UC San Diego
Jacobs School of Engineering

GENERAL ENGINEERING AND RESEARCH

Low-cost Magnetocaloric Materials Discovery

Phase II STTR Project ID PD172

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2018 DOE Annual Merit Review
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Overview

Timeline

Phase I Project Start Date: 06/13/2016
Phase II Project Start Date: 07/31/2017
Phase II Project End Date: 07/30/2019

Barriers

H. High-Cost and Low Energy Efficiency of Hydrogen Liquefaction

Ultimate Target: Energy Required < 6 kWh/kg of LH2 at 300,000kg/day facility.

Budget

Total Project Budget: $1,150,000
- Phase I - $150,000
- Phase II - $1,000,000
- Total DOE Funds Spent*: $450,000

- As of 3/31/18 – late start due to delay in funds

Partners

UCSD – Project Partner

US DOE – Project sponsor and funding

California Energy Commission – additional business development funding

San Diego Region Energy Innovation Network- Incubator for CleanTech companies

Interactions/collaborations
- Hydrogen Delivery Tech Team
- Other Industrial Partners

Relevance

Objective:
Develop low cost energy efficient magnetic refrigeration technology for hydrogen liquefaction.

Barrier

H. High-Cost and Low Energy Efficiency of Hydrogen Liquefaction

- Energy required for hydrogen liquefaction at point of production too high.
- Hydrogen boil-off from cryogenic liquid storage tanks needs to be minimized.

PNNL Task (PD131)

Developing magnetocaloric hydrogen liquefaction prototype to establish viability of concept.

GE&R Task

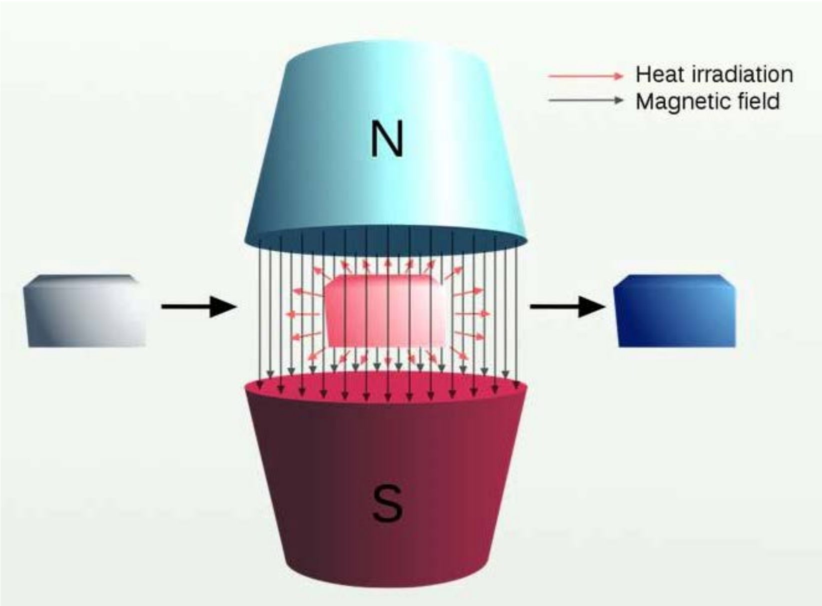
Discover, develop, and commercialize low cost high performance MCE alloys to enable magnetic refrigeration to move from prototype to production.

DOE Current Targets	FY 2015 Status	FY 2020 Target	Ultimate Target
Small Scale Liquefaction (30,000 kg H2/day)			
Installed Capital Cost ($)	70 million	70 million	-
Energy Required (kWh/kg of H2)	15	12	-
Large Scale Liquefaction (300,000 kg H2/day)			
Installed Capital Cost ($)	560 million	560 million	142 million
Energy Required (kWh/kg of H2)	12	11	6

Relevance

Magnetic refrigeration is a promising breakthrough technology to replace conventional compression based systems.

Magnetocaloric Effect (MCE)
The variation in temperature of a magnetic material when exposed to a change in magnetic field.



