Low Cost High Performance Magnetocaloric Materials for Sub 50K Refrigeration Applications

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Materials Science Department

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Outline

- Who we are
- Motivation
- Background
  - Define MCE
  - Current state of the Industry
  - Magnetic Refrigeration Challenges
- Phase I Work
  - Objectives
  - Results
- Future Work
GE&R Background

- Founded in 2009
  - Industry Experience – Semiconductor/ Pharmaceuticals/ Medical Device/ Oil refining, Licensed Patent Agent
  - GE&R Advisor Board
    - Ted Taylor - Micron R&D Fab Manager / Director at Cymer
    - Steve Oldenburg – President of NanoComposix
    - Professor Jan Talbot – Head of UCSD ChemE dept.
- Current employees
  - 4 full time employees, 3 UCSD graduate students, 2 Prof.

Thermoelectrics
R&D Grant NRL – $2.4M for 6 yrs - Cooling Technology

Magnetocalorics
- DOE STTR Phase I Awarded June 2016 –
- Phase II award pending (July 31)
- CALSeed Awarded June 2017

CMP Slurries
NSF SBIR Funded (I,II, IIB)
Development of nano-capsules
Stober Silica Nanoparticles

Other Applications

BioApplications
- Drug Delivery
- Bone Tissue Engineering

Collaboration with UCSD

UC San Diego Jacobs School of Engineering
Team Members

PI – Dr. Robin Ihnfeldt, GE&R -nanomaterials

Professor Emeritus Sungho Jin, UCSD -Magnetic materials -nanomaterials

Professor Chen, UCSD -nanomat.

Dr. Xia Xu -magnetic nanomaterials

Grad. Student – Kim Jeong

Grad. Student – Lizzie Caldwell
Motivation

Magnetocaloric Effect

The variation in temperature of a magnetic material when exposed to a change in magnetic field, $H$.

Enable Fuel Cells Vehicles - Hydrogen
Hydrogen Storage – Liquid
Magnetic Refrigeration utilizes the magnetocaloric effect (MCE) – Efficient and Green

VCC for Hydrogen liquefaction – low efficiency (~12% of Carnot) [Haberbusch 2009]

Magnetic hydrogen liquefaction - Dr. Numazawa at the National Institute for Materials Science in Japan achieved ~60% of Carnot.

Magnetic Refrigeration promising – majority of work focused on room temperature applications
MCE Material Costs

- MCE Materials typically Rare-Earth - $ to $$$$.
- Processing to obtain MCE properties – cost varies.
- Limited Commercially Available MCE materials
  (the materials available are not that good).

### Rare Earth

<table>
<thead>
<tr>
<th>Element</th>
<th>Cost (USD/kg)</th>
<th>Cost (USD/kg)</th>
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<tbody>
<tr>
<td>Ce</td>
<td>7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>110</td>
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<tr>
<td>Dy</td>
<td>350&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
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<tr>
<td>Er</td>
<td>650&lt;sup&gt;b&lt;/sup&gt;</td>
<td>280</td>
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<td>Eu</td>
<td>200000&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Gd</td>
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<td>235</td>
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<td>Ho</td>
<td>8600&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>La</td>
<td>7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>110</td>
</tr>
<tr>
<td>Nd</td>
<td>60&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Tb</td>
<td>50000&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
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<tr>
<td>Tm</td>
<td>70000&lt;sup&gt;b&lt;/sup&gt;</td>
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### Non Rare Earth

<table>
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<tr>
<td>Co</td>
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<td></td>
</tr>
<tr>
<td>Cu</td>
<td>6&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>Ga</td>
<td>2200&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>1200&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1720</td>
</tr>
<tr>
<td>Mn</td>
<td>2.80&lt;sup&gt;b&lt;/sup&gt;</td>
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</tr>
<tr>
<td>Ni</td>
<td>2.35&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>300&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>1.40&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>18&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

