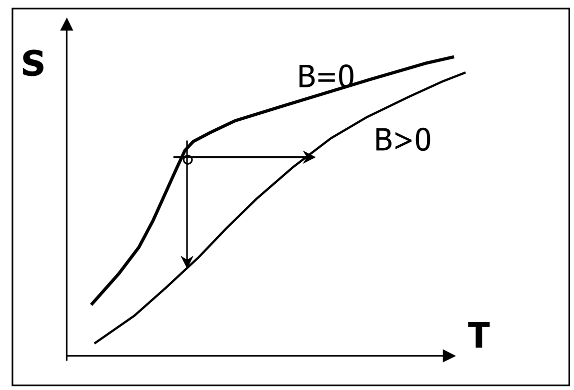




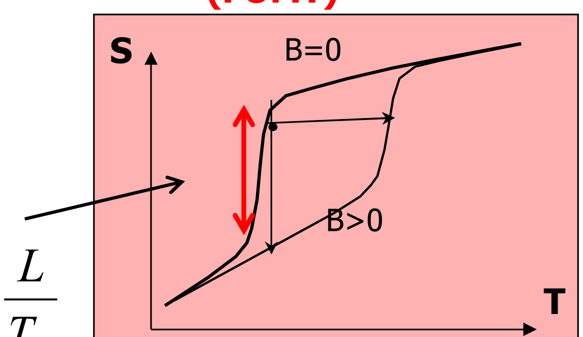
Room-temperature MCE



Second-Order Phase Transition (SOMT)



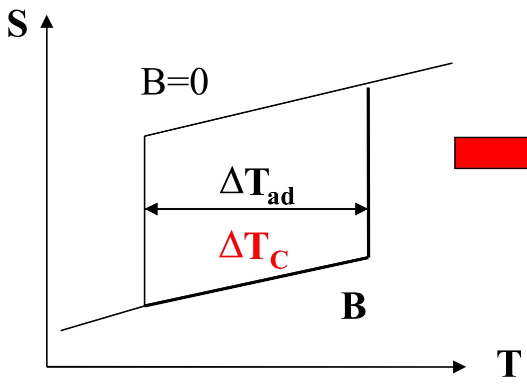
First-Order Phase Transition (FOMT)