PROS

- Solid state material – NO HFCs
- Lasts forever
- High Efficiency (H_2 liquefaction >50% energy reduction)*

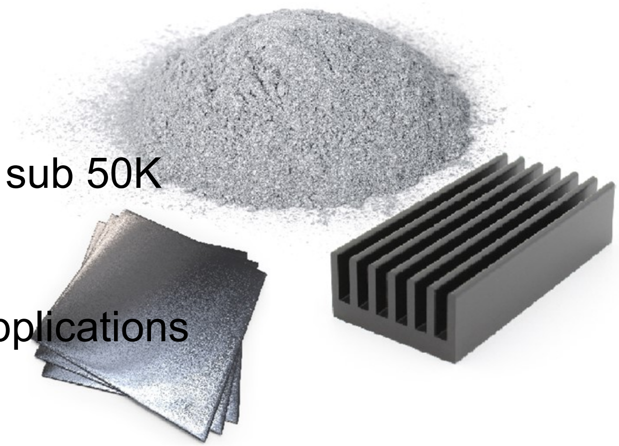
CHALLENGES

- Rare-Earth - $ to $$$$
- Not easy to make - Processing $$$$
- Limited commercially available materials
- Limited work demonstrating these systems
- MCE material only works at its curie temp, Tc

*Magnetocaloric Hydrogen Liquefaction, Jaime Holladay, Pacific Northwestern National Laboratory, June 2016. Accessed here: https://www.hydrogen.energy.gov/pdfs/review16/pd131_holladay_2016_o.pdf

Approach

Objective: Discover, develop, and commercialize low cost high performance MCE alloys to enable magnetic refrigeration to move from prototype to production.



Phase I Milestones - Completed

1.1 Discover low cost high performance MCE materials for sub 50K

Phase II Milestones – In progress

2.1 Discover novel MCE materials for >50K temperature applications

2.2 Testing in Magnetic Refrigeration Environment
- a) Characterize ΔT.
- b) Evaluate heat capacity/thermal transport – *Build prototype*

New!
Small scale, room temp. Will need additional funding to achieve low temp.

2.3 Optimize material synthesis processing to achieve:
- a) High performance – need ΔT equivalent or better than Gd
- b) Low cost – Target selling price of $5,000/kg
- c) High stability form - spheres or thin plates

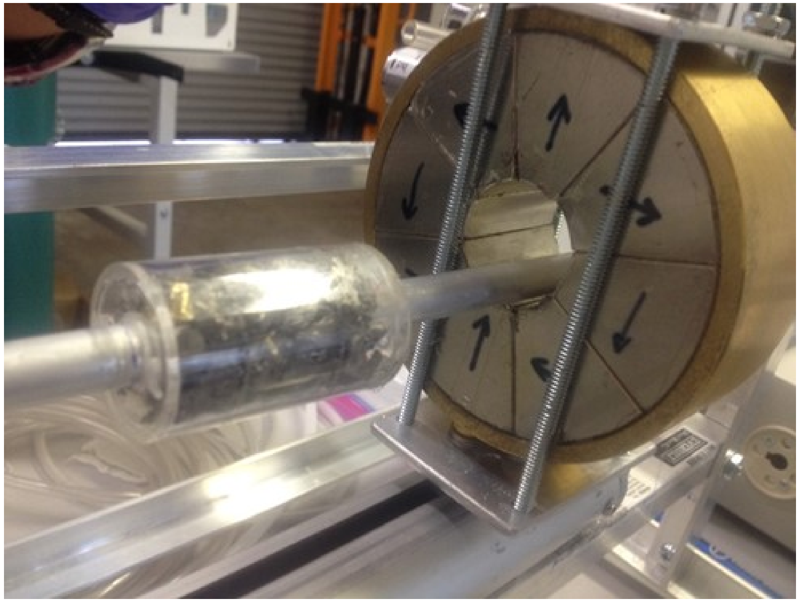
2.4 Commercially Available MCE Products on www.geandr.com webstore.

Approach

MCE material cost vs. Magnetic Field Cost

Lots of work on MCE Materials in last few decades

- No known commercial magnetic refrigerators yet for >4K applications.



Traditional Approach to MCE Materials Research

- Maximize ΔS
  - GdSiGe
  - LaFeSi
- Avoid rare–earth materials due to cost/availability
  - MnFeAs
  - NiMnSn

ΔS not a good measure of performance for 1st order materials.

