Magnetocaloric Materials not only for cooling applications

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Fundamental Aspects of Materials and Energy,

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Introduction

Magnetic cooling

Giant magnetocaloric effect

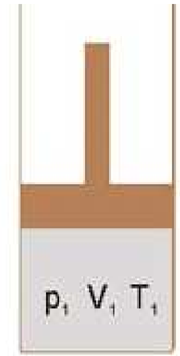
power generation

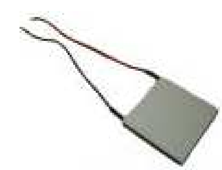
Review: E. Brück, Magnetic refrigeration near room temperature, Handbook of magnetic materials Vol 17 chapt. 4 (2007) ed. K.H.J. Buschow

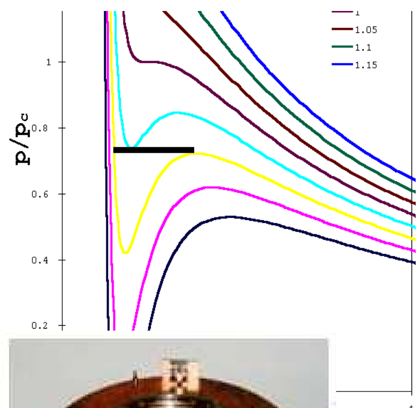
Introduction

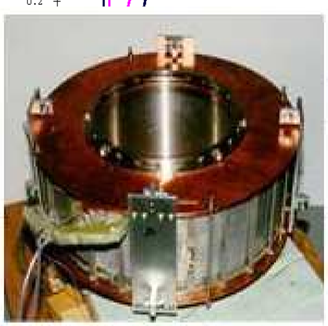
Cooling techniques

Physical principle	Application
Expansion ideal gas	Stirling-cooler Claude-turbine
Joule-Thomson effect	Liquefactor (Linde)
Peltier effect	Electronics Infrared visors
Evaporation	House-hold refrigerator Cool box
Adiabatic demagnetization	Low-temperature physics









BASF The Chemical Company

Introduction Magnetic cooling: Debye and Giauque 1926

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

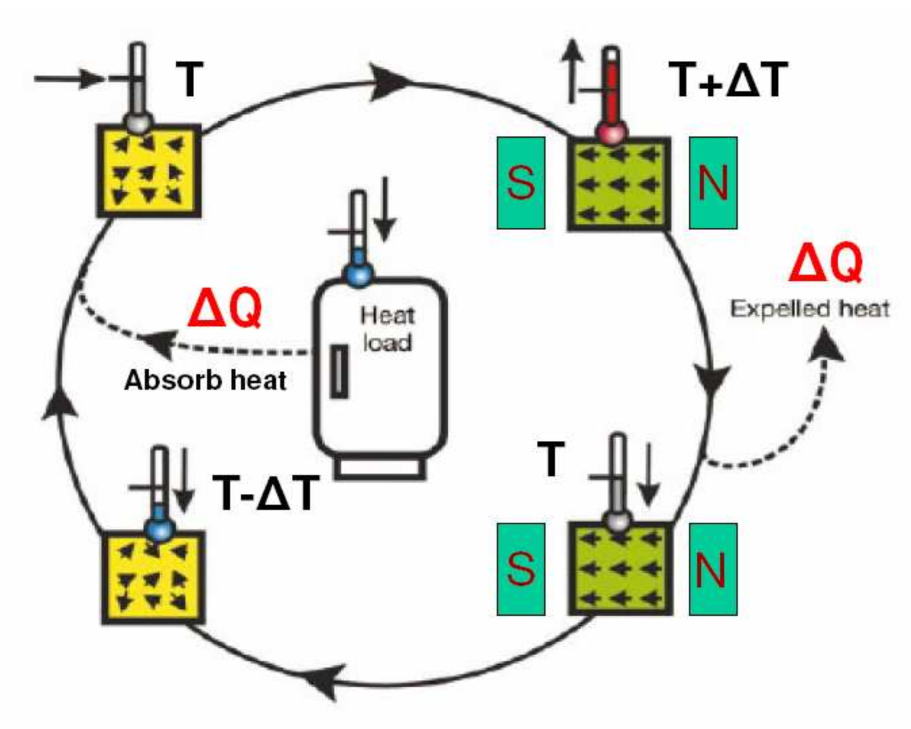
Department of Chemistry,
University of California,
Berkeley, California,
April 12, 1933.

61g $Gd_2(SO_4)_3 \cdot 8H_2O$, ΔB=0.8T, 1.5K →0.25K Nobel prize 1949

FOM stw

Introduction

- Magnetic refrigeration is based on magnetocaloric effect (MCE)



$$\Delta S_m(T,\Delta B) = -\int_{B_i}^{B_f} \left(\frac{\partial M}{\partial T}\right) dB$$

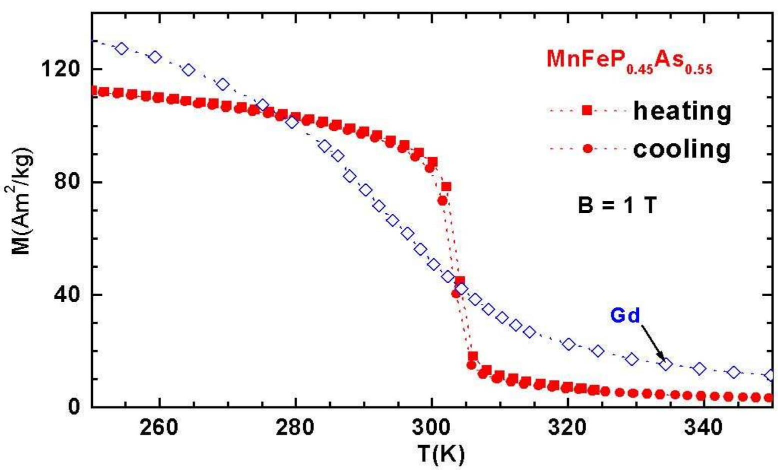
$$\Delta T(T,\Delta B) = -\int_{B_i}^{B_f} \frac{T}{C_{p,B}} \left(\frac{\partial M}{\partial T}\right) dB$$

- ΔS^{max} important for <u>cooling capacity</u>
- ΔT important for <u>heat flow</u>

Giant MCE

First-order field-induced magneto-structural transition

$Gd_5(Si_xGe_{1-x})_4$	1997
$MnAs_{1-x}Sb_x$	2001
$La(Fe_{1-x}Si_x)_{13}$	2001
$MnFeP_{1-x}As_x$	2002
$Ni_{0.5}Mn_{0.5-x}Sn_x$	2005



Determination of MCE

1. Magnetic measurements

$$\Delta S_m(T,\Delta B) = \sum_i \frac{M_{i+1}(T_{i+1},B) - M_i(T_i,B)}{T_{i+1} - T_i}\Delta B$$

2. Specific-heat measurements

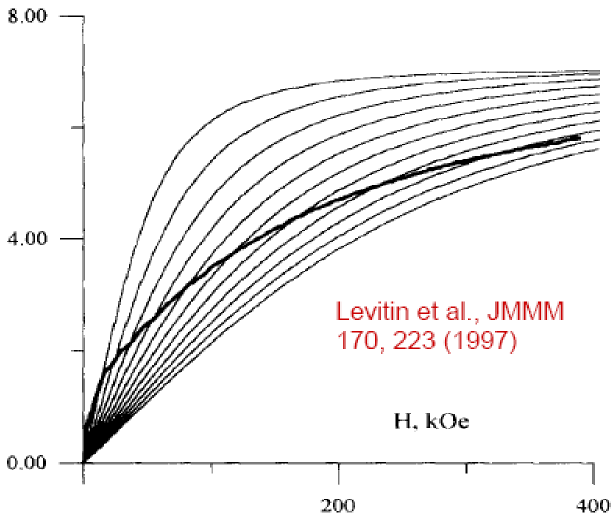
$$\Delta S_m(T,B) = \int_0^T \frac{C(T',B) - C(T',0)}{T'} dT'$$

$$\Delta T_{ad}(T,B) = -\int_0^B \frac{T}{C(T,B')}\left(\frac{\partial M}{\partial T}\right)_B dB'$$

3. Direct measurement of change of *T*

4. Pulse field technique

- Pulse field magnet allows fast magnetic measurements
- *Thermocouple* enables to measure the temperature more accurate before and after the pulse taking place
- An adiabatic M(H) curve will intersect the isothermal curves obtained at higher temperatures



Transition-metal compounds

High abundance (low price)

Intermediate magnetic moment (moderate MC effect)

Frequently Curie temperatures exceeding RT

Strong coupling to lattice (Simultaneous magnetic and structural transitions or metamagnetism)

Fe_2P related materials

Hexagonal Fe_2P type of structure

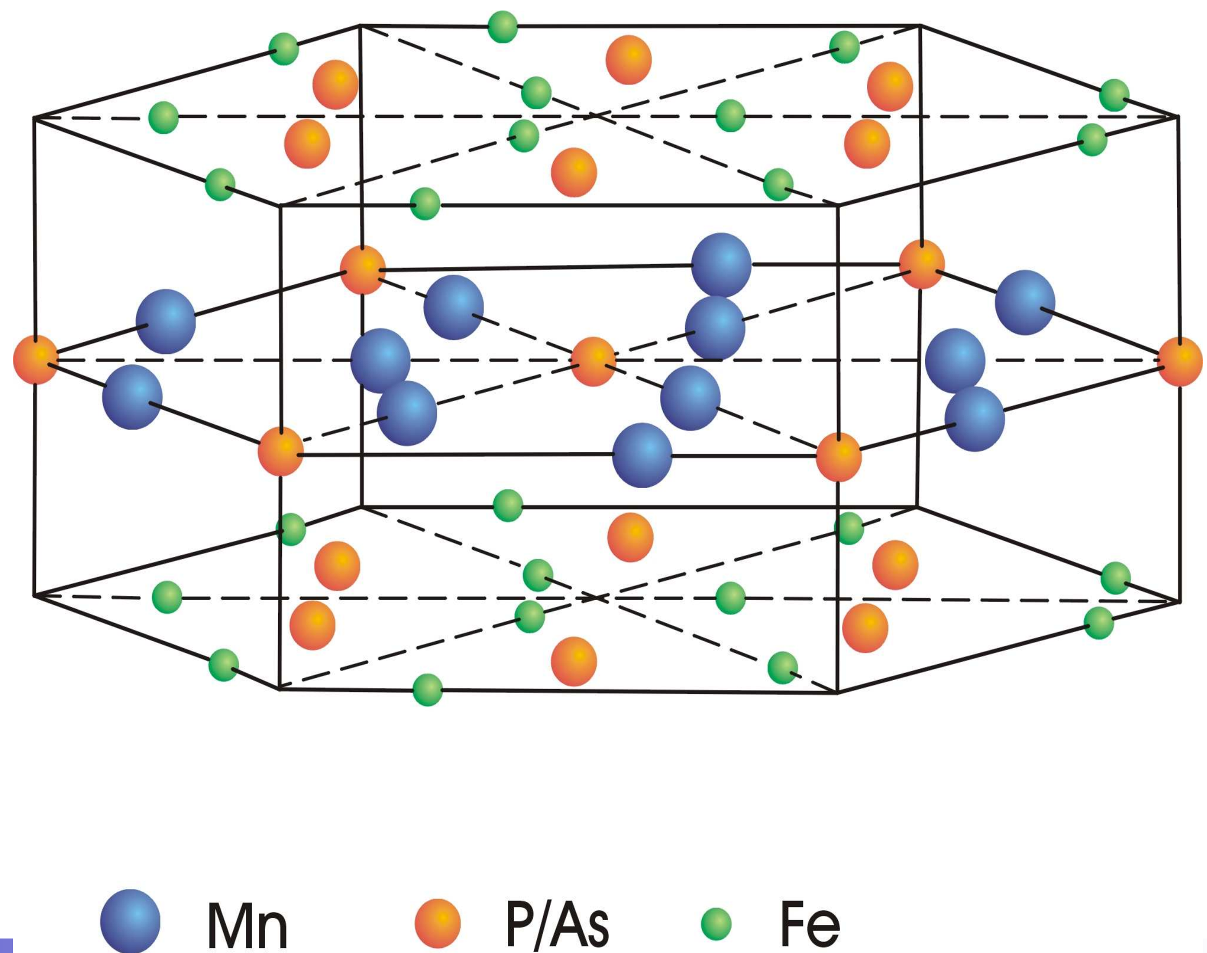
Space group:

$P\bar{6}2m$

Mn 3g sites

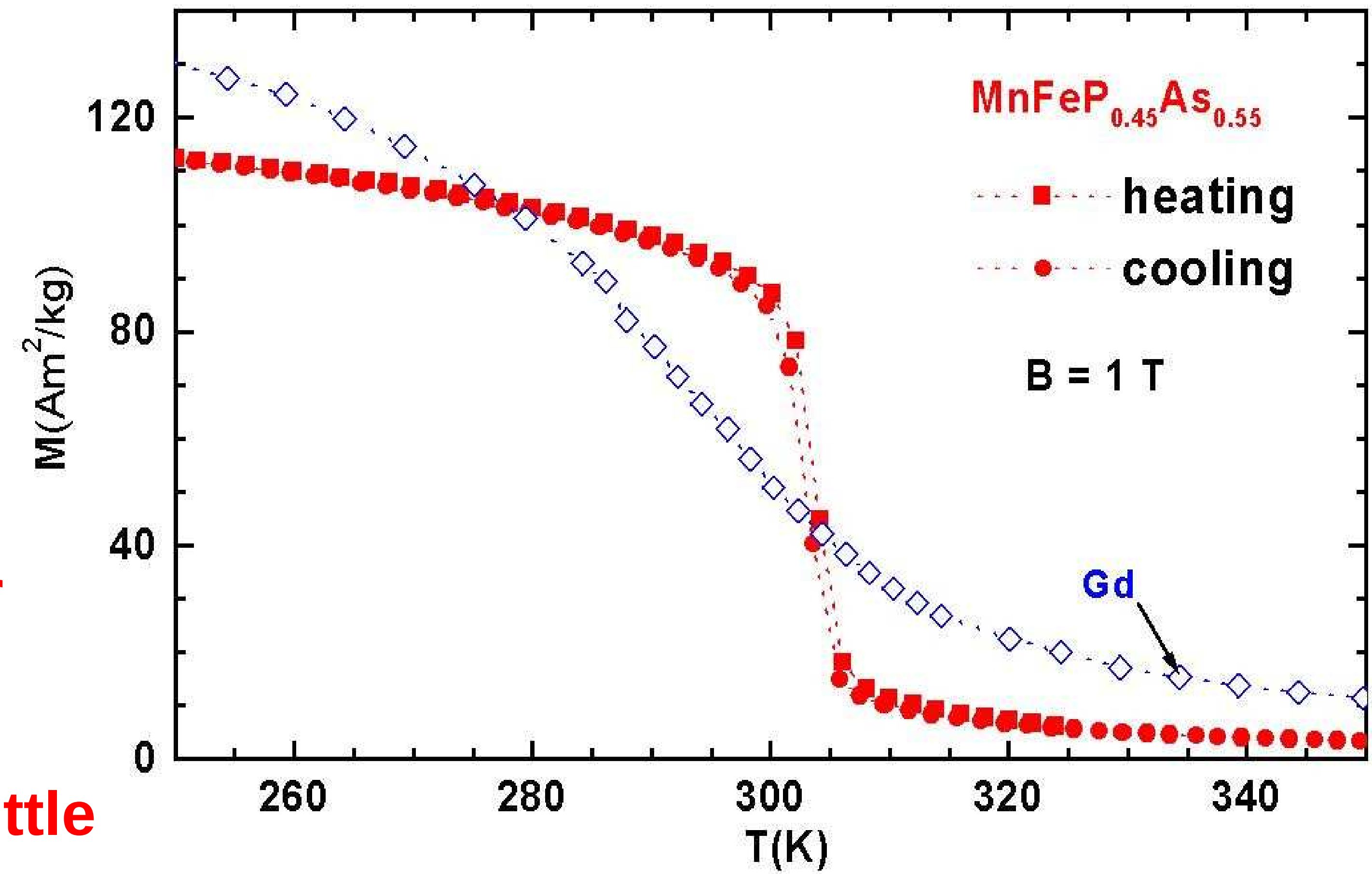
Fe 3f sites

P/As 1b&2c sites



Bacmann, JMMM 1994

Temperature dependence of magnetization

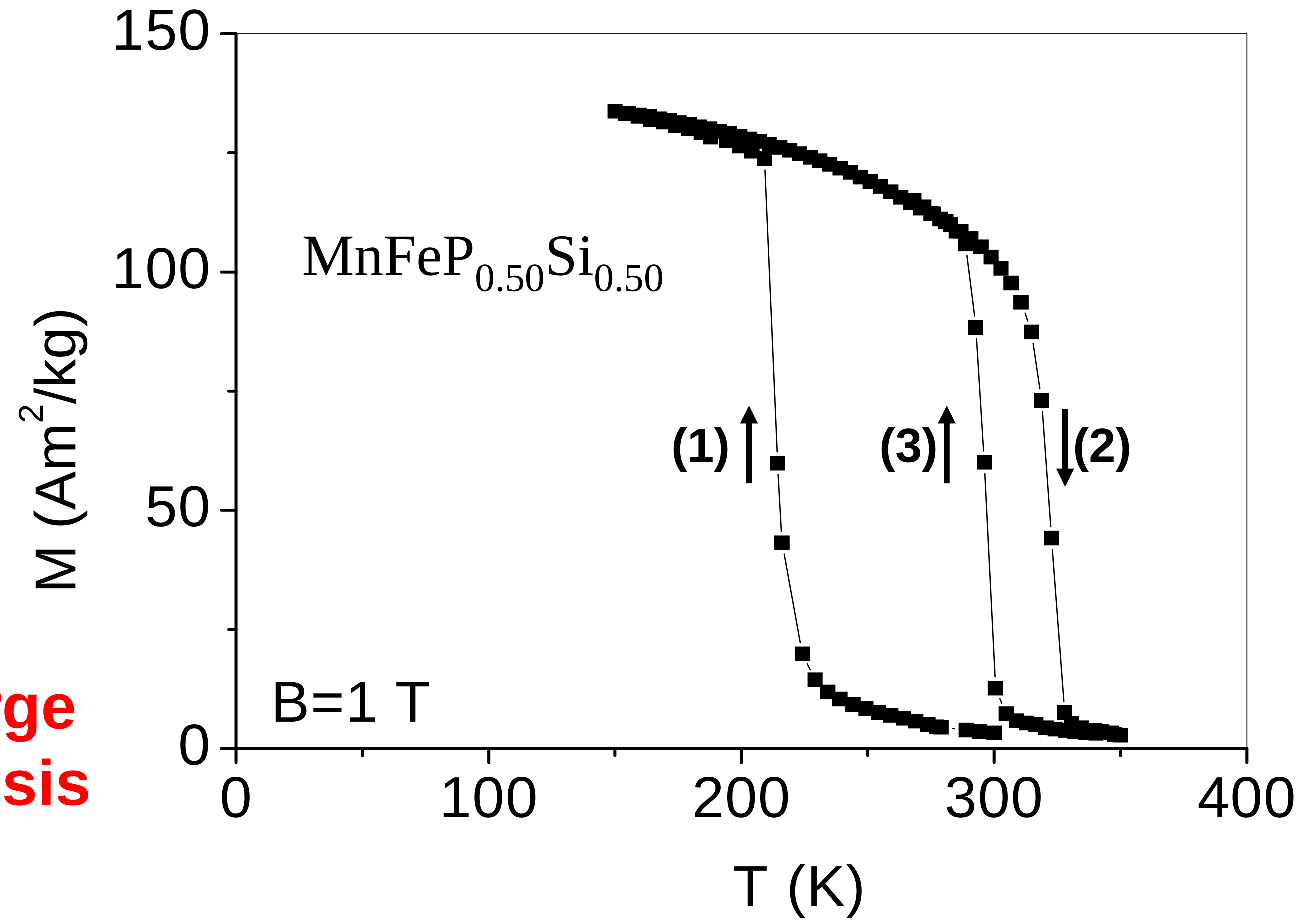


Step-like transition

first order

but very little hysteresis

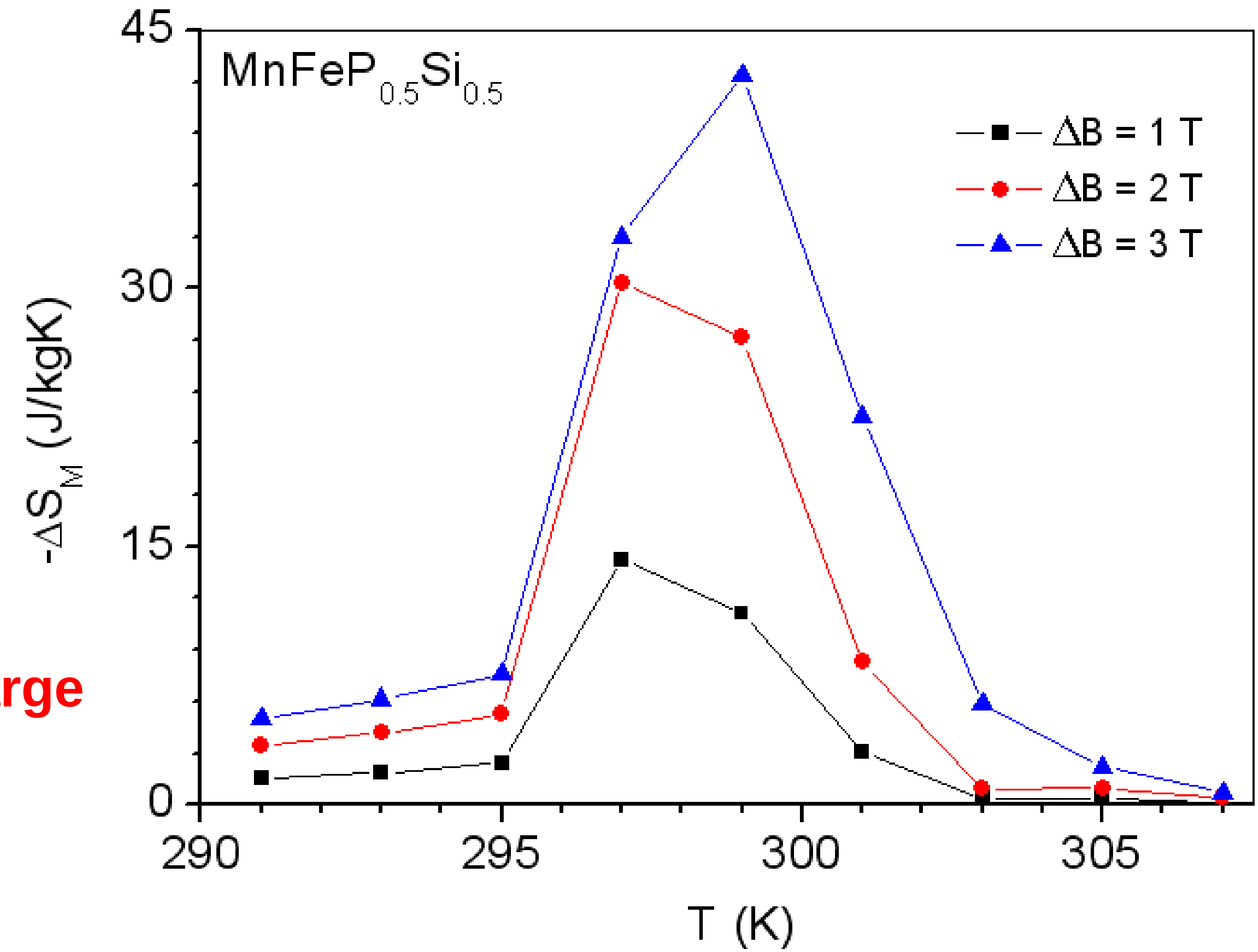
Replacing As by Si



very large hysteresis

(1) virgin effect, (2)heating, (3) subsequent cooling