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c) Quote from Hefa Rare Earth for 1kg quantity

Magnetocaloric Effect (MCE)

- MCE material only works near $T_c$ – need different materials to cover wide range
- Require porous matrix of MCE material – spheres or thin plates
- Heat removed using an external coolant
- Magnetic Field force
  - Permanent magnet (<1T)
  - Electromagnet or superconducting (up to 10T)
- For RT applications, permanent magnet >70% of costs*
  - Vmag
  - Hmag
- Cooling capacity of MR depends on MCE performance ($\Delta S$)
  - MCE materials typically expensive rare-earth

Balance MCE material cost with Magnetic Field Cost

Need high PERFORMANCE MCE materials to keep cost for magnetic field reasonable!!!

MCE Compositions

$$\text{Gd}_5\text{Ge}_2\text{Si}_{2-x}\text{Sn}_x$$

| $x$ | $T_c$ (K) | $|\Delta S_{\text{max}}|$ (J kg$^{-1}$ K$^{-1}$) | Thermal hysteresis (K) |
|-----|-----------|---------------------------------|------------------------|
| 0.5 | 210       | 14.9 (3T)                        | 4                      |
| 0.7 | 185       | 14.5 (3T)                        | 3                      |
| 0.9 | 160       | 14.2 (3T)                        | 2                      |

- RC = DS $\times$ FWHM
First order vs. Second order transition

- **Gd** - Second order
  - Reversible
  - Typically require significant rare-earth

- **Gd₅Si₂Ge₁.₃Sn₀.₇** - First order
  - Giant MCE
  - Not entirely reversible – bad for high frequency MR
  - Thermal expansion \( \Delta L/L = (L(T) - L(T=4K))/L(T=4K) \)
    - Thermal hysteresis \( \Delta T = 4K \)
  - Relative volume change \( \Delta V/V = 2.7 \times 10^{-3} \)
  - Clausius-Clapeyron relation \( dT_C/dp = 3.2 \text{ K/kbar} \)
Hysteresis Loss in First Order Transitions

\[
\text{Ni}_{48}\text{Mn}_{35}\text{Sn}_{15}\text{Cu}_2
\]

### Table

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tc (K)</th>
<th>Max $\Delta S$ at 3T (J/kg*K)</th>
<th>Hysteresis @ Tc (K)</th>
<th>FWHM</th>
<th>RCP (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsubscript{48}Mn\textsubscript{35}Sn\textsubscript{15}Cu\textsubscript{2}</td>
<td>135</td>
<td>3.07</td>
<td>15</td>
<td>15</td>
<td>46.05</td>
</tr>
</tbody>
</table>

MCE will only take place where $\Delta S$ curves overlap!
## Known MCE Materials

### For 100-300K applications

<table>
<thead>
<tr>
<th>Material</th>
<th>Tc</th>
<th>H</th>
<th>ΔS max (J/kgK)</th>
<th>FWHM (K)</th>
<th>RC (J/Kg)</th>
<th>phase transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>293</td>
<td>5T</td>
<td>9.5</td>
<td>80</td>
<td>760</td>
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<tr>
<td>Gd$<em>{0.72}$Dy$</em>{0.27}$</td>
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<td>10.5</td>
<td>120</td>
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<td>Gd$<em>{5}$Si$</em>{2}$Ge$_{2}$</td>
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<td>5T</td>
<td>9.5</td>
<td>25</td>
<td>475</td>
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<tr>
<td>Gd$<em>{5}$Si$</em>{1.9}$Ge$_{0.1}$</td>
<td>305</td>
<td>5T</td>
<td>65</td>
<td>7</td>
<td>455</td>
<td>1st</td>
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<tr>
<td>LaFe$<em>{11.5}$Si$</em>{1.5}$</td>
<td>194</td>
<td>5T</td>
<td>24.6</td>
<td>26</td>
<td>615</td>
<td>1st</td>
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<tr>
<td>LaFe$<em>{10.88}$Co$</em>{0.95}$Al$_{1.17}$</td>
<td>300</td>
<td>5T</td>
<td>9</td>
<td>55</td>
<td>495</td>
<td>1st</td>
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<tr>
<td>Ni$<em>{50}$Mn$</em>{31}$Sn$_{13}$</td>
<td>310</td>
<td>3T</td>
<td>9.5</td>
<td>64</td>
<td></td>
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<tr>
<td>MnFe$<em>{0.5}$As$</em>{0.5}$P$_{0.5}$</td>
<td>286</td>
<td>5T</td>
<td>16</td>
<td>20</td>
<td>320</td>
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</table>