Performance is too low

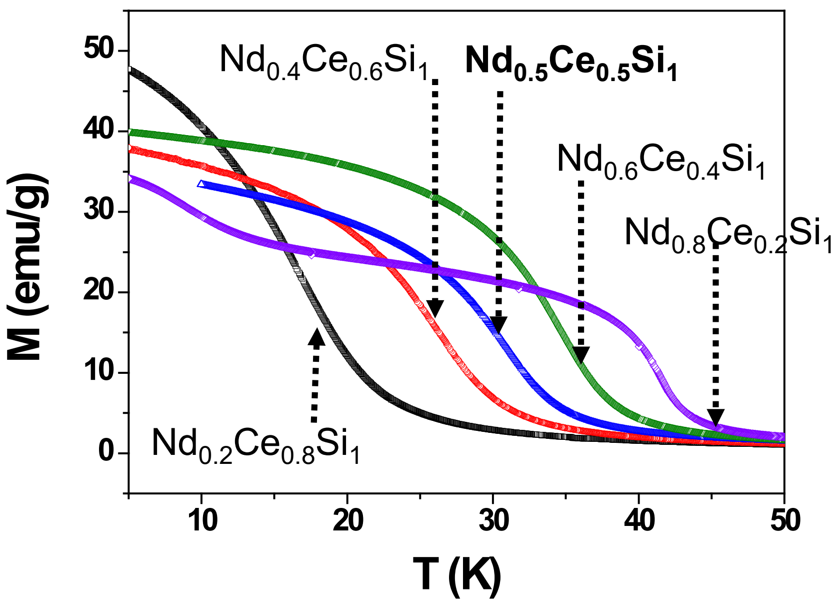
GE&R Approach to MCE Materials – stems from experience building magnetic refrigeration devices

- Materials with 2nd order only response
  - Maximize ΔT – high cooling power
  - Mechanically stable
- Use low cost rare-earth (Ce, Nd, Gd)
  - Need high performance to keep cost of Magnetic field reasonable

