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

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UC San Diego
Jacobs School of Engineering

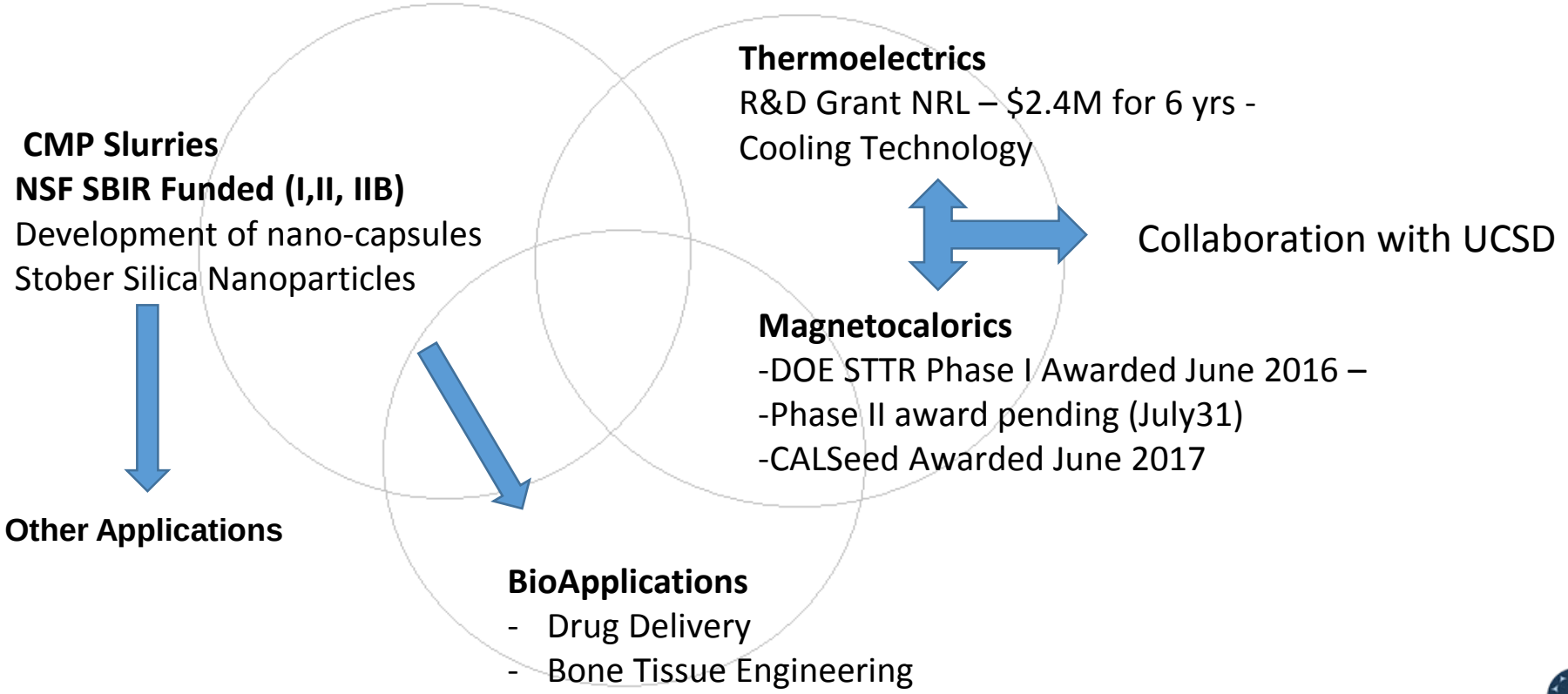
GENERAL ENGINEERING AND RESEARCH

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.



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

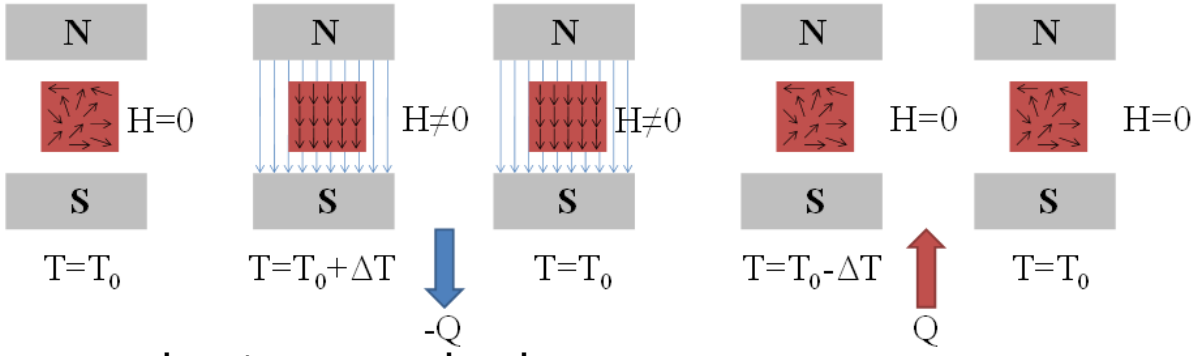
Grad. Student – Lizzie Caldwell

Motivation

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

magnetic entropy, specific heat capacity decreases

magnetic entropy, specific heat capacity increases



heat removed using an external coolant

Energy absorbed from the environment.