### For <100K applications

<table>
<thead>
<tr>
<th>Material</th>
<th>Tc</th>
<th>H</th>
<th>ΔS max (J/kgK)</th>
<th>FWHM (K)</th>
<th>RC (J/Kg)</th>
<th>phase transition</th>
<th>Cost ($/kg)</th>
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<tbody>
<tr>
<td>DyAl$_2$ [5]</td>
<td>65</td>
<td>5T</td>
<td>4.5</td>
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<td>DyCo$_2$Al [7]</td>
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<tr>
<td>HoAl$_2$ [5]</td>
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<td>5T</td>
<td>6.5</td>
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<td>10.5</td>
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<td>126</td>
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<td>$212</td>
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<tr>
<td>TmAl$_2$ [5]</td>
<td>10</td>
<td>5T</td>
<td>7</td>
<td>15</td>
<td>105</td>
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<td>$53k</td>
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<tr>
<td>TbCo$_2$Al [7]</td>
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<td>5T</td>
<td>10.5</td>
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<td>HoCo$_2$Al [7]</td>
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<td>5T</td>
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<td>TmCo$_2$Al [6]</td>
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<td>18</td>
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<td>GGG</td>
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<tr>
<td>MnSi</td>
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<td>3T</td>
<td>2.3</td>
<td>20</td>
<td>46</td>
<td>2nd</td>
<td>&lt;$3</td>
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<tr>
<td>NdSi [8]</td>
<td>45</td>
<td>5T</td>
<td>12</td>
<td>17</td>
<td>204</td>
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<td>$50</td>
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<td>CeSi [4]</td>
<td>7</td>
<td>5T</td>
<td>13.7</td>
<td>10</td>
<td>137</td>
<td>2nd</td>
<td>$92</td>
</tr>
</tbody>
</table>

Costs are for materials only and do not account for processing to achieve MCE properties.

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Discovered Low Cost High Performance MCE

CeSi
Tc~7K

NdSi
Tc~46K

Ce₀.5Nd₀.5Si
Tc~32K

New Patent:
NdₓCeₙ(1-x)Si
Tc tunable between 7K – 45K
Comparison to known MCE Materials

For <100K applications

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<th>H (T)</th>
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</tbody>
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For <100K applications

Nano-structuring

Forming micro/nanoparticles and mixing prior to anneal reduces required time

<Pellet condition>
Hand-grinding (1 hour) to form micro/nanopowder
-> hot-pressing 700 C 10 min
-> annealed at 1000 C for 4 days
Future Work

- Optimize processing
  - High performance
  - Low cost

- High stability form
  - Spheres or thin plates

- Compatibility with external coolant
  - May need to incorporate ceramic coating on material to prevent reaction with hydrogen.

- Testing in Magnetic Refrigeration Environment
  - CALSeed Funding – Awarded – build prototype
  - National Institute for Materials Science in Japan
  - Prof. Pecharsky from Caloricool
  - Industrial partners - proprietary

- Developing novel MCE materials for higher temperature applications
  - Find low cost high performance compositions for >50K applications – need to be better than current commercially available
  - Some promising techniques discovered during phase I
  - Novel compositions discovered
Acknowledgments

- Funded by the Department of Energy through a Small Business Technology Transfer Research (STTR) grant.

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