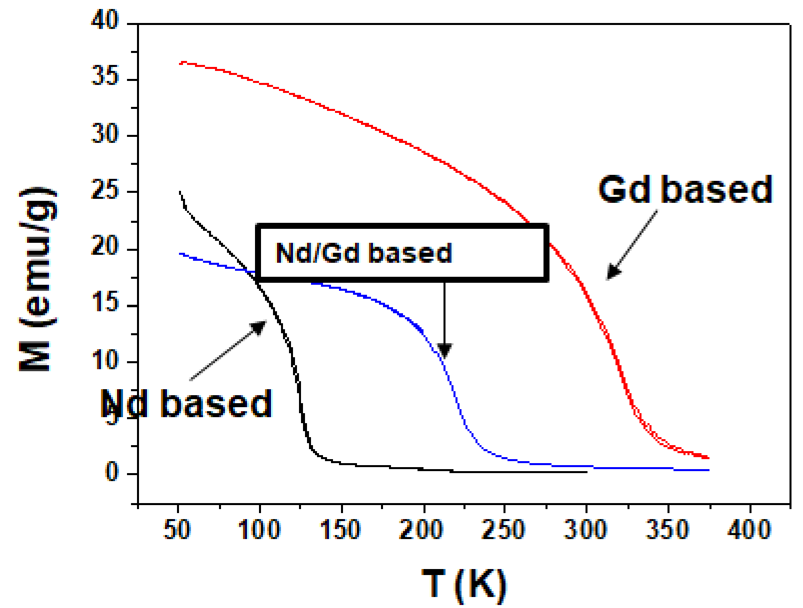
Accomplishments and Progress

MCE Materials 9K to 300K

For 9~50K,
-> **Nd/Ce based ternary**



For 50~325K,
-> Nd/Gd ternary or quaternary

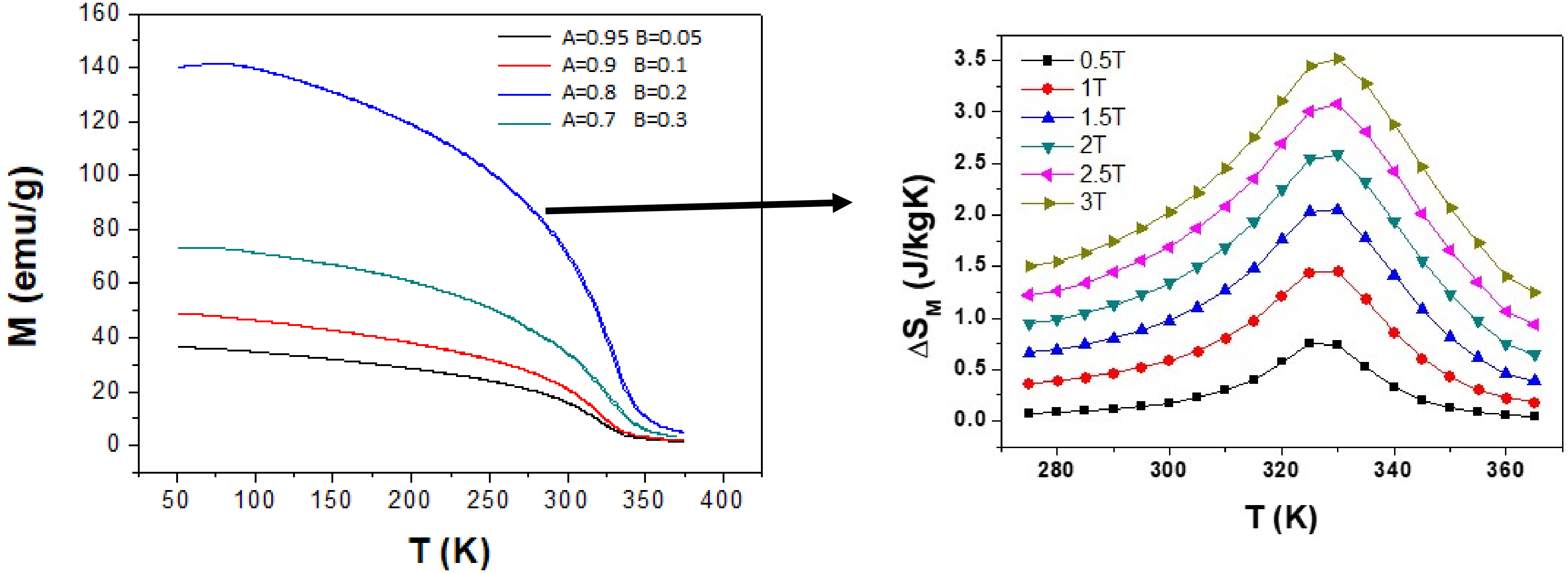


NEW PATENTS FILED
Low cost 2nd order MCE compositions discovered for entire temperature range 9K – 325K

Accomplishments and Progress

MCE Materials High Performance

Ternary Gd-A-B compound (as-cast)



Significant Improvement in Performance with composition optimization.

For further performance improvements - Long high temp anneals typically required

Challenge: low melting temperature

- Anneal may not work to improve performance
- New melt furnace installed onsite

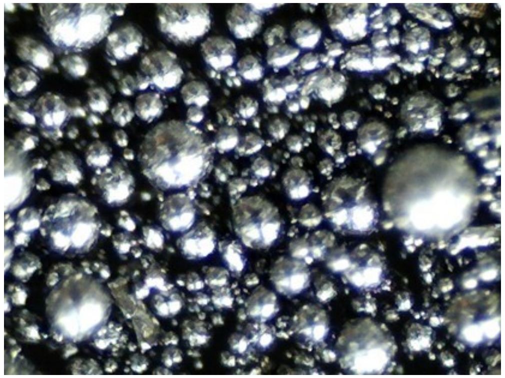
GOAL: Synthesize alloys on-site and optimize melt step to avoid additional anneal.

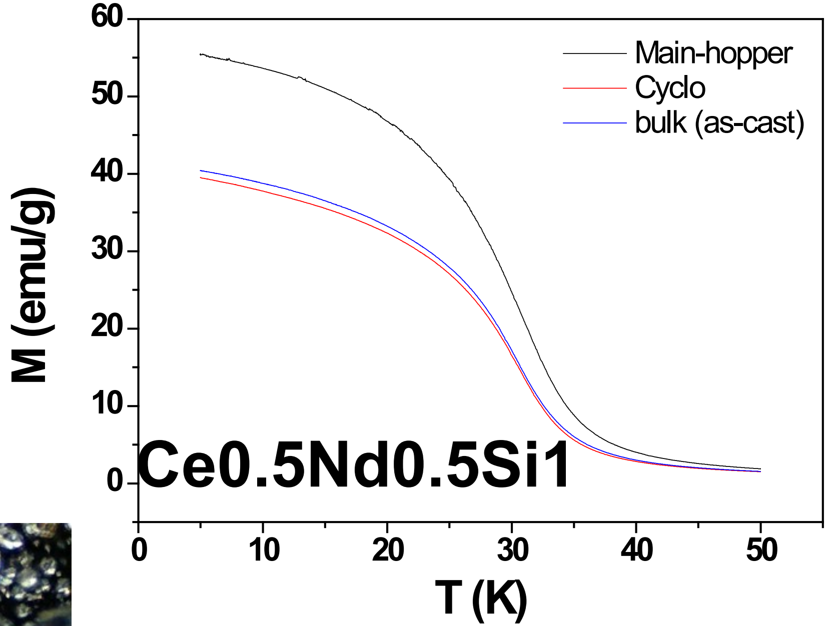
Accomplishments and Progress

High Stability Form – Spheres and Thin Plates

Rotating Disk Atomization

- Performed by Arcast Inc
  - Sub mm size spheres
  - Performance maintained (or better)
  - Reasonable cost – several kg for $1k
  - Our material works well
  - Process optimization needed
- Thin Plates – need to develop