- 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

Element	Cost (USD/kg)	Cost (USD/kg) [c]
Ce	7 [a]	110
Dy	350 [a]	
Er	650 [b]	280
Eu	200000 [b]	
Gd	120 [b]	235
Ho	8600 [b]	
La	7 [a]	110
Nd	60 [a]	
Tb	50000 [b]	
Tm	70000 [b]	

Non Rare Earth

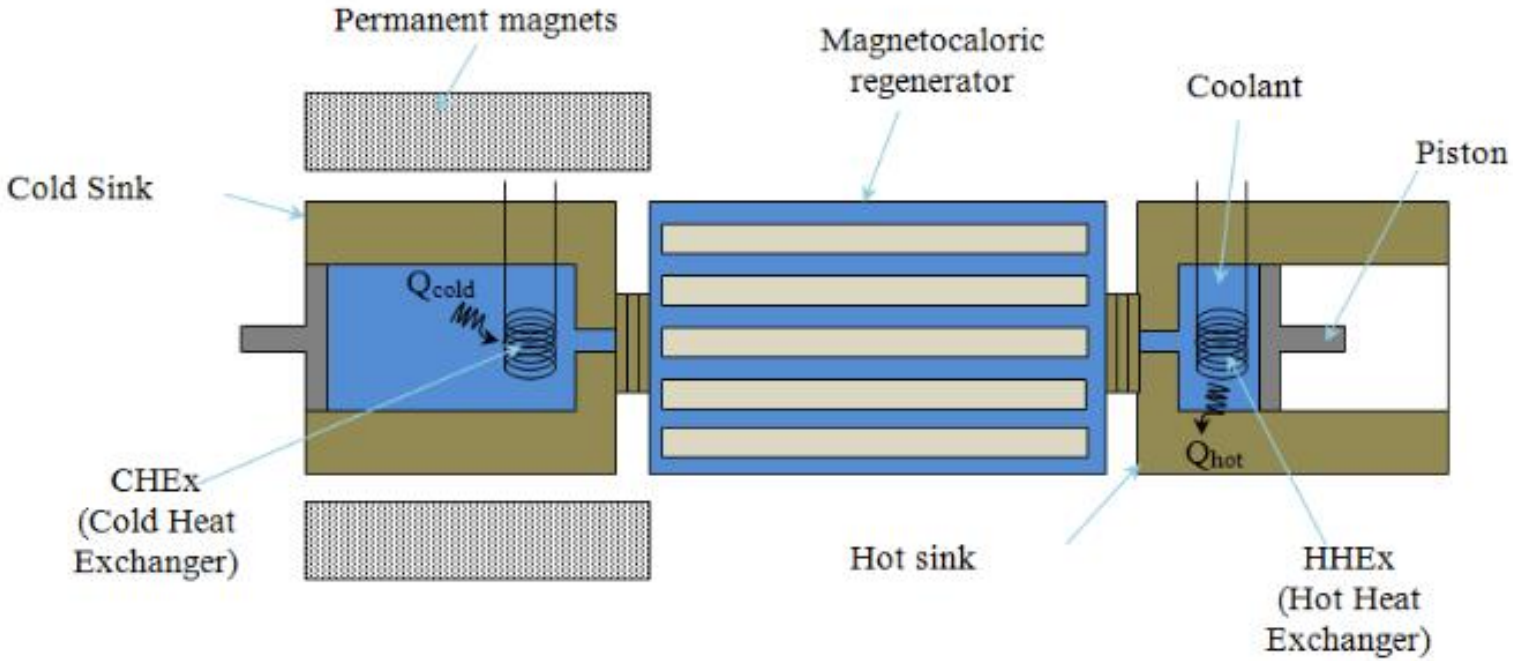
Element	Cost (USD/kg)	Cost (USD/kg) [c]
As	3200 [b]	
Co	44 [b]	
Cu	6 [b]	
Ga	2200 [b]	
Ge	1200 [b]	1720
Mn	2.80 [b]	
Ni	2.35 [a]	
P	300 [b]	
Si	1.40 [b]	
Sn	18 [b]	

a) http://mineralprices.com/default.aspx#Aluminium accessed 11/23/2016
b) http://www.chemicool.com/elements/thulium.html
c) Quote from Hefa Rare Earth for 1kg quantity
d) https://en.wikipedia.org/wiki/Thermal_conductivities_of_the_elements_%28data_page%29

Magnetocaloric Effect (MCE)

- MCE material only works near Tc – 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 (ΔS)
  - MCE materials typically expensive rare-earth

Schematic of magnetic refrigerator (MR)



Balance MCE material cost with Magnetic Field Cost

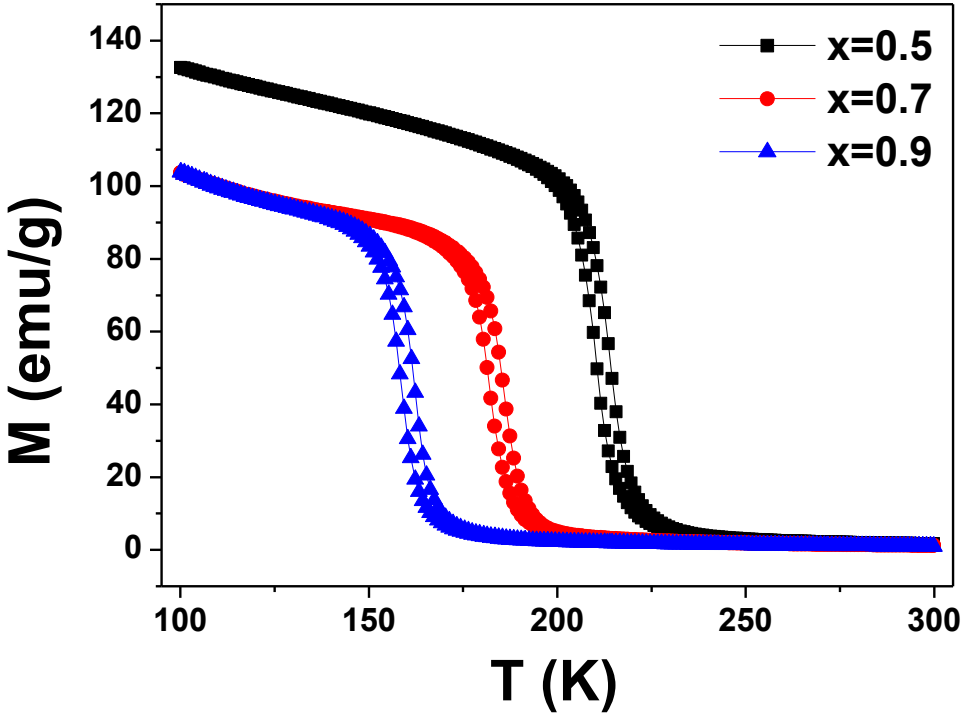
Need high PERFORMANCE MCE materials to keep cost for magnetic field reasonable!!!