Magnetic-entropy change

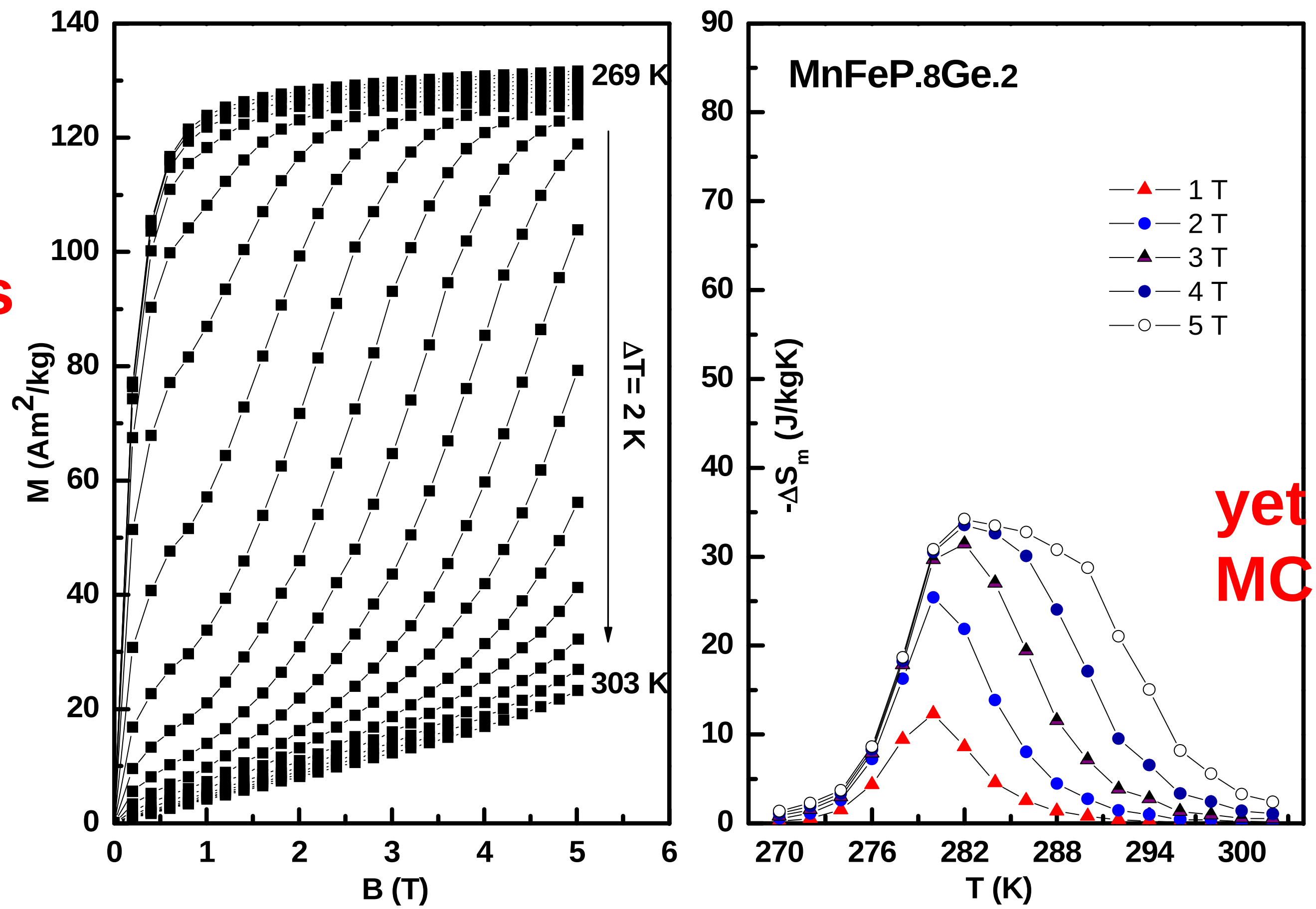


yet large MCE

Replace As by Ge

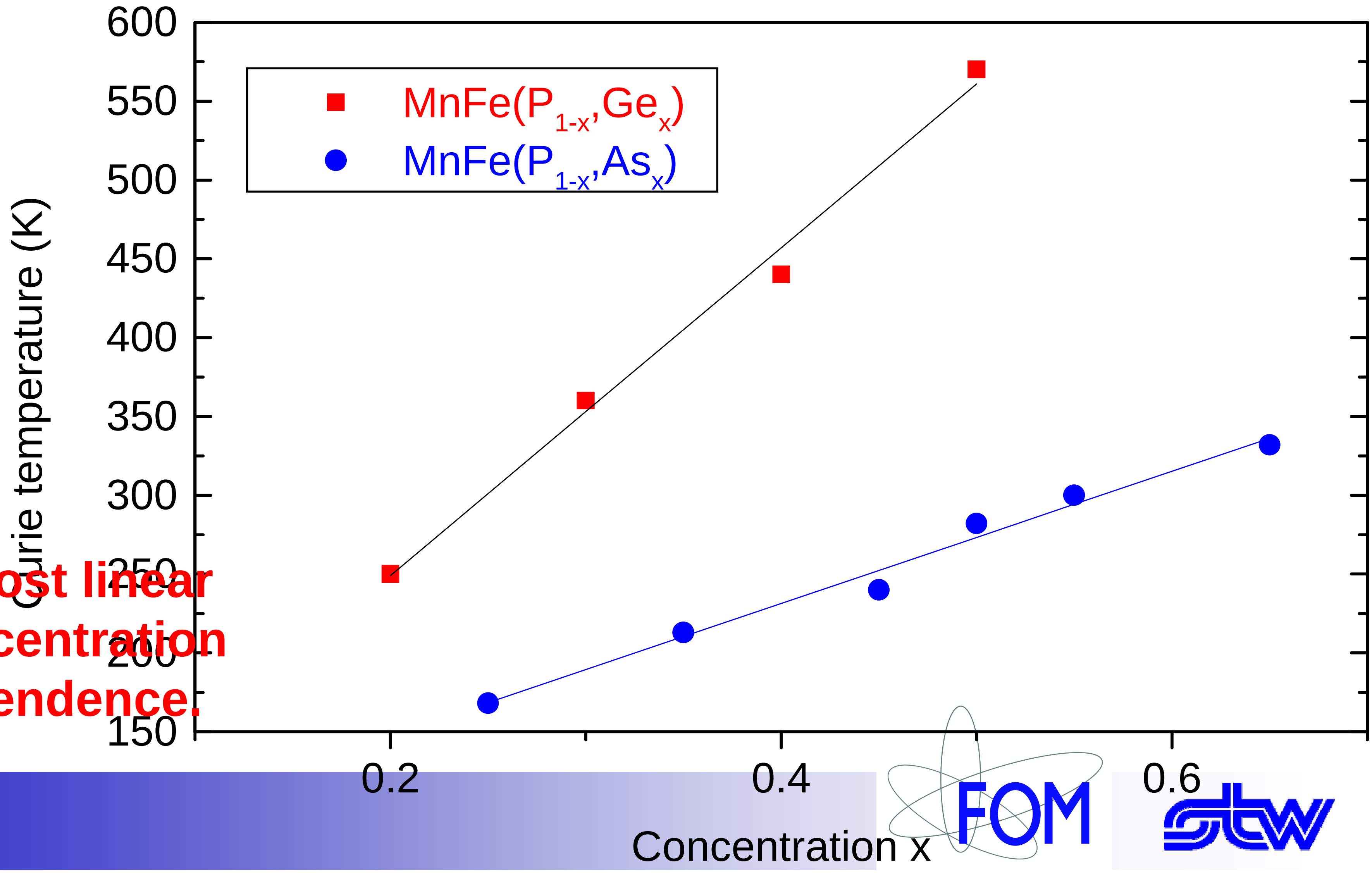
very large hysteresis

nice field induced transition



yet large MCE

Concentration dependence of T_C for Ge and As

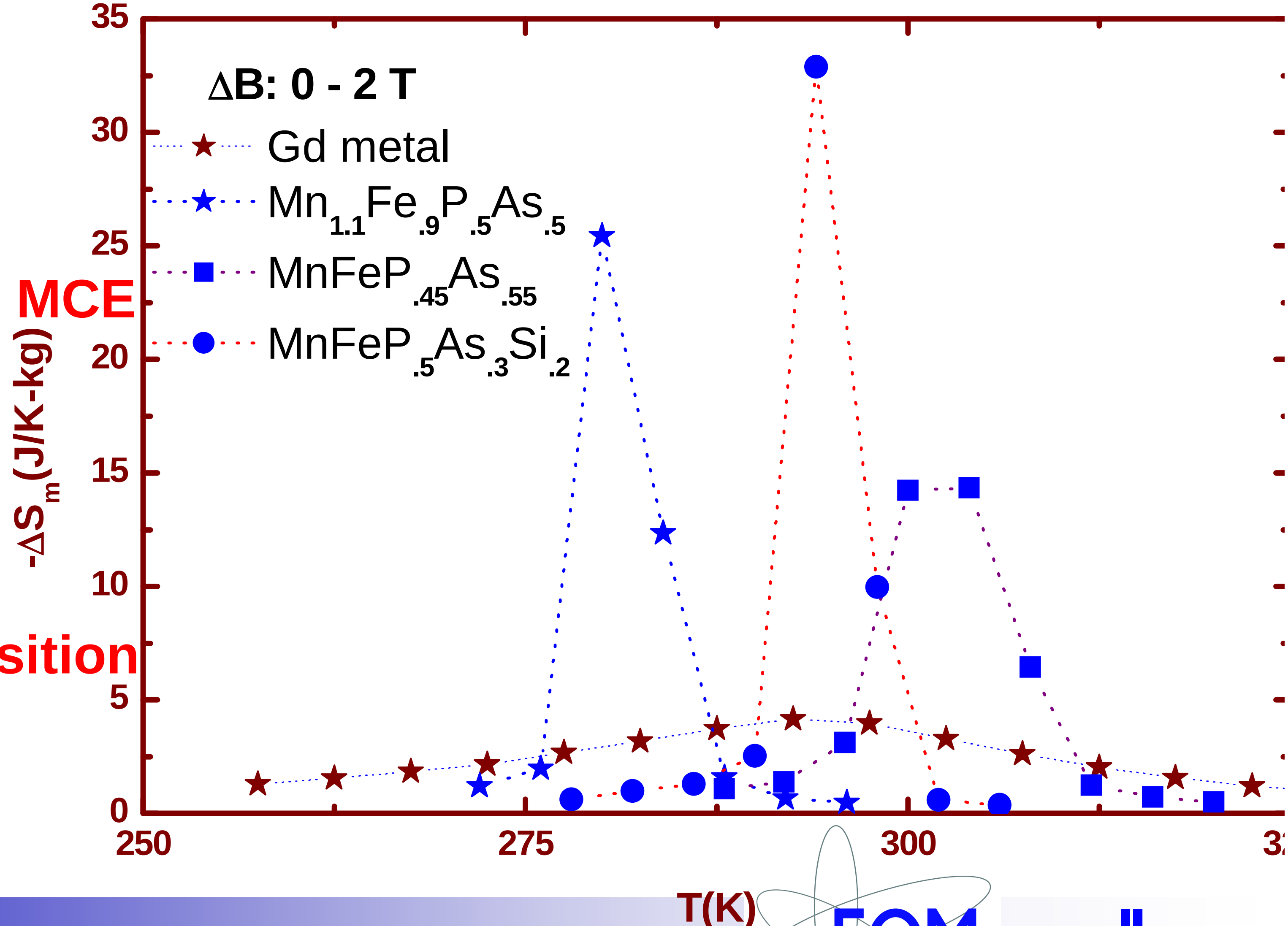


Almost linear concentration dependence.

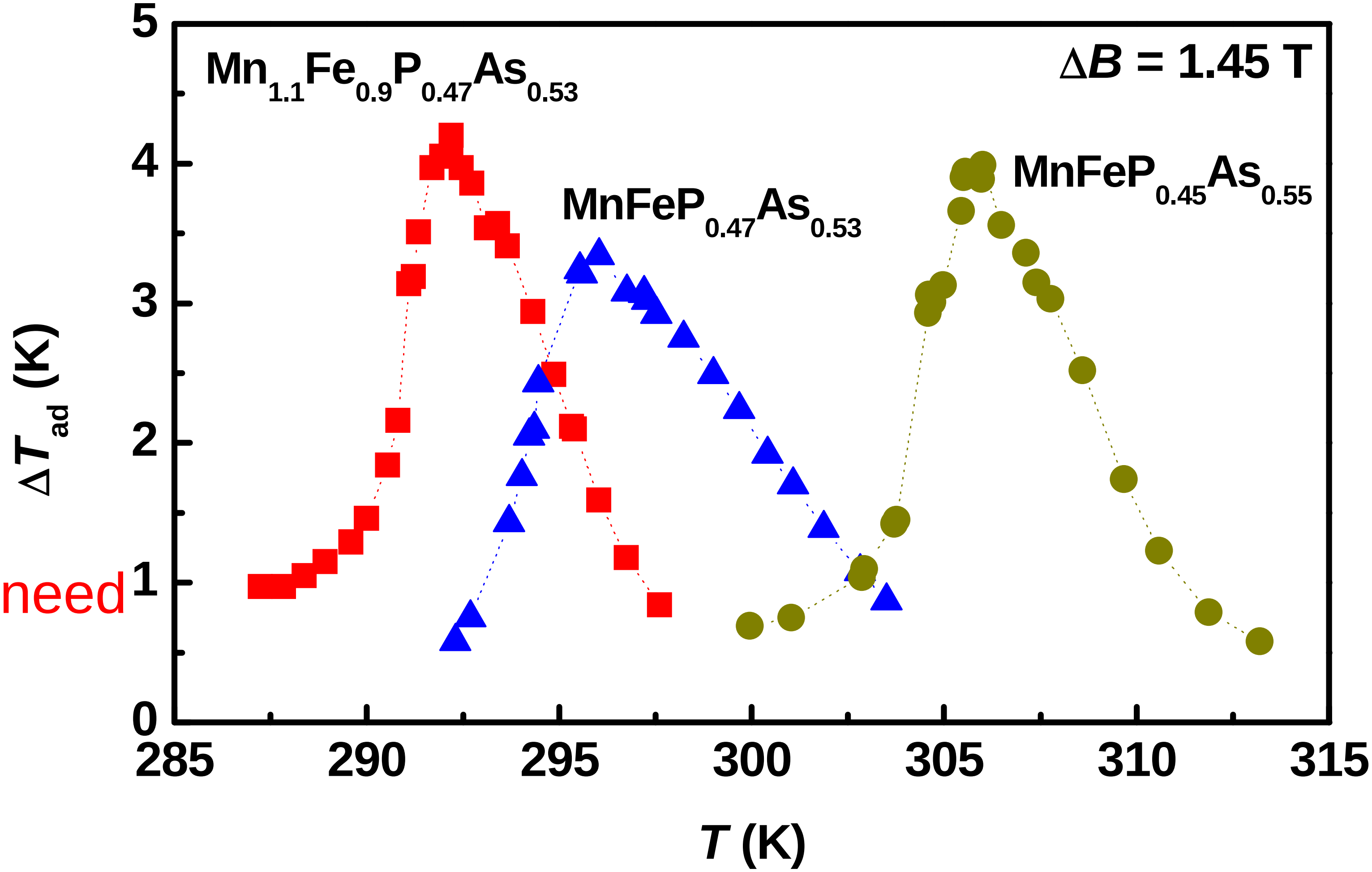