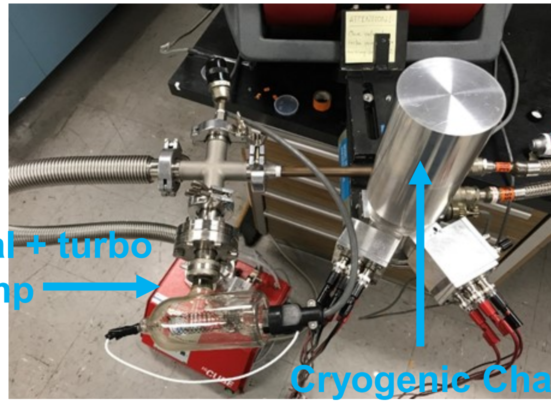


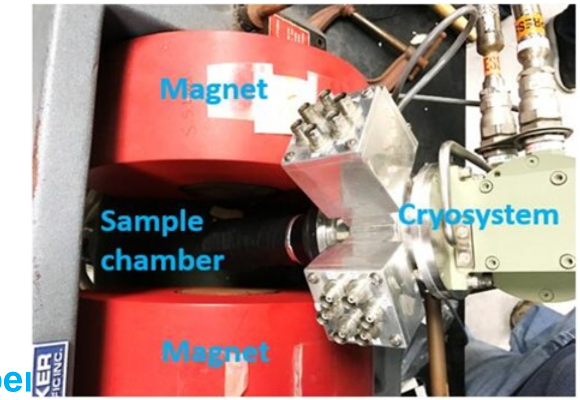


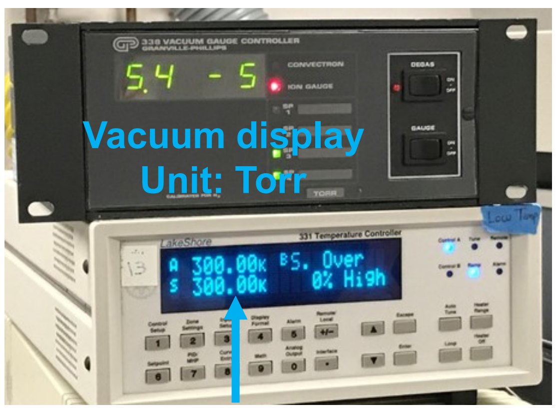
Materials Successfully formed into sub mm size spheres

Accomplishments and Progress

Cryogenic/Magnetic System







- The magnetic field can reach up to ~0.37 T.
- The cryogenic chamber can reach down to 20 K.
- The chamber can be moved in and out of magnetic field by mechanical rotation.

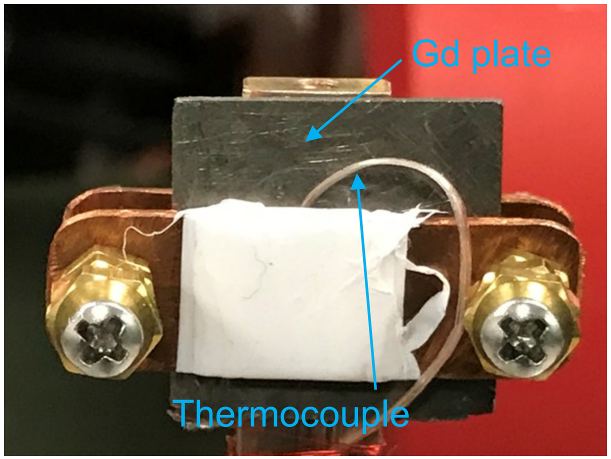
Custom built system to characterize ΔT of MCE materials.