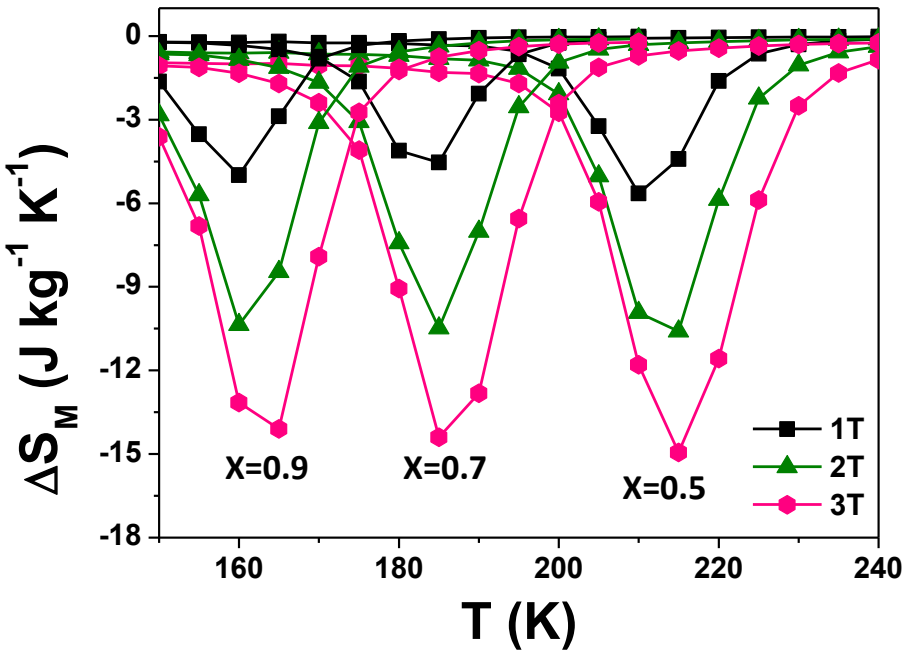
*R. Bjork, A. Smith, C.R.H Bahl, and N. Pryds, International Journal of Refrigeration, 34 (8), 1805 (2011).

MCE Compositions

$Gd_5Ge_2Si_{2-x}Sn_x$

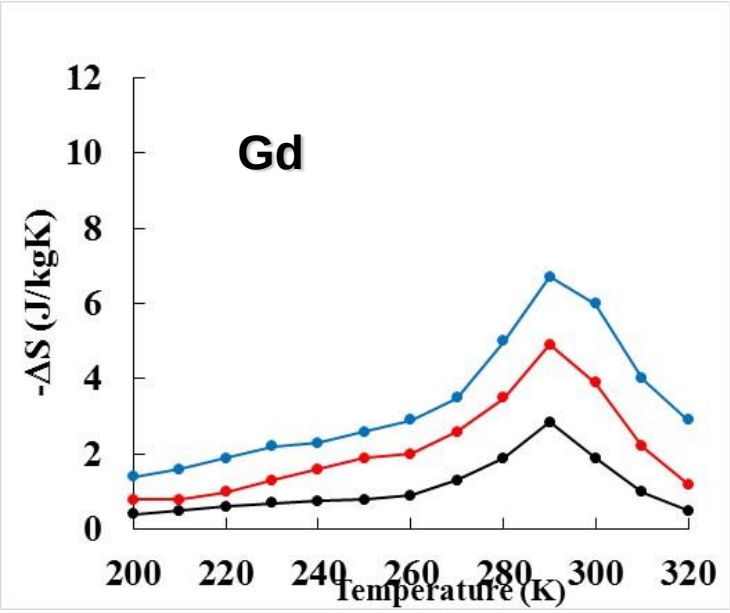
x	Tc (K)	$\lvert\Delta S_{max}\rvert$ (J kg^{-1} K^{-1})	Thermal hysteresis (K)
0.5	210	14.9 (3T)	4
0.7	185	14.5 (3T)	3
0.9	160	14.2 (3T)	2