$$\Delta S_{tr} = \frac{L}{T_C}$$

In low B,
$\Delta T_{ad} \sim L/C$

First order phase transition

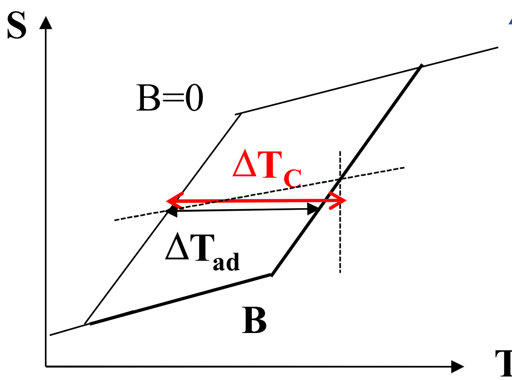


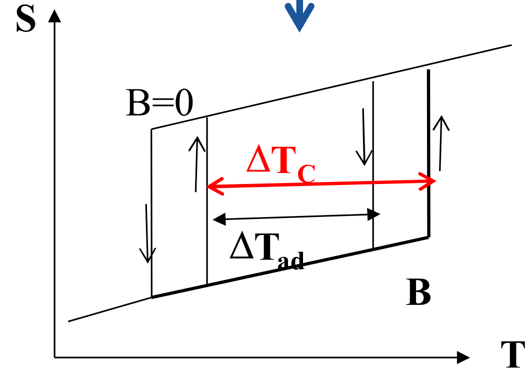
Ideal FOT

$\Delta T_{ad} = \Delta T_C$ Field induced shift of the transition

No transition width

No thermal hysteresis





Real FOT → $\Delta T_{ad} < \Delta T_C$

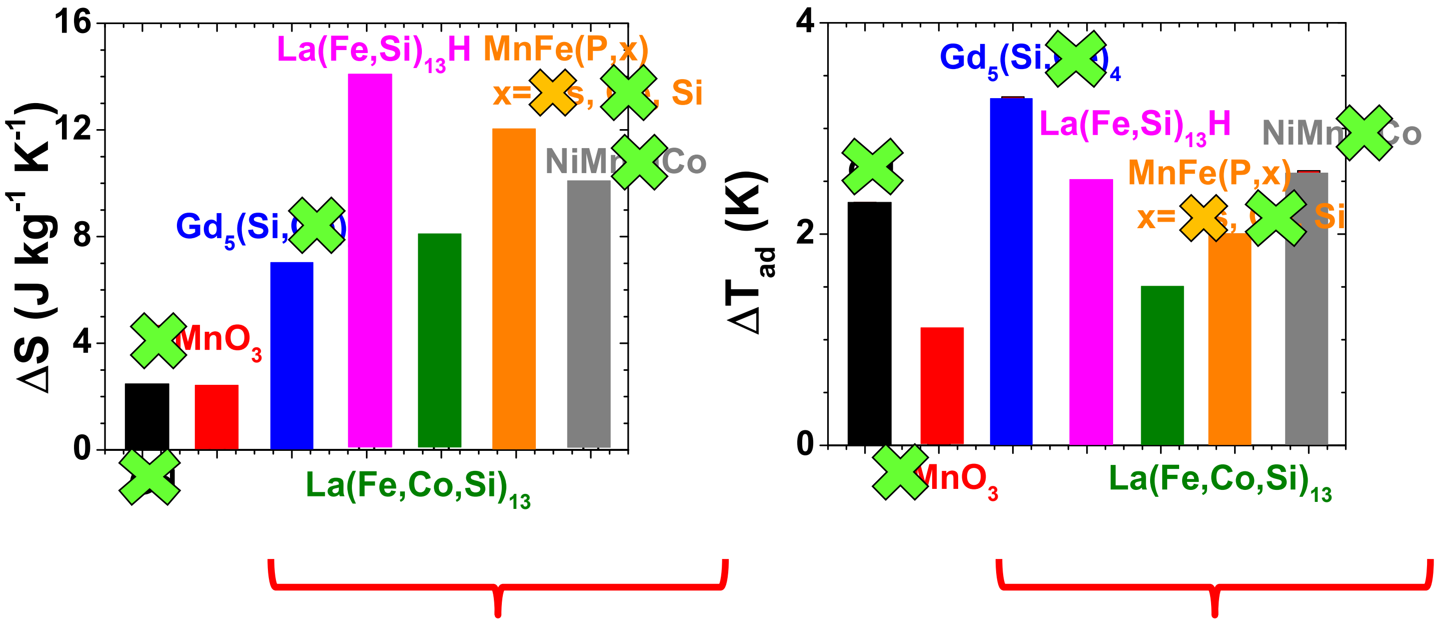
Hysteresis → Influences reversibility

$$\Delta T_C = \left(\frac{\partial T_C}{\partial B}\right)\Delta B \qquad \frac{\partial T_C}{\partial B} = \frac{T_C \Delta M}{L}$$

↗ ↘

MCE Materials

At room temperature, for ΔB= 1 T (=available with permanent magnets)



"Giant" MCE: based on first order transitions

Large-Scale Applications:

Toxicity | **Cost + availability** | **Other nonmagnetic requirements (corrosion, mechanical resistance ...)**

Figure of Merit

- Refrigerant capacity RC = ΔS·ΔT

Measure of net work in reversible cycle. Often used, but not a good FoM.

