Barocaloric effects in a novel spin-crossover compound

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Motivation
Today 3600 million AC units installed → 2050 14000 million AC units installed
**Motivation**

**COOLING DEVICES** > 15% world-electricity consumption

8% of total greenhouse emissions

**Gases:**
- HCFC
- HFC

Leaks (3%)

**Greenhouse effect**
Motivation

(UE Regulation 517/2014)

Gases:

• HCFC
• HFC

Need for an environmentally-friendly cooling alternative

Solid-state devices

• No leaks
• Promise higher efficiency
How does refrigeration work?

*Vapour compression cycle (Reverse Brayton cycle)*

*Liquid-Vapour transition*
Vapour compression cycle

Liquid-Vapour transition

Clausius-Clapeyron:

\[
\frac{\Delta V_t}{\Delta S_t} = \frac{dT}{dp}
\]
Vapour compression cycle

Liquid-Vapour transition

Clausius-Clapeyron:

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Liquid-Vapour transition

\[
\Delta V_t \frac{dT}{\Delta S_t} = \frac{dT}{dp}
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Vapour compression cycle

**Liquid-Vapour transition**

\[ p_{\text{atm}} \]

\[ T_1 \]

\[ T_0 \]

\[ T_2 \]

\[ T \]

\[ S \]

\[ +Q \]

\[ -Q \]

\[ p_1 \]

\[ p_{\text{atm}} \]

Clausius-Clapeyron:

\[ \frac{\Delta V_t}{\Delta S_t} = \frac{dT}{dp} \]
Solid-state refrigeration cycle

Vapour \longrightarrow Solid

L-G phase transition

S-S phase transition

\[ \frac{\Delta V_t}{\Delta S_t} = \frac{dT}{dp} \]

Clausius-Clapeyron: \[ \frac{\Delta V_t}{\Delta S_t} = \frac{dT}{dp} \]
BAROCALORIC EFFECTS

Clausius-Clapeyron:

$$\frac{\Delta V_t}{\Delta S_t} = \frac{dT}{dp}$$

Solid-state refrigeration cycle

Vapour

L-G phase transition

Solid

S-S phase transition

isothermal $\Delta S$

adiabatic $\Delta T$
Other types of solid-state caloric effects

Barocaloric

Elastocaloric

Magnetocaloric

Electrocaloric
Other types of solid-state caloric effects

Barocaloric

ADVANTAGES:

• Many materials with S-S transition sensitive to $p$
• No fatigue, long term cyclability
• $p$ is easier to generate
Instrumental Setup: quasi-direct method
Calculation of the caloric effects: Quasi-direct method

\[ \frac{dQ}{dT} \]

Phase diagram

\[ T_T \]

\[ P_{\text{atm}} \] \[ P_1 \] \[ P_2 \]

\[ P_1 \] \[ P_2 \]

\[ T \]
Calculation of the caloric effects: Quasi-direct method

Phase diagram

Hysteresis and Reversibility

\[ p_{\text{atm}} \quad p_1 \quad p_2 \]

\[ d\overline{Q}/dT \]

\[ T \]

\[ T_t \]

Heating

Decompression

Compression

Cooling
Calculation of the caloric effects: Quasi-direct method

\[ \Delta S_t = \int_{T_i}^{T_f} \frac{1}{T} \frac{dQ(p)}{dT} \, dT \]

I Transition entropy change

II
Calculation of the caloric effects: Quasi-direct method

II  Heat capacity

\[ S(T, p) - S(T_0, p) = \int_{T_0}^{T} \frac{C_p}{T} \, dT \]

III  Volume

\[ S(T, p) - S(T, p_{\text{atm}}) = -\int_{p_{\text{atm}}}^{p} \left( \frac{\partial V}{\partial T} \right)_p \, dp \]

X-ray diffraction, dilatometry
Calculation of the caloric effects: Quasi-direct method

\[ \Delta S(T, p \rightarrow p_{atm}) = S(T, p_{atm}) - S(T, p) \]

\[ \Delta T(S, p \rightarrow p_{atm}) = T(S, p_{atm}) - T(S, p) \]
Calculation of the caloric effects: Quasi-direct method

\[ \Delta S(T, p_{atm} \rightarrow p) = S(T, p) - S(T, p_{atm}) \]

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Calculation of the caloric effects: Quasi-direct method