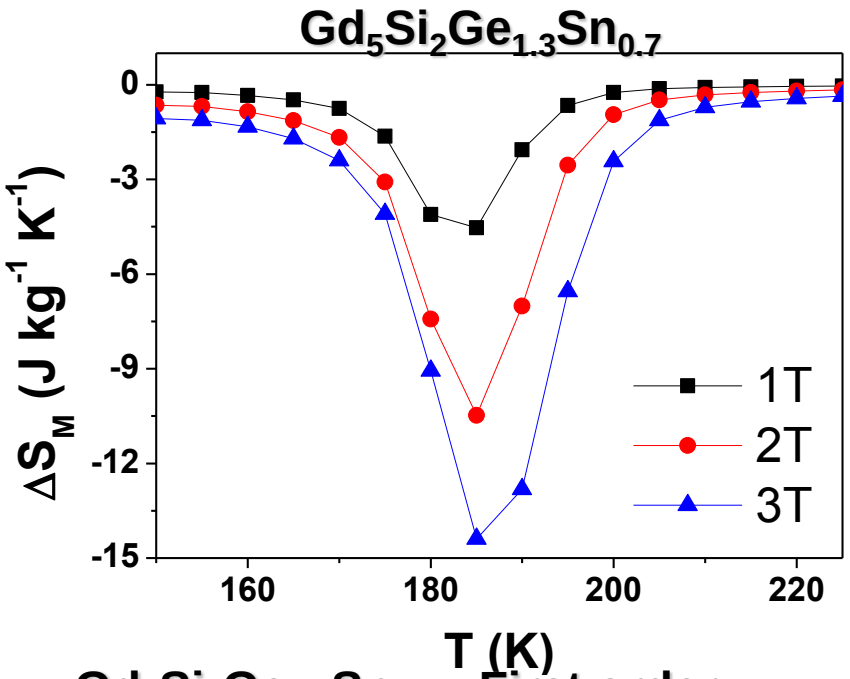




- RC = DS x FWHM

First order vs. Second order transition

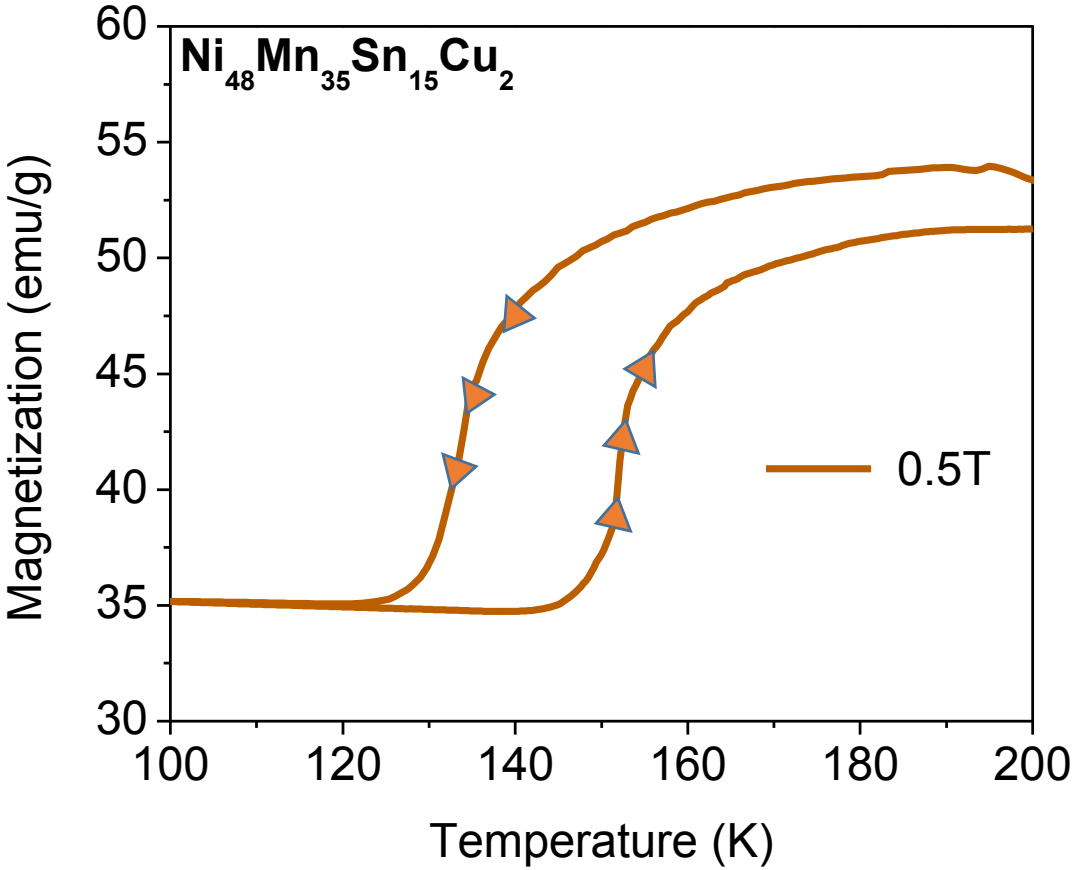


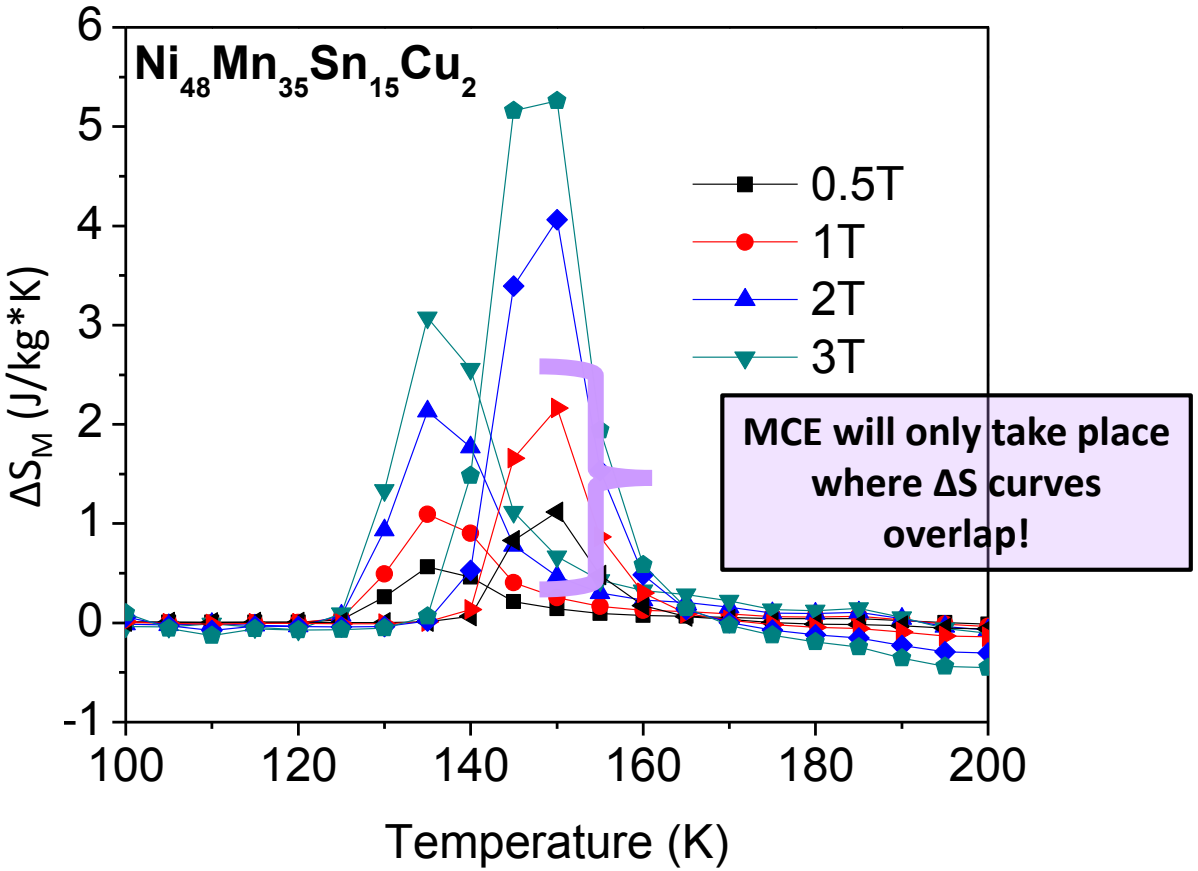


- **Gd - Second order**
  - **Reversible**
  - **Typically require significant rare-earth**
- **$Gd_5Si_2Ge_{1.3}Sn_{0.7}$ - First order**
  - **Giant MCE**
  - **Not entirely reversible – bad for high frequency MR**
  - **Thermal expansion** $\Delta L/L=(L(T)-L(T=4K))/L(T=4K)$

    Thermal hysteresis ex) $\Delta T = 4K$
  - Relative volume change ex) $\Delta V/V = 2.7\times10^{-3}$
  - Clausius-Clapeyron relation $dT_C/dp = 3.2$ K/kbar

Hysteresis Loss in First Order Transitions





Sample	Tc	Max ΔS at 3T	Hysteresis @ Tc	FWHM	RCP
$Ni_{48}Mn_{35}Sn_{15}Cu_2$	135 K	3.07 J/kg*K	15 K	15	46.05 J/kg

Known MCE Materials

For 100-300K applications

Material	Tc	H	ΔS max (J/kgK)	FWHM (K)	RC (J/Kg)	phase transition