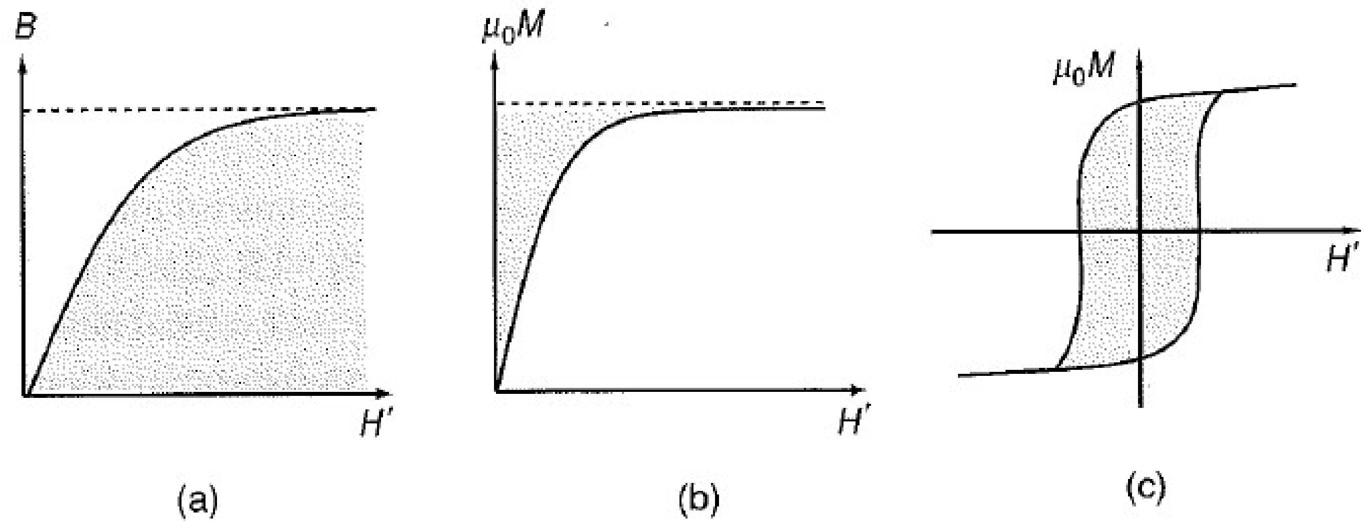
Coefficient of Refrigerant performance CRP

$$CRP = \frac{refrigerant\ capacity}{positive\ work\ on\ refrigerant} = \frac{\Delta S \Delta T}{\int_0^{B_{max}} M(T_C, B) dB'}$$

Dimensionless Figure of Merit which can be used to compare different materials even gas compression

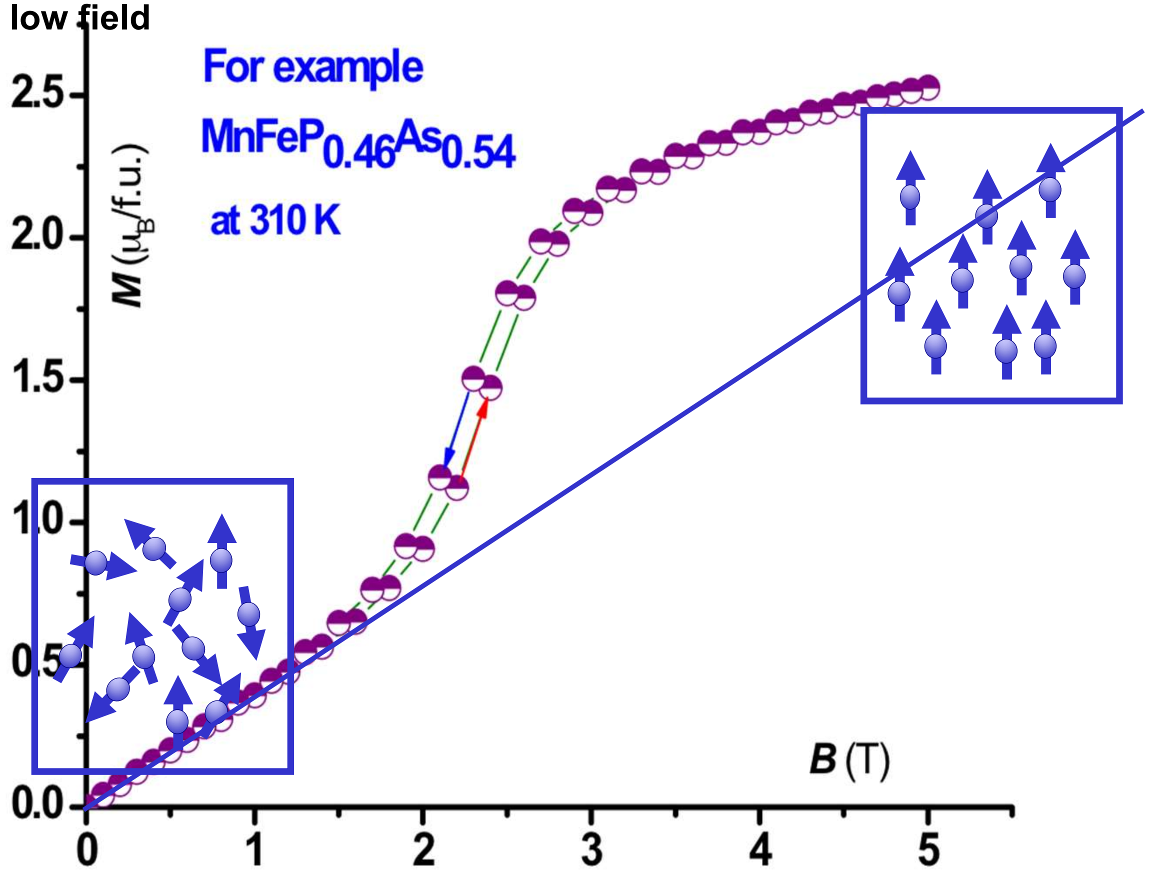
Wood & Potter Cryogenics 1985

Which work (shaded area) is here relevant?