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Reversible caloric effects and hysteresis

\[ \Delta S_{\text{rev}}(T, p_{\text{atm}} \rightleftharpoons p_2) = S_{\text{cool}}(T, p_2) - S_{\text{heat}}(T, p_{\text{atm}}) \]

\[ \Delta T_{\text{rev}}(T, p_{\text{atm}} \rightleftharpoons p_2) = T(S_{\text{cool}}, p_2) - T(S_{\text{heat}}, p_{\text{atm}}) \]
Reversible caloric effects and hysteresis
Reversible caloric effects and hysteresis

minimum pressure to achieve reversible barocaloric effects
Materials for the solid-state refrigeration cycle

Should have:

- 1st order transition close to room T, with large $\Delta H$
- T high sensibility to applied field
- Small hysteresis
- Low toxicity
- Low cost
- High density
- High thermal conductivity
Materials for the solid-state refrigeration cycle

Need of material with solid transition accompanied by large $\Delta H$:

order-disorder transitions under the application of an external field

- Change in the magnetization
  - Ex: Alloys based on MnNi-Co-Mn-Ga, Ni-Mn-In
- Change in the polarization
  - Ex: salts $\text{KNO}_3$, $\text{BaTiO}_3$
  - Molecular Crystals $\left(\text{C}_5\text{H}_7\text{N}_2\right)^+\text{ClO}_4^-$
- Change in the orientation
  - Ex: NPA, NPG, Adamantane Derivatives
- Change in the ionic conductivity
  - Ex: AgI
Materials for the solid-state refrigeration cycle

Need of material with solid transition accompanied by large $\Delta H$:

**order-disorder transitions under the application of an external field**

<table>
<thead>
<tr>
<th>Magnetostructural</th>
<th>Ferroelectrics</th>
<th>Plastic crystals</th>
<th>Superionic conductors</th>
<th>Spin Crossover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic</td>
<td>Polar (Positional/rotational)</td>
<td>Orientational</td>
<td>Positional (diffusion)</td>
<td></td>
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- **Change in the magnetization**
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- **Change in the polarization**
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- **Change in the orientation**
  - Ex: NPA, NPG, Adamantane Derivatives

- **Change in the ionic conductivity**
  - Ex: AgI

- **Change in spin state (LS-HS)**
  - Ex: $\text{Fe(qnal)}_2$
  - $\text{Fe}_3(\text{bntrz})_6(\text{tcnset})_6$
Spin-crossover material (SCO)

switching between LS-HS state by changes in T, p or light irradiation
Giant and Reversible Barocaloric Effect in Trinuclear Spin-Crossover Complex Fe₃(bntrz)₆(tcnsset)₆

Properties

- abrupt one-step spin transition
- negligible hysteresis
- $\Delta S_t (p_{amb}) \sim 80 \text{ J kg}^{-1} \text{ K}^{-1}$
- sharp volume change at spin transition

$\frac{|\Delta V_t|}{V_i} \sim 3\%$
Differential Thermal Analysis measurements

- \( \frac{dT}{dp} \sim 25.0 \, K \, kbar^{-1} \)
- Clausius-Clapeyron:
  \( \frac{dT}{dp} = \frac{\Delta V_t}{\Delta S_t} \sim 25.6 \, K \, kbar^{-1} \)
- Small hysteresis: \sim 2 \, K \, / \sim 65 \, bar
Reversible barocaloric effect:

\[ S(T_p) - S(250, p_{atm}) \text{ [J K}^{-1} \text{ kg}^{-1}] \]

\[ p \text{ [kbar]} \]
- 0.0
- 0.5
- 1.1
- 1.6
- 2.0
- 2.5

ΔS: 80 → 120 J K\(^{-1}\) kg\(^{-1}\)

ΔT: 6 → 35 K
<table>
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<tr>
<th>Sample</th>
<th>$\Delta p$ (kbar)</th>
<th>$\Delta S_{\text{rev}}$ (JK$^{-1}$kg$^{-1}$)</th>
<th>$\Delta T_{\text{rev}}$ (K)</th>
<th>$\Delta T_{\text{hyst}}$ (K)</th>
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Refrigerant Capacity (RC)

FBT

$0.6 \rightarrow 5.8 \text{ J/g}$

$(0.3 \rightarrow 2 \text{ kbar})$
Conclusions:

• Solid-state caloric effects are a possible alternative to current refrigeration systems that use harmful gases.

• Advantages of solid-state refrigeration systems: higher efficiencies, more compact devices, no leaks

• There is a need of finding new materials for implementation.

• Results on SCO: stimuli for further research of the barocaloric effect in such compounds and for the design of novel SCO materials
Thank you for the attention