Entropy change; effect of different element substitutions.

More Mn increases moment and MCE

Si produces sharper transition



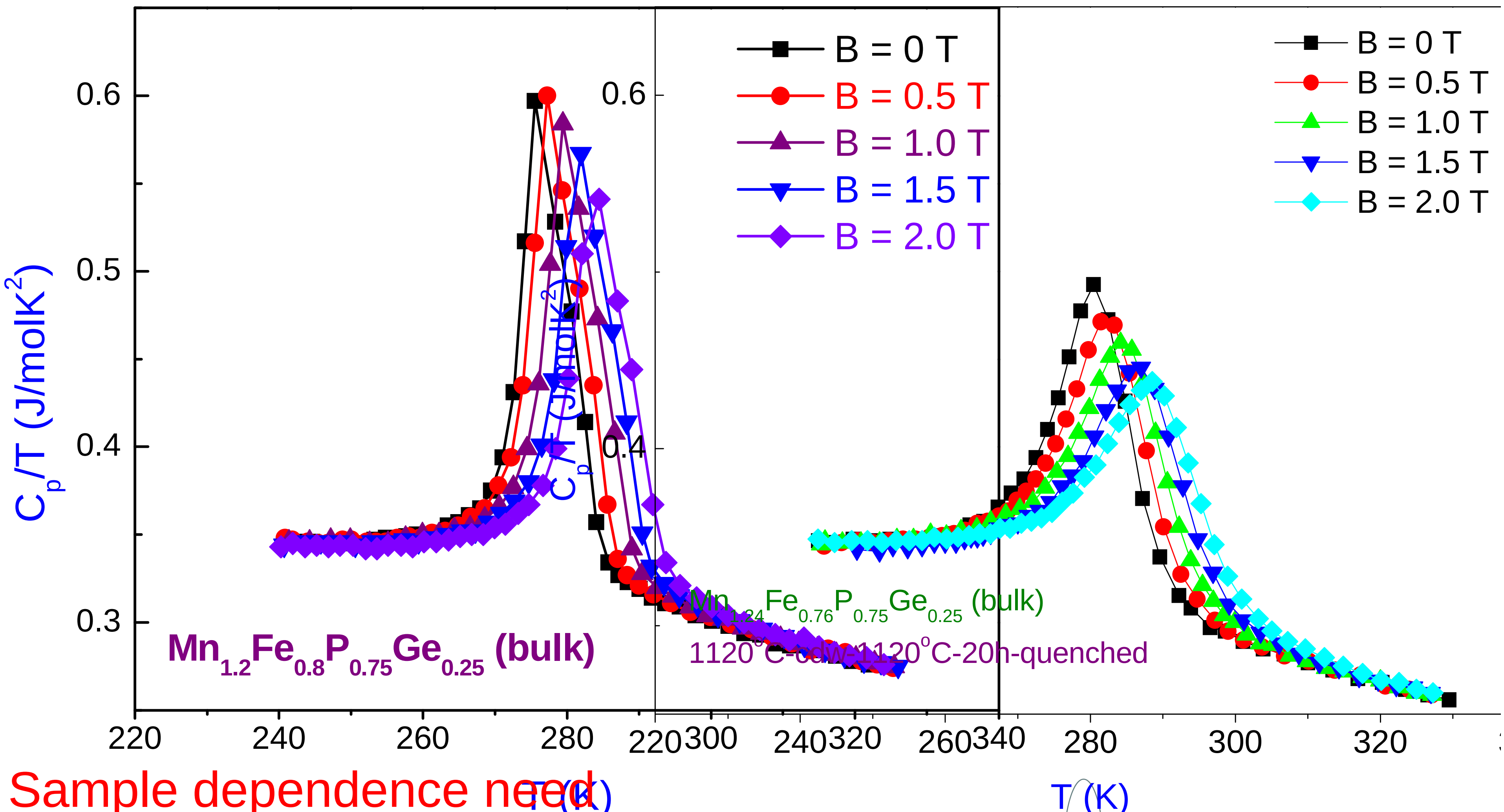
Adiabatic temperature-change



Sample dependence need for careful preparation

Direct measurements MSU

specific heat in field

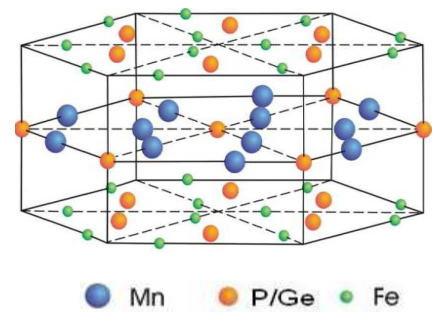


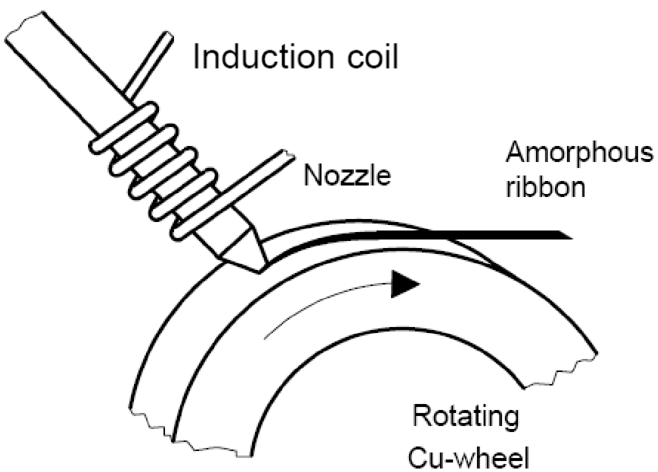
Sample dependence need
for careful characterization