Applied field work | Magnetizing work | Hysteresis loss

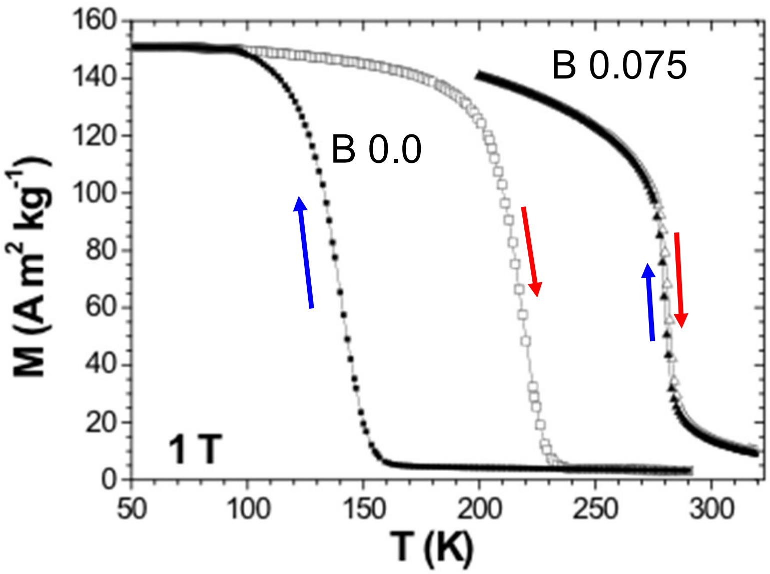
Desired Magnetization processes as we want large change in magnetizaton in low field

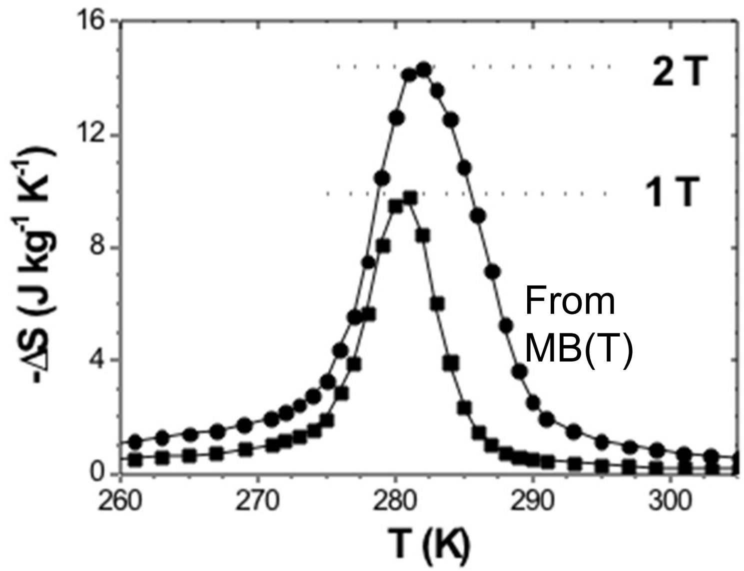


Material with field induced first order phase transition.

