Magnetocaloric Materials not only for cooling applications

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Introduction
Magnetic cooling
Giant magnetocaloric effect
power generation

## Cooling techniques

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**Introduction**
Introduction  Magnetic cooling: Debye and Giauque 1926

LETTERS TO THE EDITOR

Attainment of Temperatures Below 1° Absolute by Demagnetization of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ 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 $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ 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.

$61\text{g }\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}, \Delta B=0.8\text{T}, 1.5\text{K} \rightarrow 0.25\text{K}$ Nobel prize 1949
Introduction

- Magnetic refrigeration is based on magnetocaloric effect (MCE)

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

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

- \( \Delta S_{\text{max}} \) important for cooling capacity
- \( \Delta T \) important for heat flow
Giant MCE

First-order field-induced magneto-structural transition

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$_2$P related materials

Hexagonal Fe$_2$P type of structure

Space group: P62m
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

$\text{MnFeP}_{0.50}\text{Si}_{0.50}$

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

ΔB: 0 - 2 T

-ΔS_m (J/K-kg)

T(K)

Gd metal
Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.5}
MnFeP_{0.45}As_{0.55}
MnFeP_{0.5}As_{0.3}Si_{0.2}
Sample dependence need for careful preparation
specific heat in field

Sample dependence need for careful characterization
Improved Sample preparation

- Melt-spinning
  - $\text{Mn}_{2-x}\text{Fe}_x\text{P}_{0.75}\text{Ge}_{0.25}$ ($x = 0.70, 0.76, 0.78, 0.80$)
  - Ar gas pressure $\sim 1$ atm.
  - surface speed of the wheel $v = 40\text{m/s}$
  - ribbons were annealed for $\pm 10\text{ min.}$
Small thermal hysteresis, $T_c = 288$ K

Large MCE observed at low operation field
The Magnetocaloric effect is directly observed with a field sweep rate of 300 Tesla/sec at a field sweep rate of 100 ms ($f = 10$ Hz). It indicates an adiabatic condition.

Magnetocaloric effect is directly observed.
$\Delta T_{ad} (H)$ is constructed via the crossing points of the adiabatic curve with the set of isothermal curves.

For $x = 0.80$: $\Delta T_{ad} \approx 3 \text{ K/Tesla}$
Experimental results

$T_c$ decreases with increasing the Mn/Fe ratio

$\text{Mn}_{2-x}\text{Fe}_x\text{P}_{0.75}\text{Ge}_{0.25}$ compounds:

+ Small thermal hysteresis
+ Large range of working temperature
+ Large MCE
Specific heat measurements

\[ S_{\text{tot}} = S_{\text{lat}} + S_{\text{m}} + S_{\text{e}} \]

Magnetic field induces a shift of transition temperature \( \sim 4 \text{ K/T} \)
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.

\( \text{MnFe(P,As)} \text{ hexagonal above magnetic transition} \)

\( \text{hexagonal below.} \)

Hardly any volume change ( <0.1 %) but change of c/a.
Magnetocaloric power-generation

Heat input $\rightarrow$ temperature change
magnetization change

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

\[ W_{\text{elect}} = I^2 R = -\frac{N^2 S^2}{R} \left( \frac{dB}{dt} \right)^2 \]
Edison's machine from 1892 directly employing the heat from the coal fire. Interesting design with very low efficiency.
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

\[ \varepsilon \approx 20\% \]

\[ \text{sunlight} \rightarrow \text{solar cell} \rightarrow \text{electricity} \]

\[ \text{Other heat} \rightarrow \text{Magnetocaloric energy converter} \]

\[ 400K \text{ in} \]
\[ 300K \text{ out} \]

\[ \varepsilon \approx 25\% \]
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. $\Delta T_{ad}$ is calculated by comparing the $M(H)$ curves obtained in isothermal and adiabatic process

3. $\text{Mn}_{2-x}\text{Fe}_x\text{P}_{0.75}\text{Ge}_{0.25}$ 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!