Gd	293	5T 10T	9.5 19	80 120	760 2280	2nd
$Gd_{0.73}Dy_{0.27}$	275	10T	18.5	110	2035	2nd
$Gd_5Si_2Ge_2$	270	5T	19	25	475	1st
$Gd_5Si_2Ge_{1.9}Fe_{0.1}$ Hysteresis reduced	305	5T	7	65	455	1st
$LaFe_{11.5}Si_{1.5}$	194	5T	24.6	25	615	1st
$LaFe_{10.88}Co_{0.95}Al_{1.17}$ Hysteresis reduced	300	5T	9	55	495	1st
$Ni_{50}Mn_{37}Sn_{13}$	310	3T	6.7	9.5	64	1st
$MnFeAs_{0.5}P_{0.5}$	286	5T	16	20	320	1st

For <100K applications

Material	Tc	H	DS max (J/kgK)	FWHM	RC (J/Kg)	phase trans.	Cost ($/kg) *
DyAl2 [5]	65	5T	4.5	35	158	1st	$226
DyCoAl [7]	37	5T	16.3	38	619	1st	$207
HoAl2 [5]	32	5T	6.5	17	111	1st	$6.5k
ErAl2 [5]	18	5T	10.5	12	126	1st	$212
TmAl2 [5]	10	5T	7	15	105	1st	$53k
TbCoAl [7]	70	5T	10.5	40	420	2nd	$33k
HoCoAl [7]	10	5T	21.5	30	645	2nd	$5.6k
TmCoAl [6]	7.5	5T	18	9	162	2nd	$46k
GGG	2	4T	36	6	216	2nd	$5k
MnSi	32	3T	2.3	20	46	2nd	<$3
NdSi [8]	45	5T	12	17	204	2nd	$50
CeSi [4]	7	5T	13.7	10	137	2nd	$92