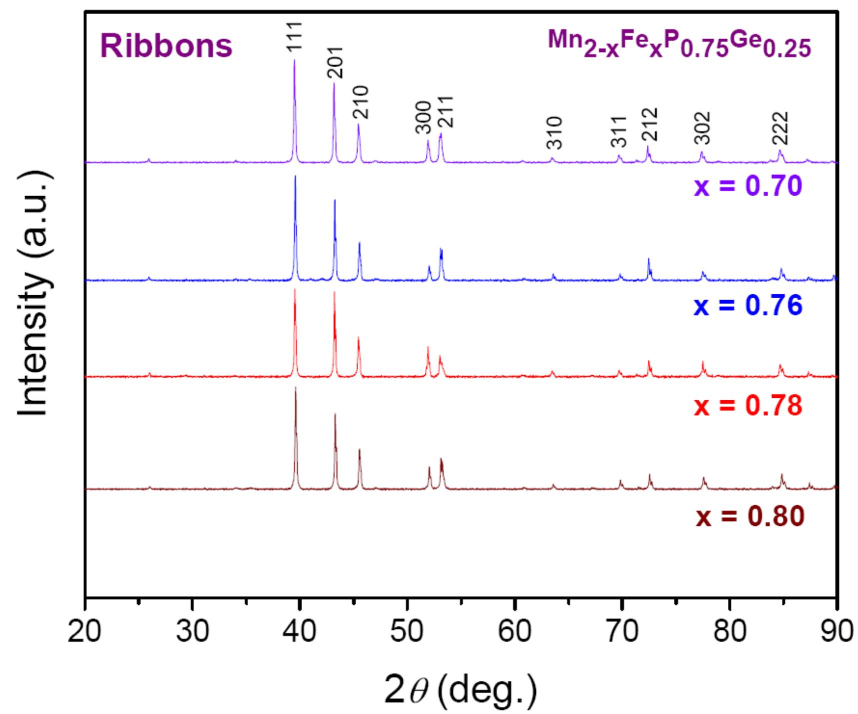
Improved Sample preparation

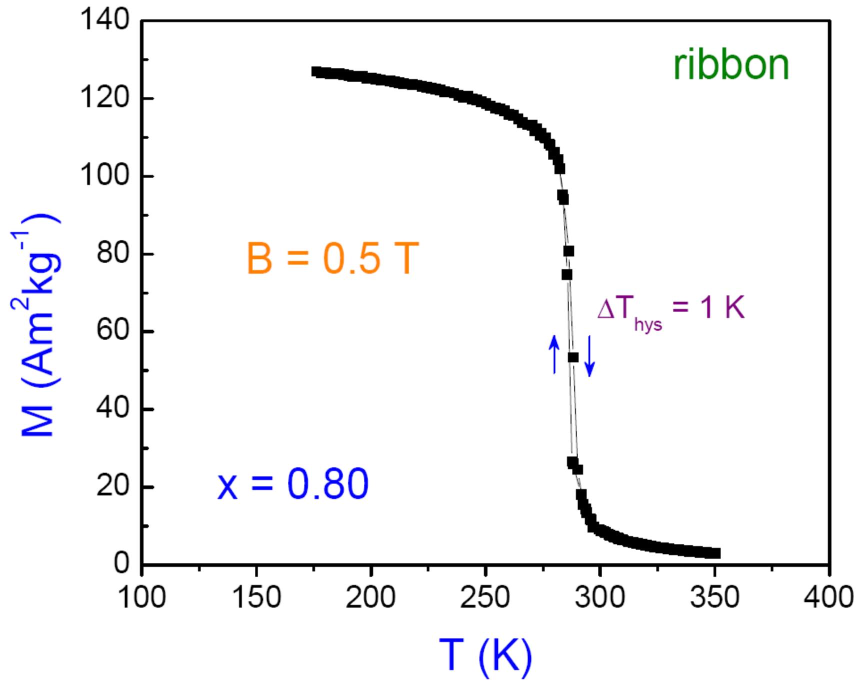
- Melt-spinning
  - + $Mn_{2-x}Fe_xP_{0.75}Ge_{0.25}$ (x = 0.70, 0.76, 0.78, 0.80)
  - + Ar gas pressure ~ 1 atm.
  - + surface speed of the wheel v = 40m/s
  - + ribbons were annealed for ± 10 min.