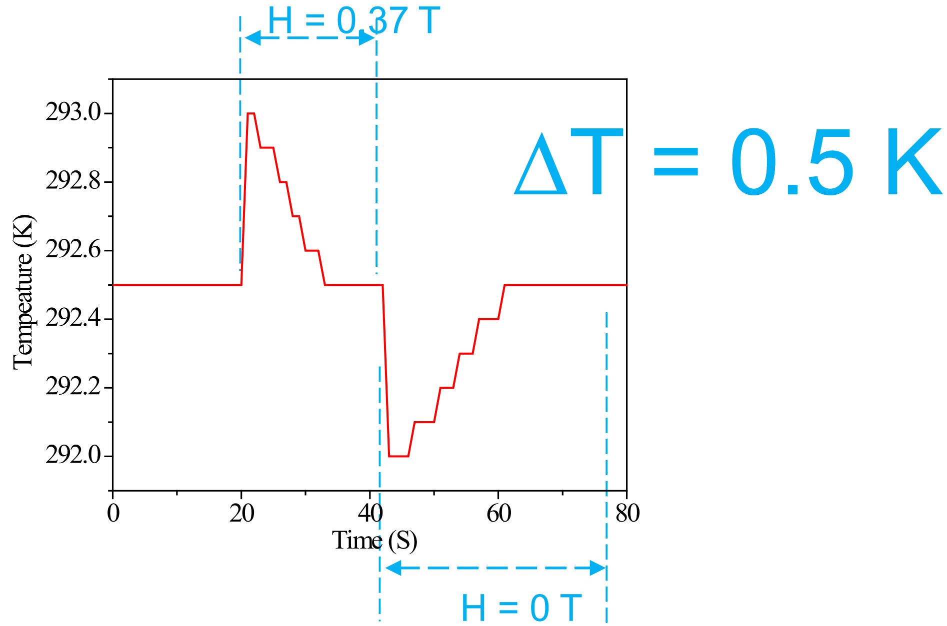
- Measure ΔT - This is a better indicator of performance
  – not easy to measure