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

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[3] R. Szymczak, N. Nedelko, S. Lewinska, E. Zubov, A. Sivachenko, I. Gribanov, I. Radelytskyi, K. Dyakonov, A. Slawska-Waniewska, V. Valkov, V. Varyukhin, V. Dyakonov, and H. Szymczak, Solid State Sciences, 36, 29, 2014.
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[5] P.J. von Ranke, N.A. de Oliveira, M.T. Tovar Costa, E.P. Nobrega, A. Caldas, I.G. de Oliveira, Journal of Magnetism and Magnetic Materials, 226, 970, (2001).
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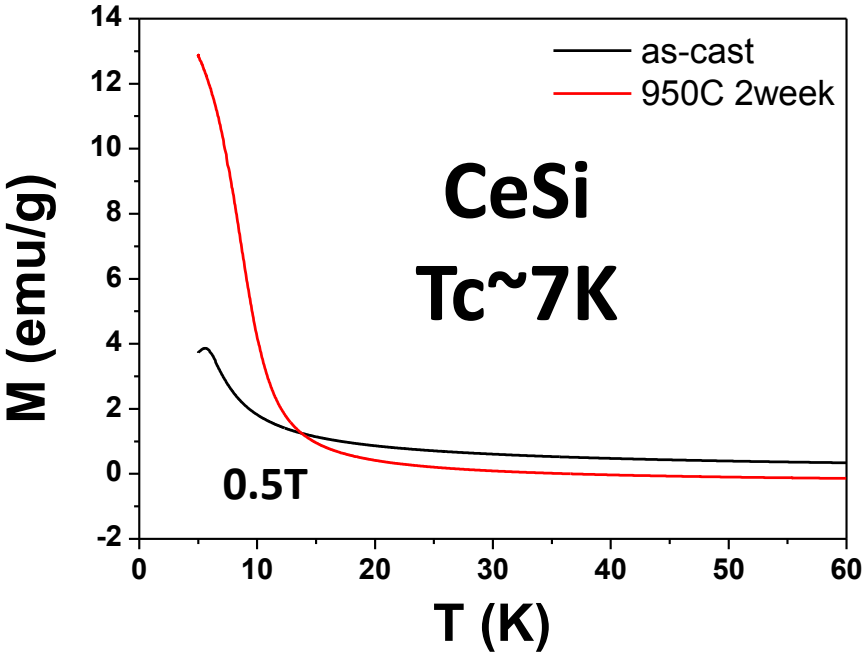
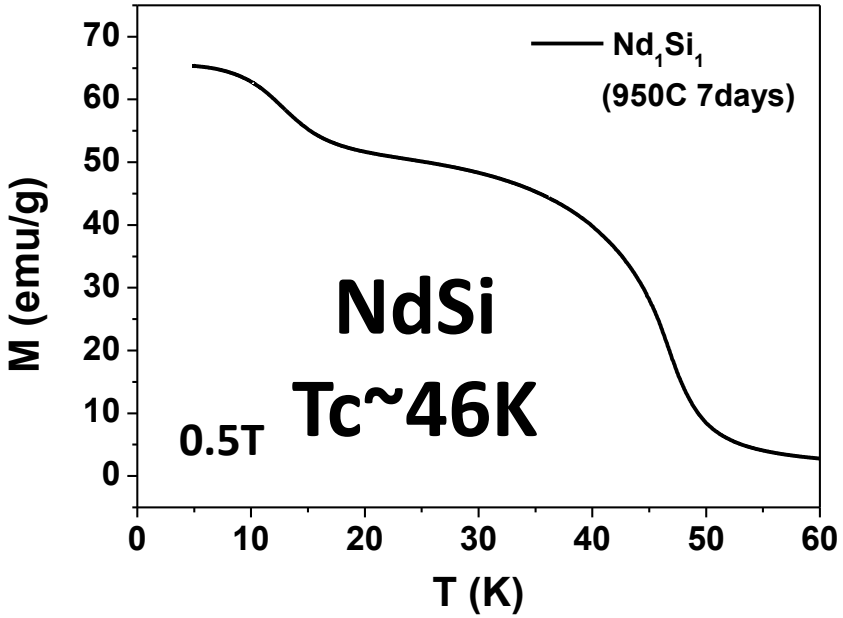
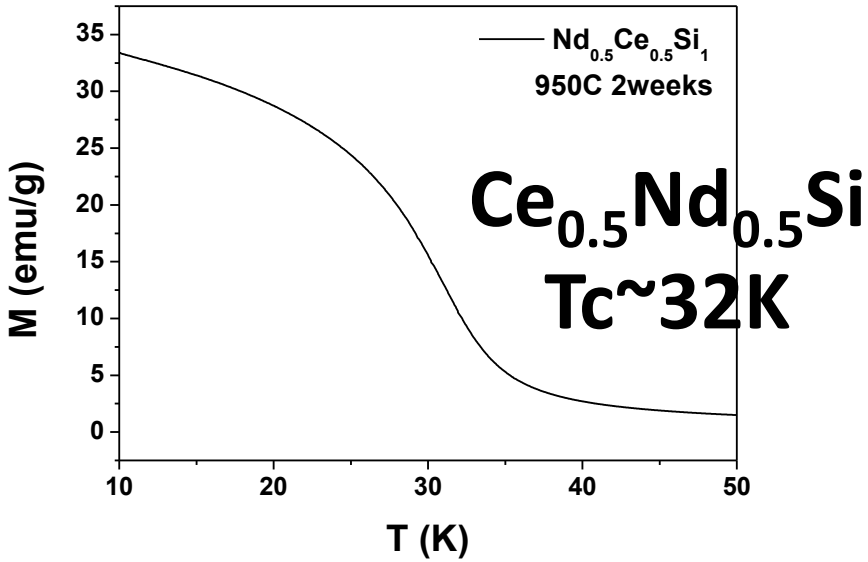
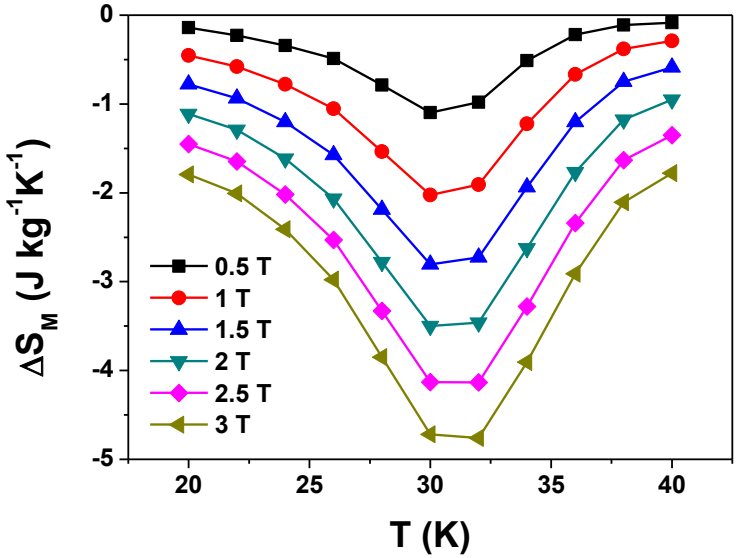
[8] Q.M. Zhang, R.L. Gao, L. Cui, L.C. Wang, C.L. Fu, Z.Y. Xu, Z.J. Mo, W. Cai, G. Chen, and X.L. Deng, Physica B, 456, 258 (2015).