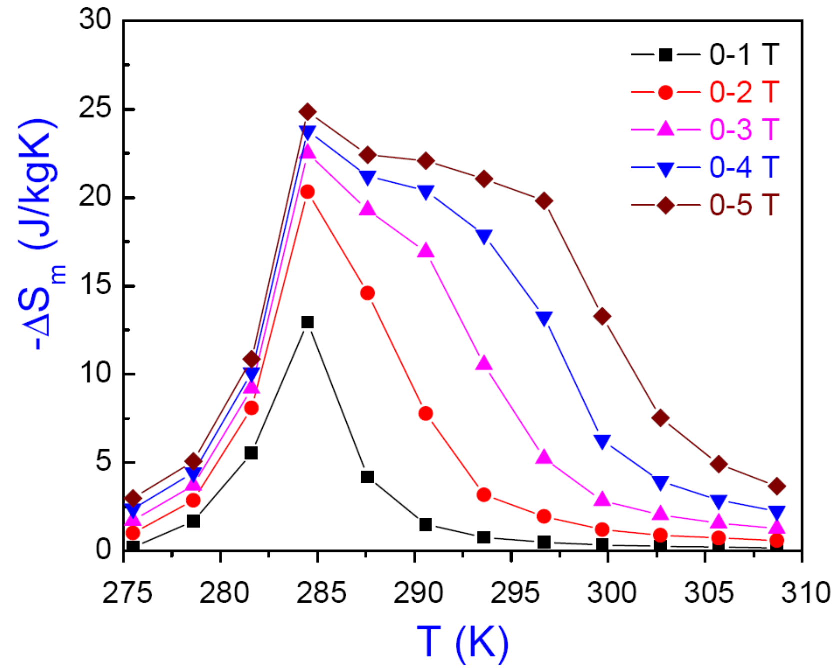
Hexagonal Fe_2P-type structure



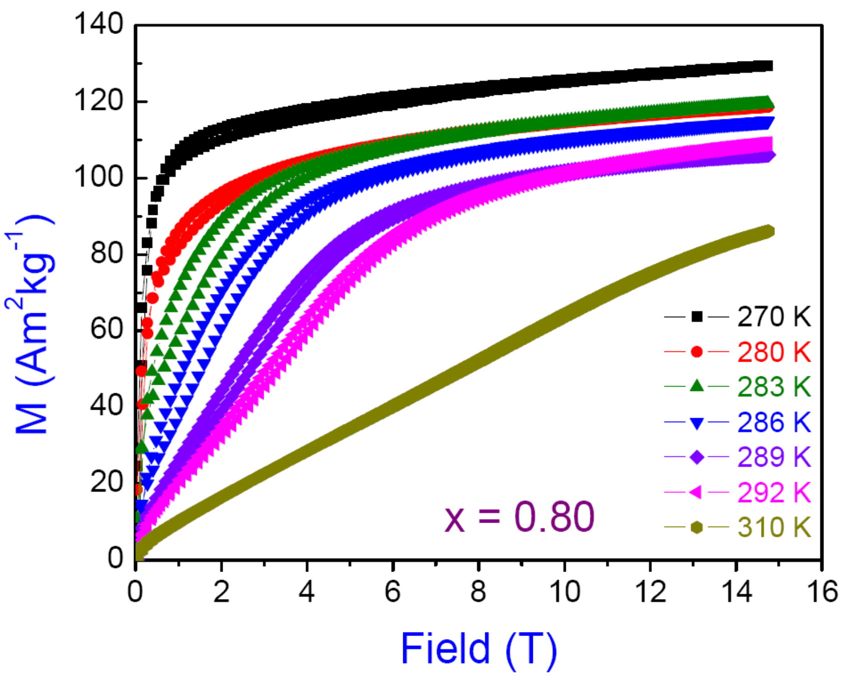


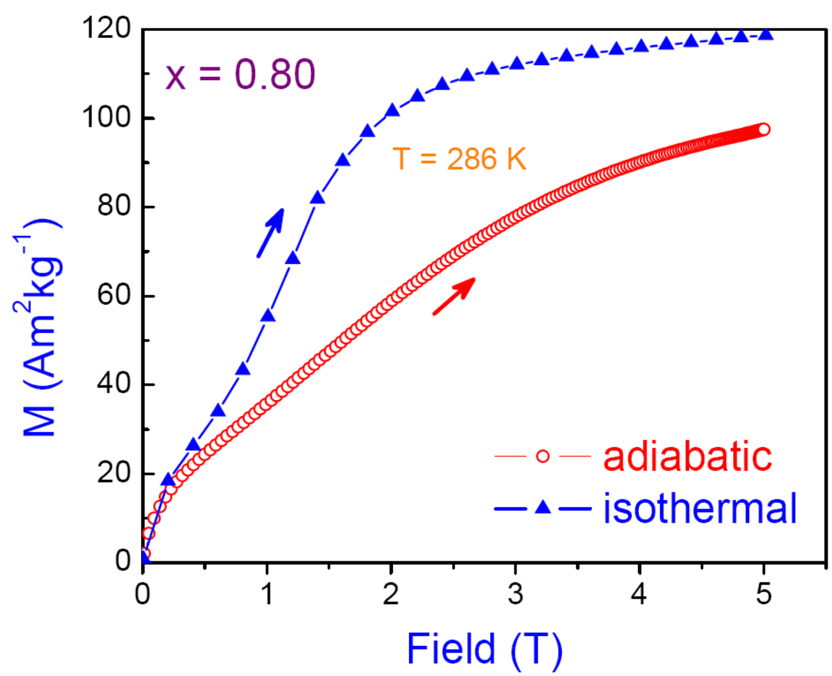




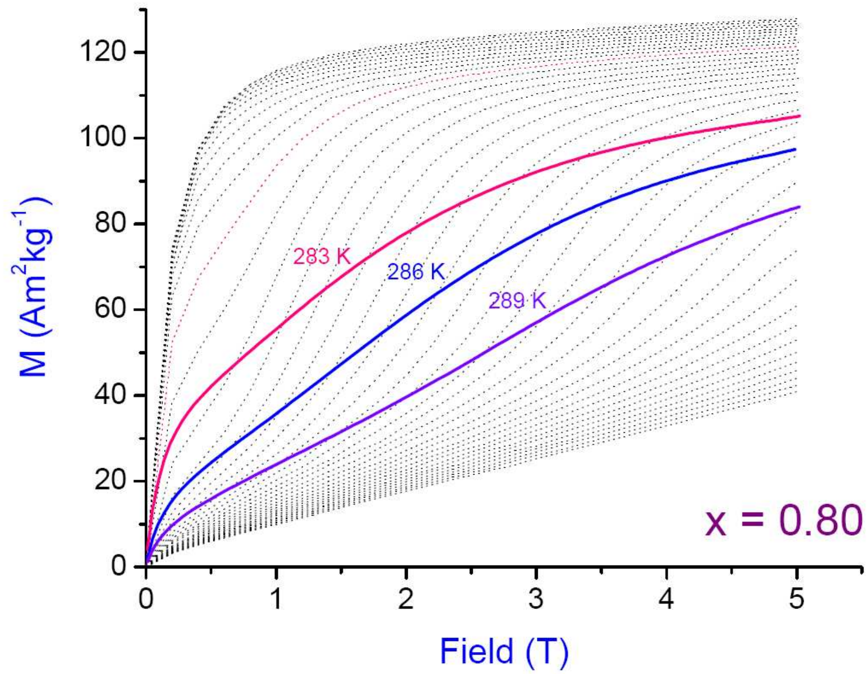


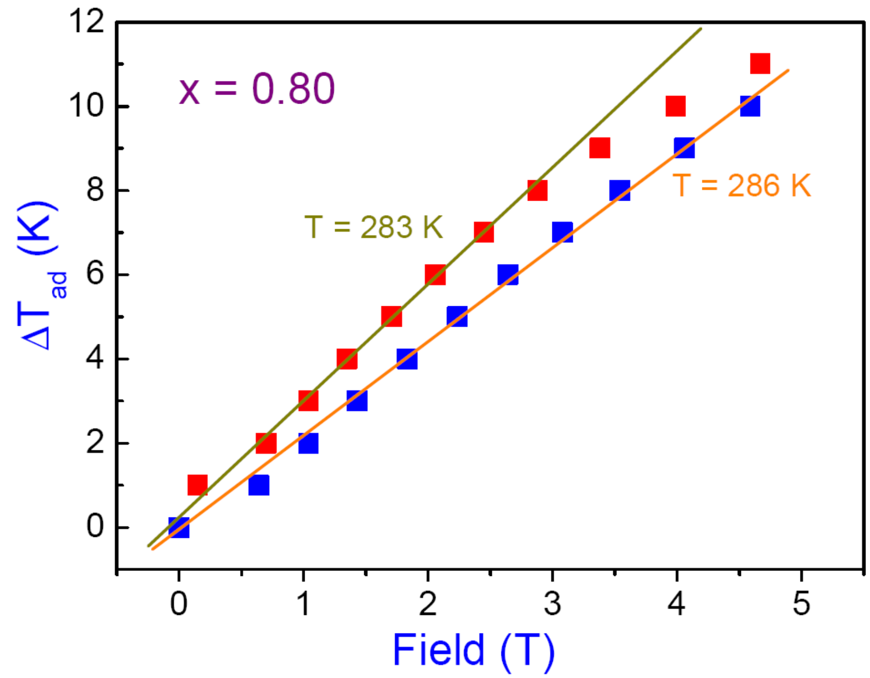
- Small thermal hyteresis, T_c = 288 K
- Large MCE observed at low operation field



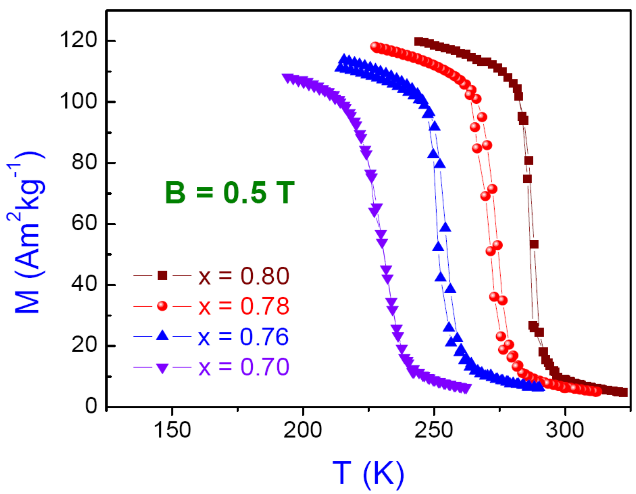


- τ = 100 ms (f = 10 Hz): field sweep rate of 300 Tesla/sec. ⟶ adiabatic condition
- Magnetocaloric effect is directly observed

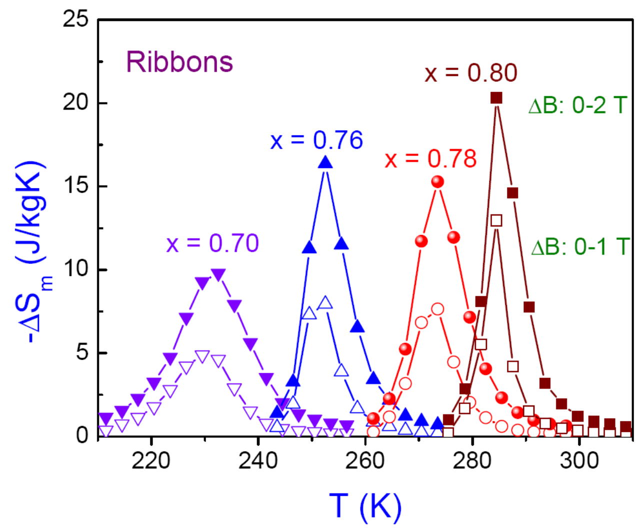




- ΔT_{ad} (*H*) is constructed via the crossing points of the adiabatic curve with the set of isothermal curves
- For x = 0.80: $\Delta T_{ad} \approx$ 3 K/Tesla

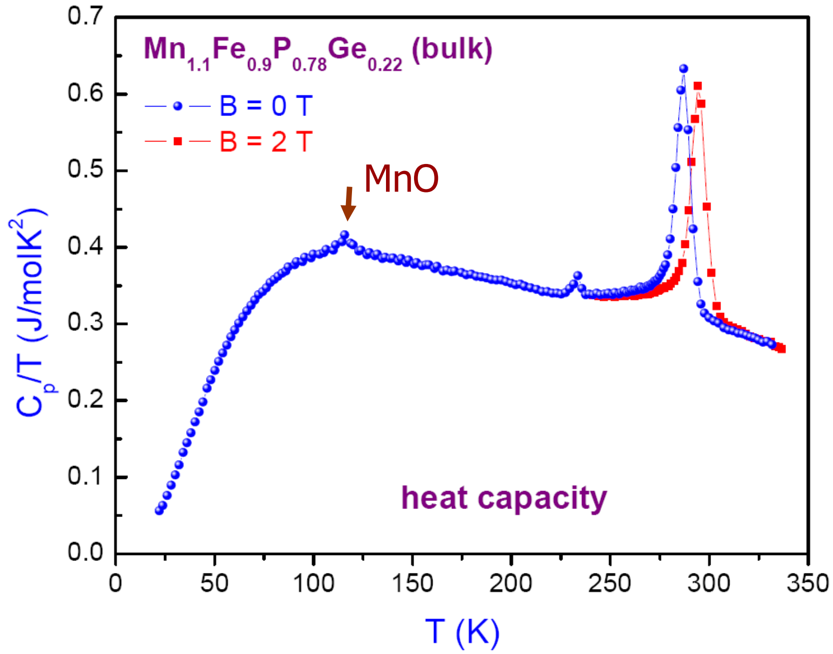


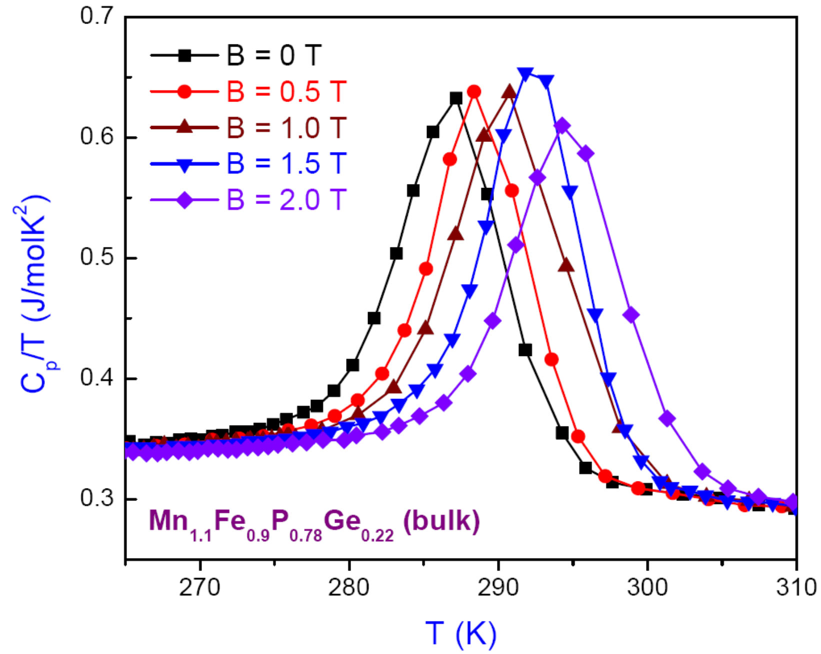
x	c/a	ΔT_{hys} (K)	T_c (K)	$-\Delta S_{m,max}$ (Jkg^{-1}K^{-1})	$\Delta T_{ad,max}$ (K/T)
0.80	0.5626	1	288	20.3	3.0
0.78	0.5638	2	274	15.3	2.5
0.76	0.5646	2	254	16.4	2.6
0.70	0.5651	0	230	9.8	-



- T_c decreases with increasing the Mn/Fe ratio
- $Mn_{2-x}Fe_xP_{0.75}Ge_{0.25}$ compounds:
  - + Small thermal hysteresis
  - + Large range of working temperature
  - + Large MCE