Accomplishments and Progress

Characterizing MCE materials in Refrigeration Environment

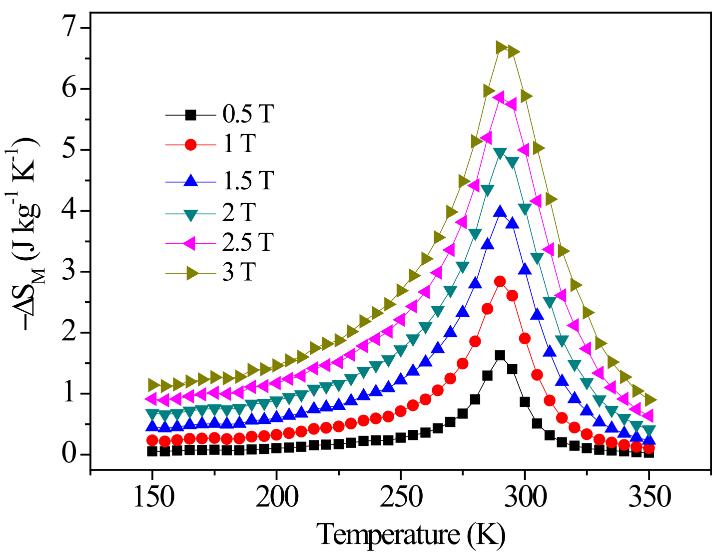
ΔT of Gd





Calculated ΔT (based on DS curve) ~1.9K @ 0.37T

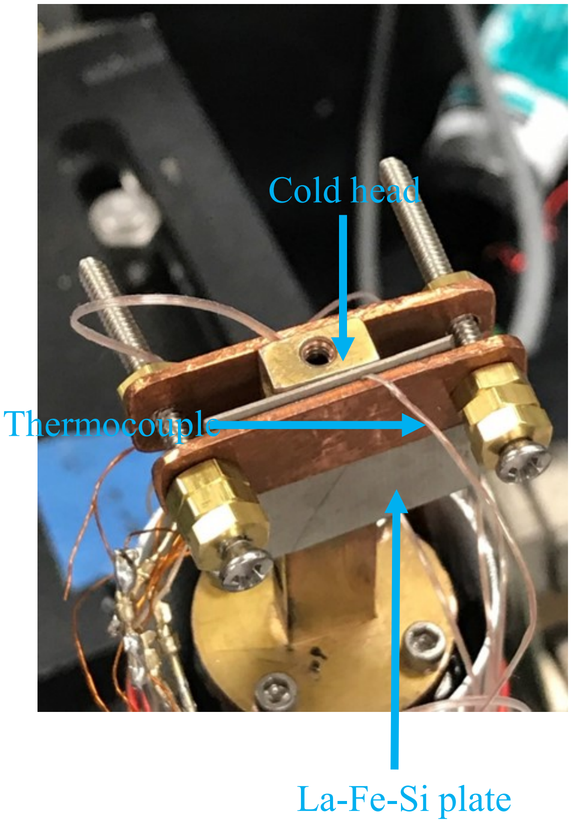
Measured ΔT ~0.5K



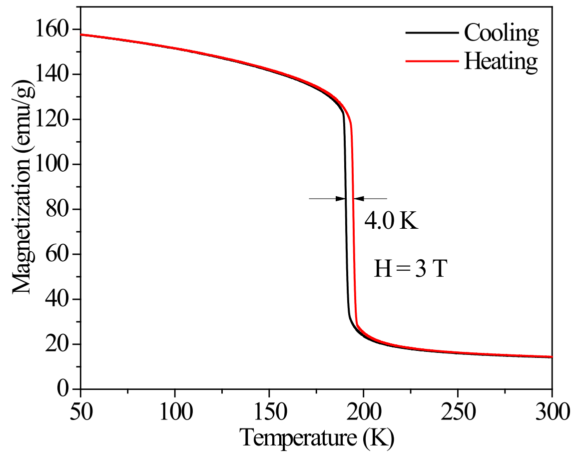
Measured ΔT of Gd

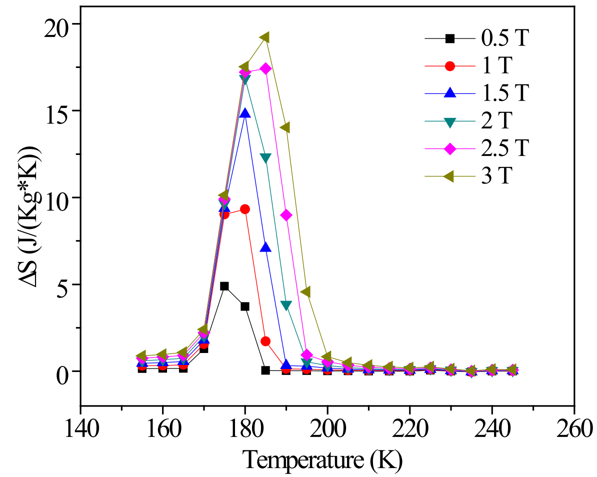
Accomplishments and Progress

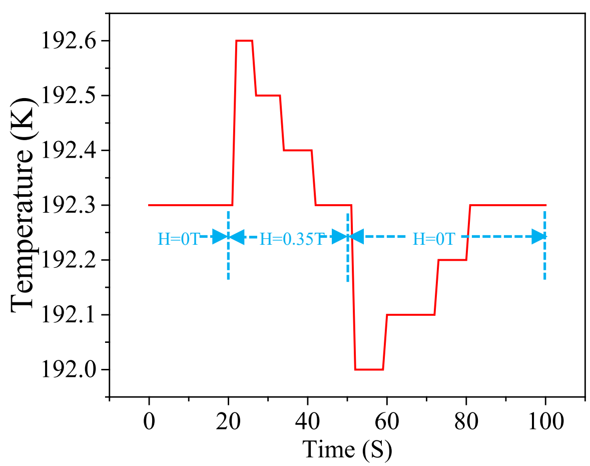
Characterizing MCE materials in Refrigeration Environment