Discovered Low Cost High Performance MCE



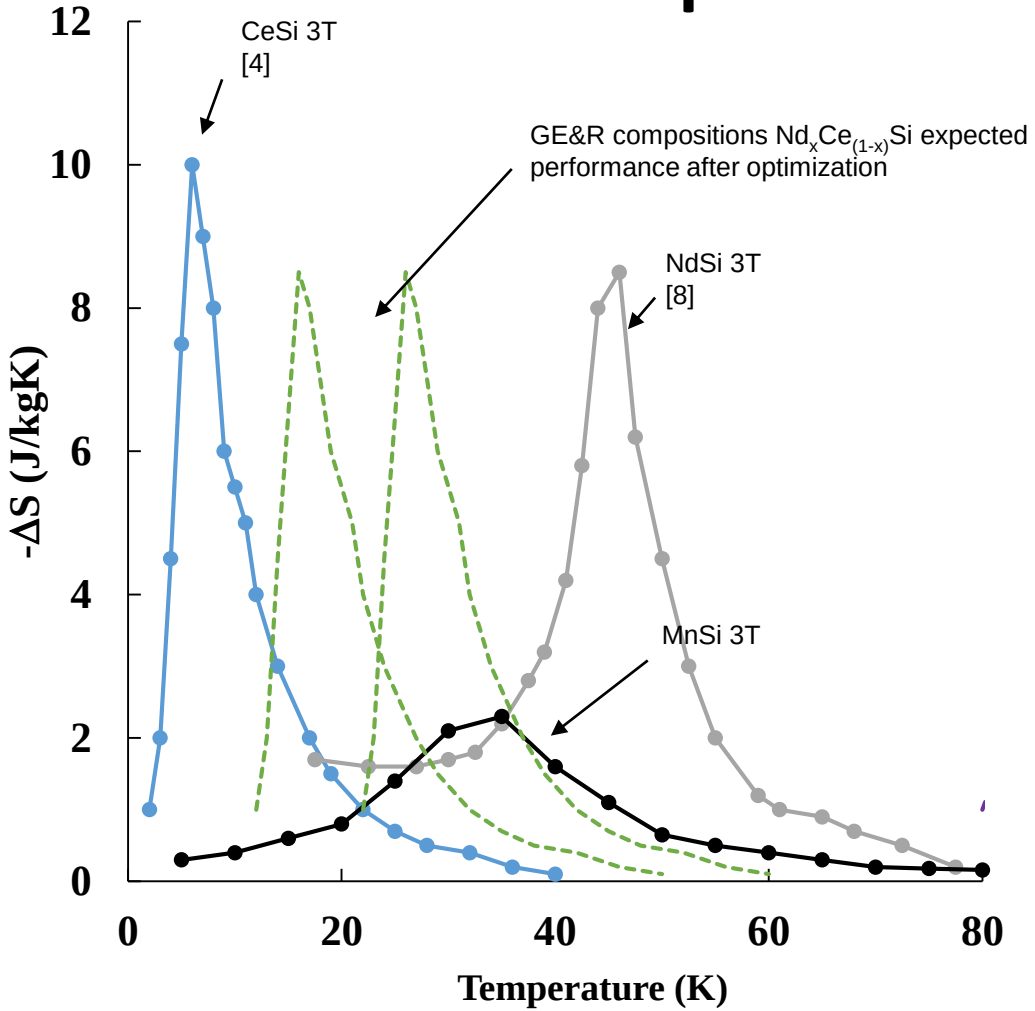






New Patent:
$Nd_xCe_{(1-x)}Si$
Tc tunable between
7K – 45K

Comparison to known MCE Materials



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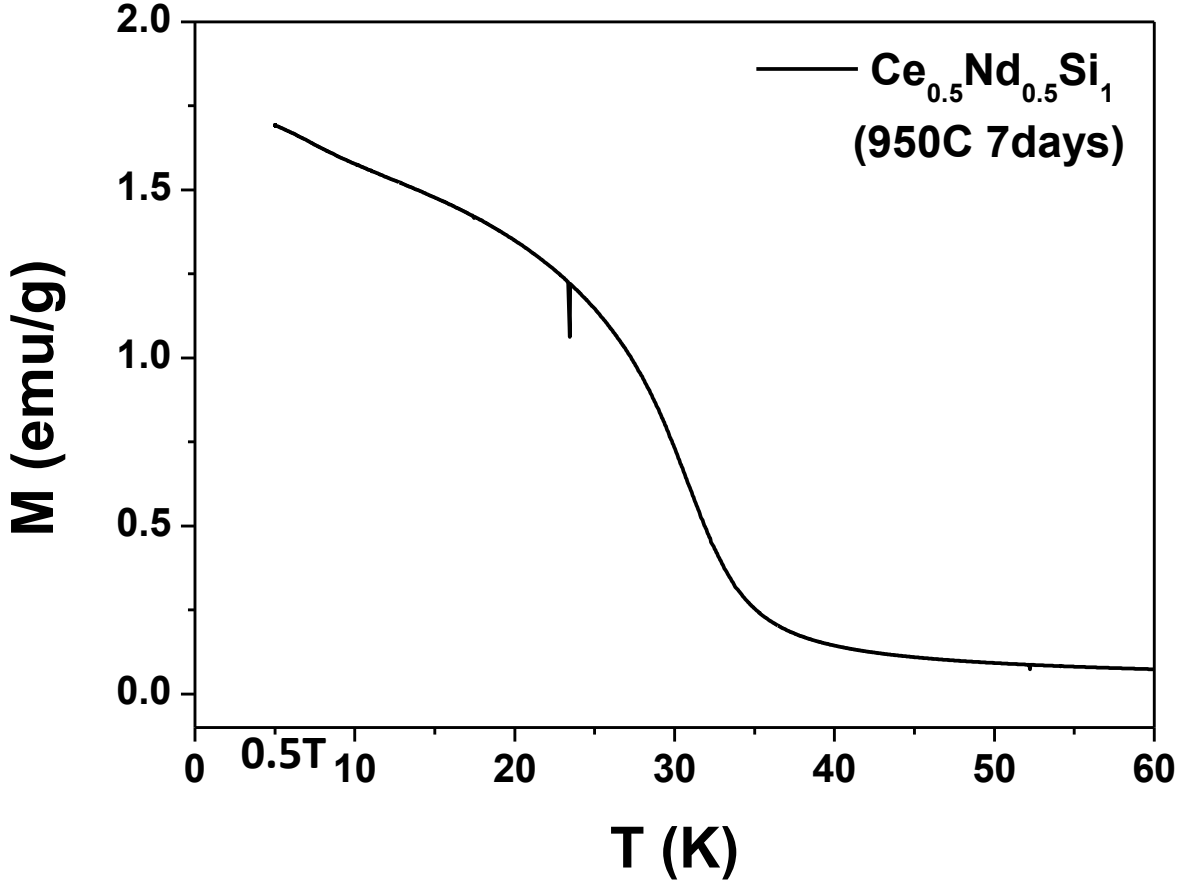