Specific heat measurements

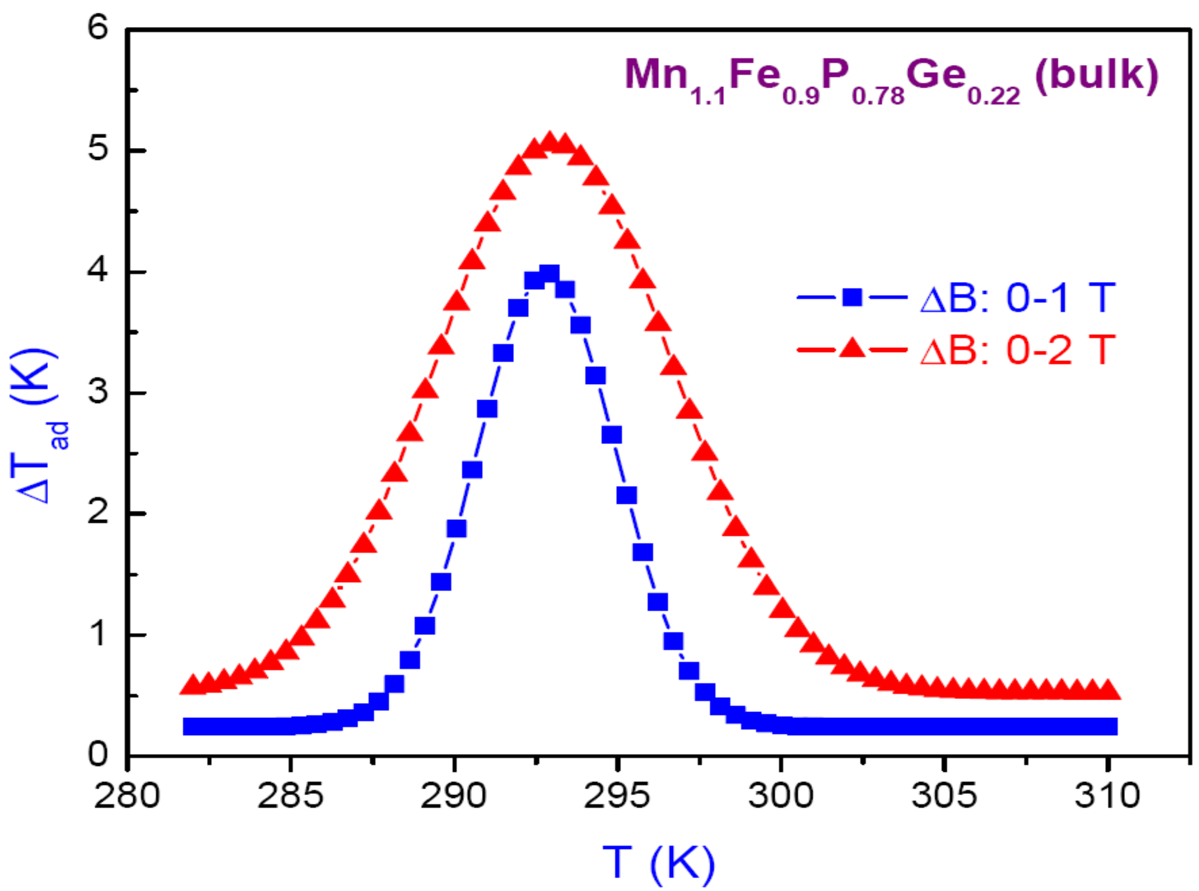




- $S_{tot} = S_{lat} + S_m + S_e$
- Magnetic field induces a shift of transition temperature ~ 4 K/T

Adiabatic temperature change

$$\Delta T_{ad}(T,\Delta B) = -\int_0^B \frac{T}{C(T,B')}\left(\frac{\partial M}{\partial T}\right)_B dB'$$



Summary MnFe(P,As,Si,Ge)

Field driven 1st order magnetoelastic transition 150 K < T_c < 450 K .

MnFe(P,As) hexagonal above magnetic transition

hexagonal below.

Hardly any volume change(<0.1 %) but change of c/a.

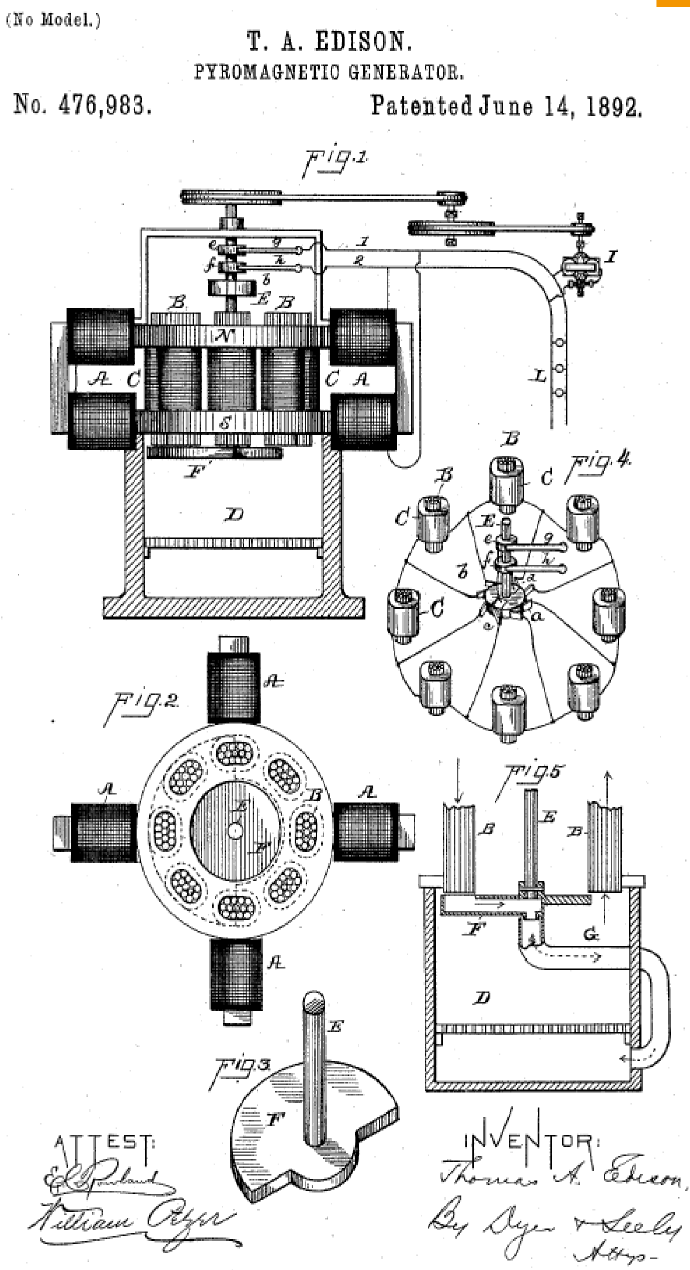
Magnetocaloric power-generation

Heat input → temperature change
magnetization change

$$dQ = TdS = c_p dT + T\frac{\partial M}{\partial T}dB$$

$$W_{elect} = I^2R = -\frac{N^2S^2}{R}\left(\frac{dB}{dt}\right)^2$$

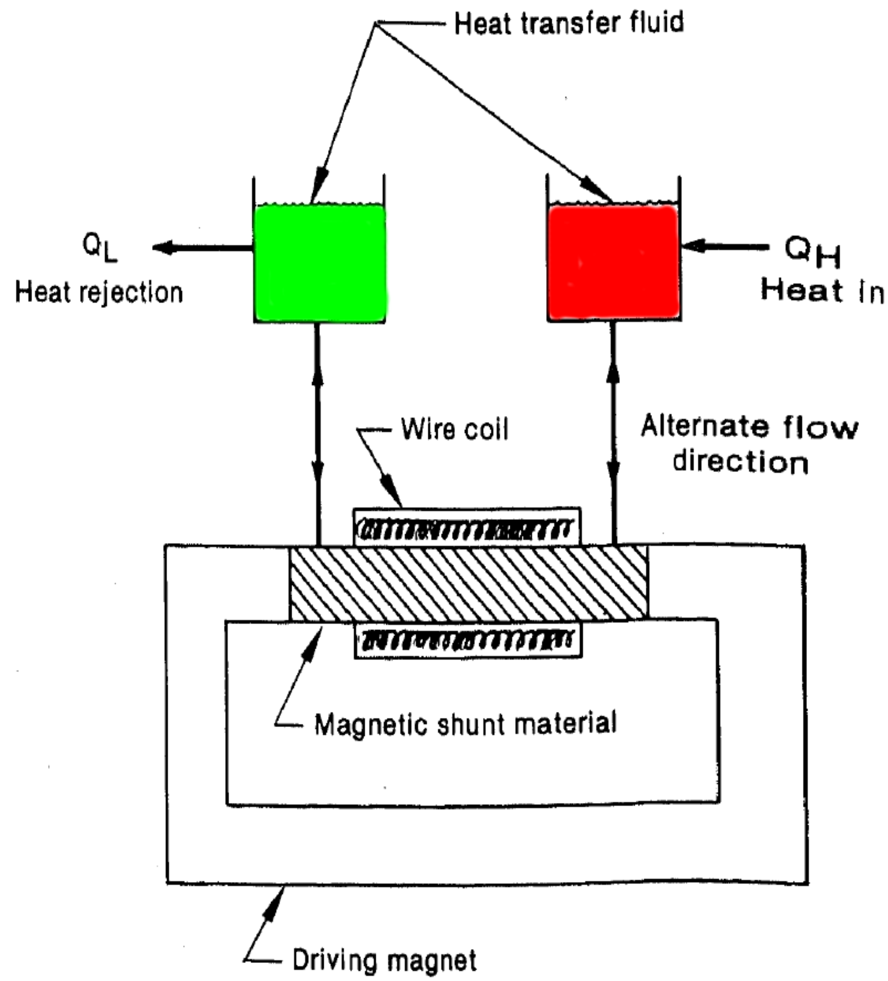
Edison's machine from 1892
directly employing the heat from the coal fire.
Interesting design with very low efficiency.