Taming the first order transition

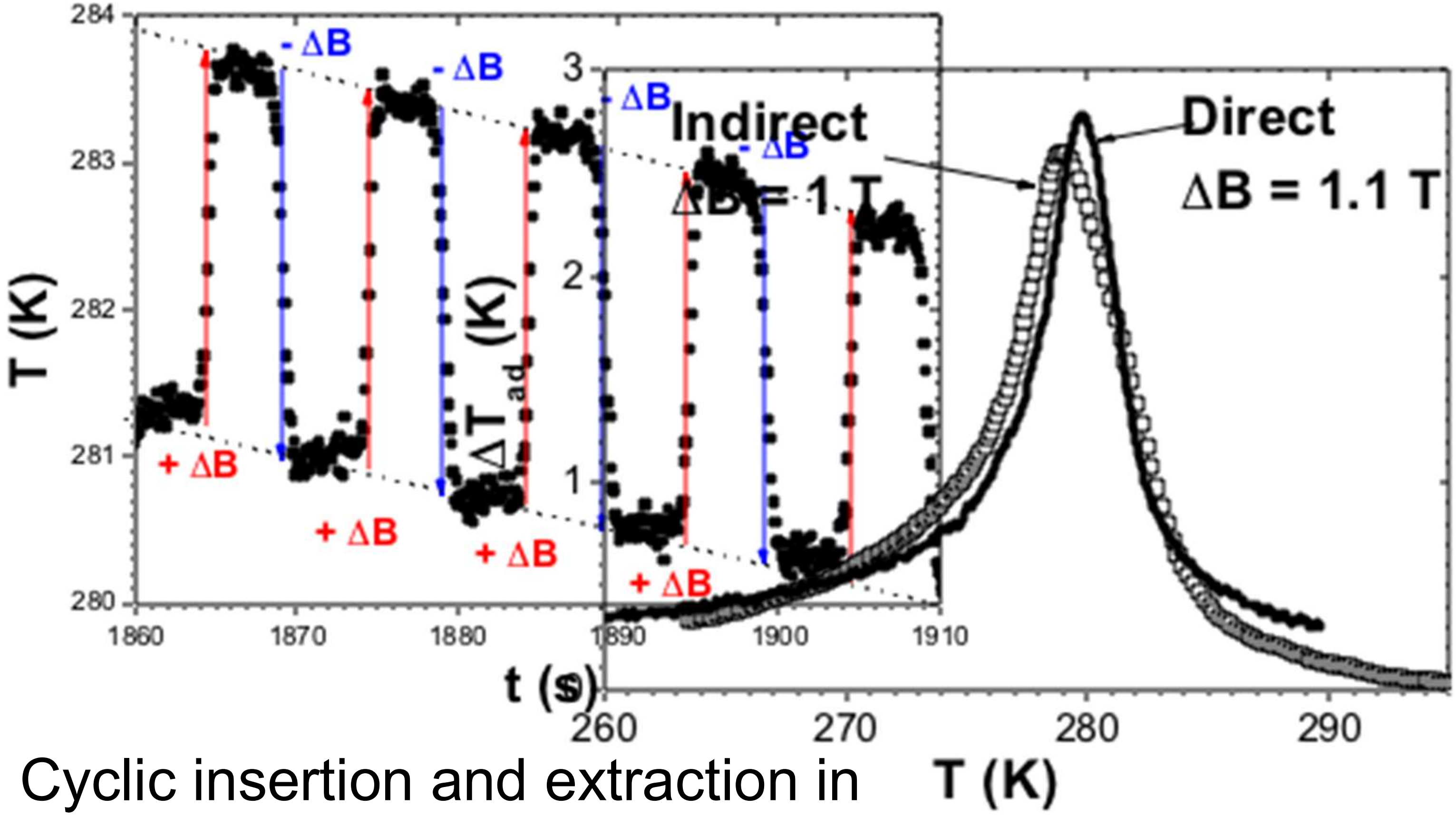
$MnFe_{0.95}P_{0.595}B_{0.075}Si_{0.33}$





F. Guillou et. al. Adv. Mat. (2014)

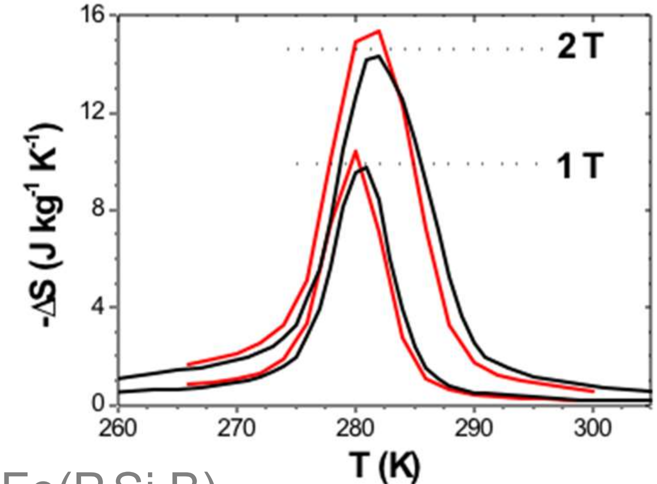
$MnFe_{0.95}P_{0.595}B_{0.075}Si_{0.33}$