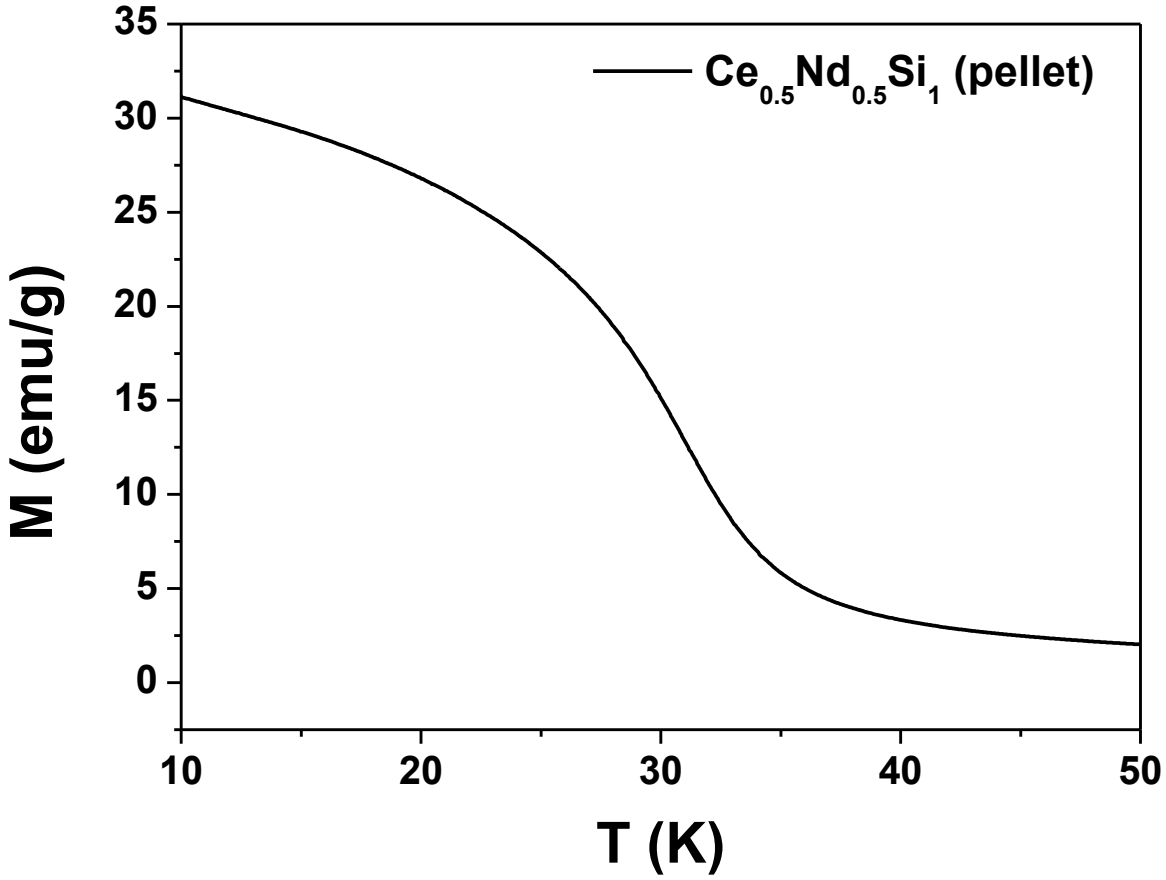
Nano-structuring





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

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

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

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