BASF The Chemical Company

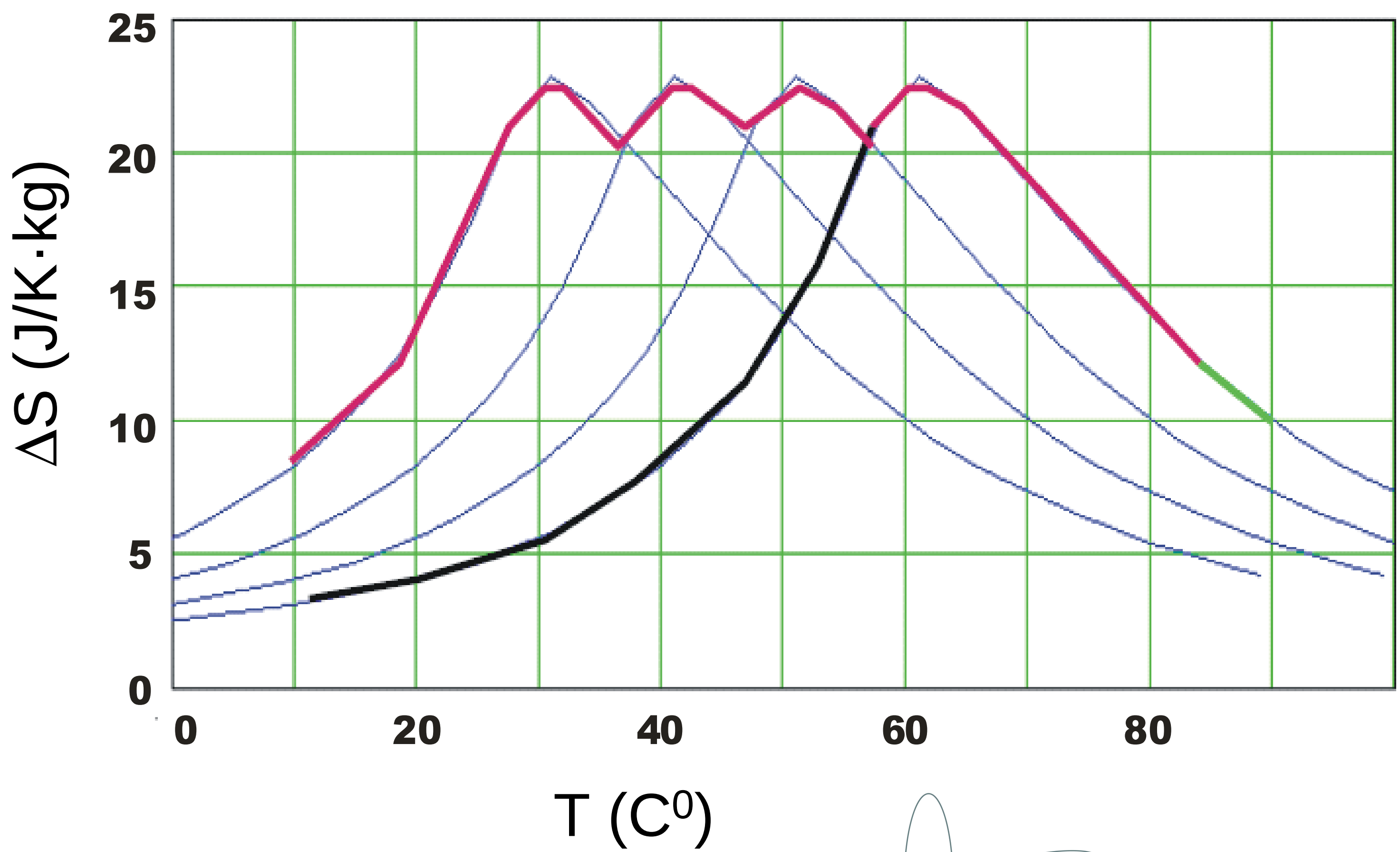
Modern design without moving parts.

Increased efficiency with regenerator.
From numerical modeling 75% Carnot-efficiency derived.

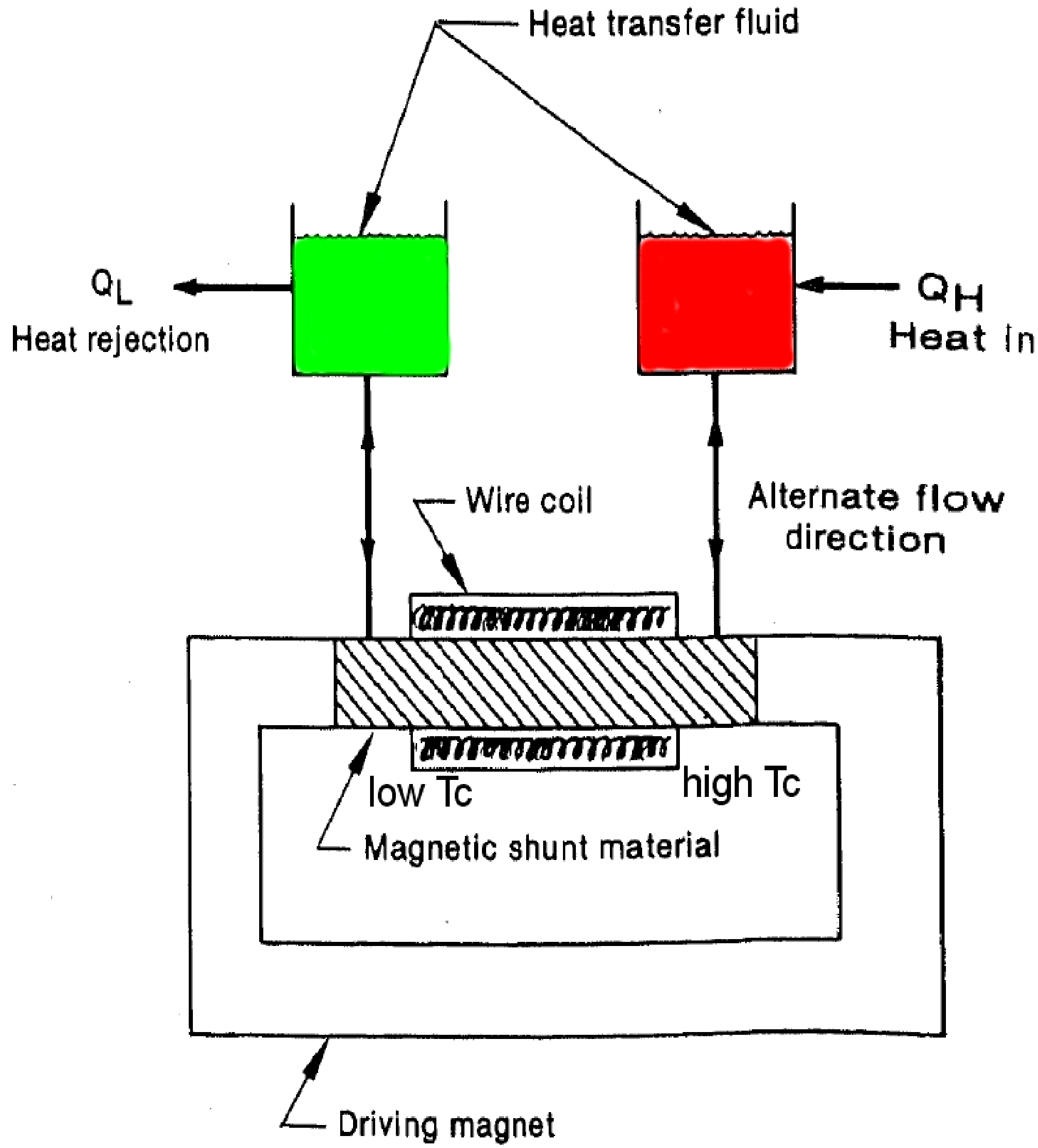


Kirol & Mills JAP

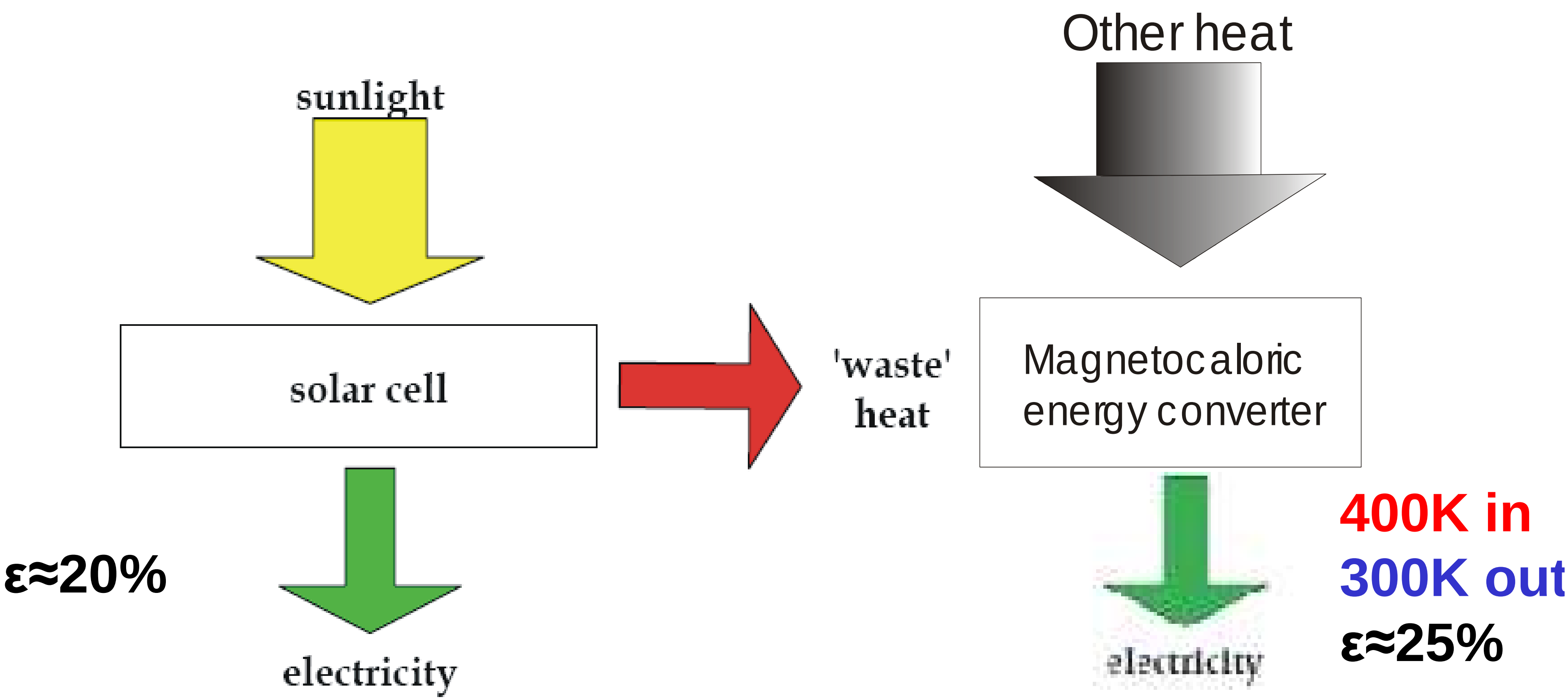
Increased T span with active magnetic regenerator containing different materials with tailored T_c



High efficiency with locally only small ΔT but working in series over large T span and thus larger power output.



Possible scenario to increase efficiency of solar cells



Conclusions I

- First order magnetic transition common to giant MCE!
- Structural transition may cause extra hysteresis.
- Control of hysteresis very important but possible.
- Evaluation of entropy change needs care.
- Fe and Mn based systems with much lower materials costs.
- Relevant T range covered by MnFe(P,As,Si,Ge).
- Sample preparation simplest for MnFe(P,As) with As replaced by other element.

Conclusions II

1. Pulse field magnet provides a good approach for directly monitoring the MCE
2. ΔT_{ad} is calculated by comparing the M(*H*) curves obtained in isothermal and adiabatic process
3. $Mn_{2-x}Fe_xP_{0.75}Ge_{0.25}$ ribbons exhibit excellent magnetocaloric properties
4. MnFe(P,As,Ge,Si) compounds can be used as magnetocaloric medium working at high frequencies

Thank you for your attention !