La-Fe-Si Plate





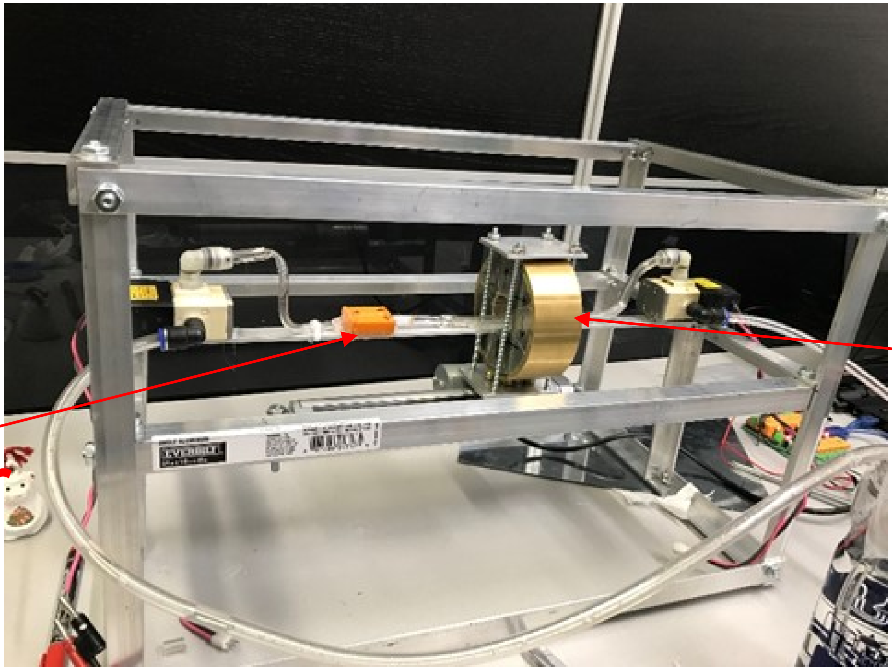


- Cryogenic chamber temperature: T = 190 K (temp of max ΔT)
- Magnetic field: H = 0. 37 T
- La-Fe-Si plate temperature change: ΔT = 0.3 K

ΔT of LaFeSi is lower than Gd, even though ΔS is nearly triple

Accomplishments and Progress

Small Room Temperature Magnetocaloric Cooler Prototype



In progress. Testing material performance, compatibility, etc.

Reviewer Responses

This project was not reviewed last year.

A Collaborative Project

Partner	Project Role
US DOE	Project sponsor and funding
University of California, San Diego (UCSD)	Project partner. Subcontractor. Assisting with materials development and optimization.
California Energy Commission (CEC)	Additional funding provided for business development through CALSeed Program. Participation in CleanTech Open business accelerator program.
San Diego Regional Energy Innovation Network (SDREIN)	Networking incubator for CleanTech companies in San Diego. GE&R officially accepted into program. They provide network / mentor resources.
Hydrogen Delivery Tech Team	Annual reporting provided to HDTT
Other Industry Partnerships	In Progress - Proprietary

Remaining Challenges and Barriers

Magnetic Refrigeration

For MCE Materials Commercialization:

- MCE Materials - need continued process development and optimization to hit performance targets ($\Delta T \sim 1^oC$ in 1T field) to be viable in magnetic refrigeration systems.
- Commercialization – MCE materials market is small. Very few entities are actually working on systems.
    - Need more resources to work on system development – we added small prototype development to our Phase II milestones. Additional resources will be needed to develop commercial systems.

For Hydrogen Liquefaction:

- Both large scale magnetic refrigeration production plants and small scale magnetic refrigeration systems to prevent boil-off at point of use are needed.

- Only two known entities working on systems (Pacific Northwestern National Lab and Japanese National Institute of Material Science). Need industrial effort to move magnetic refrigeration technology forward.

Proposed Future Work

Remainder FY2018 and FY2019

Phase II Milestones	Description	Percent Complete
1	Discover MCE for >50K applications - Low cost compositions with 2nd order response to cover 9-300K range have been discovered. We will investigate material doping to improve performance. Additional material set (such as known and public domain alloys of Gd, Dy, Er) may be investigated if needed.	80%
2	Evaluate performance in magnetic refrigeration environment - We have a custom built platform to evaluate ΔT of materials. - We are working on a small scale room temperature prototype. Additional funding/ resources will be needed to develop: - LH2 production facility using Magnetic Refrigeration - Zero boil-off magnetic refrigeration system for 1000kg LH2 gas station storage	50%
3	Optimize processing to achieve high performance, low cost, and stability. - New furnace installed for on-site alloy synthesis. We will develop melting/cooling conditions to achieve high performance and methods to form material into thin plates. Phase II Goal: 1kg available for $5000	50%
4	Commercially Available MCE Products on www.geandr.com webstore. - Webstore is built. Just need to add products.	50%

Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

Additional Funding Received

- CALSeed Grant from the California Energy Commission is supporting business development activities for our Magnetic Refrigeration technologies.

Potential Future Funding

- Applied for ARPA-E funding to develop Zero boil-off LH2 storage system.
- Applied for NASA SBIR Phase I to develop Zero boil-off LH2 storage system.
- We will compete in the CALSeed Phase II pitch competition in Sept 2018 to raise additional funds for prototype development.
- Industrial Funding Sources – In progress.

Patents

- PCT application (US2018/012836) filed for our ternary based compounds.
- New provisional application (US 62/634078) filed on our quaternary compounds.
- New provisional application (US 62/551148) filed to cover zero boil-off LH2 storage system.

Summary Slide

- Novel 2nd order response MCE material set for entire temperature range 9 - 325K discovered with promising potential for high refrigeration performance.
- System to characterize ΔT developed.
- In-house manufacturing capabilities in progress.
- Additional CEC funding obtained for magnetic refrigeration development.

Technical Back-Up Slides