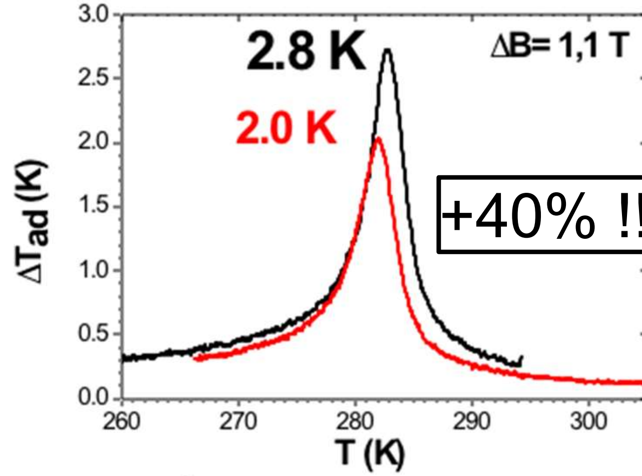


Cyclic insertion and extraction in 1.1 T field

Resulting ΔT

MnFe(P,Si,B) *vs* $Mn_{1.25}Fe_{0.7}P_{0.5}Si_{0.5}$





MnFe(P,Si,B)

$Mn_{1,25}Fe_{0,7}P_{1/2}Si_{1/2}$

Reminder: $$\frac{dT_C}{dB} = \frac{\Delta M}{\Delta S_{tr}} = \frac{\Delta M . T_C}{L}$$

Sample	$\Delta S_{tr} = L/Tc$ (J kg^{-1} K^{-1})	ΔM (A m^2 kg^{-1})	dT_C/dB (K/T)	Transit. Width (K)	ΔS ***MCE*** B=1T (J kg^{-1} K^{-1})
Boron 7.5%	***21.1***	***65***	***4.4 ±0.2***	***7.5***	***-10.5***
	-36%	+6%	+40%		
Mn rich	***29.8***	***61***	***3.2 ±0.2***	***8.0***	***-10.5***

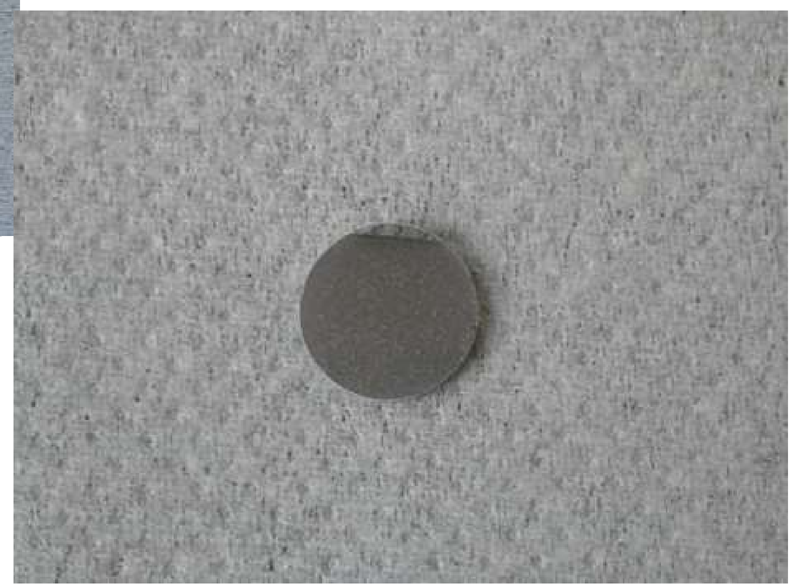
Consequences of no volume change

$MnFe_{0.95}P_{0.587}B_{0.078}Si_{0.34}$

$\Delta V/V \leq 0.05$ %

$Mn_{1.3}Fe_{0.7}P_{0.5}Si_{0.5}$

$\Delta V/V \leq 0.2$ %



Summary Magnetocalorics

- **Magnetoelastic transition enhances MCE in low fields**
- **Small changes in composition strongly affect properties**
- **Materials with high Curie-temperatures may be suited for waste–heat recovery**

Desired properties:

Not toxic

Not expensive

Good mechanical stability

Easy tunability of T_C

Thank you for your attention

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