

Danish Days on Caloric Materials and Devices Book of Abstracts

DTU Risø Campus, Roskilde, Denmark 2-3 October 2017



Department of Energy Conversion and Storage

Danish Days on Caloric Materials and Devices

Book of Abstracts

Acknowledgements

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Welcome to the Danish Days on Caloric Materials and Devices 2017

Dear Colleague,

We are pleased to welcome you to the Danish Days on Caloric Materials and Devices 2017. This meeting is a continuation of the series of 'Delft Days on Magnetocalorics' hosted by Professor Ekkes Brück in Delft, The Netherlands, since 2009. We are grateful to Ekkes for inviting us to continue this tradition here in Denmark.

Over the last few years, the scientific community working on caloric materials and devices has expanded significantly and no longer only encompass magnetocalorics, but also elastocalorics, barocalorics and electrocalorics. There are many similarities between the different caloric effects, both in regards to the understanding of materials properties and to the design and construction of devices. By broadening the scope of this meeting to include all the caloric effects we hope to encourage knowledge sharing across the whole community, between researchers in different areas of caloric materials research, and between materials scientists and machine designers.

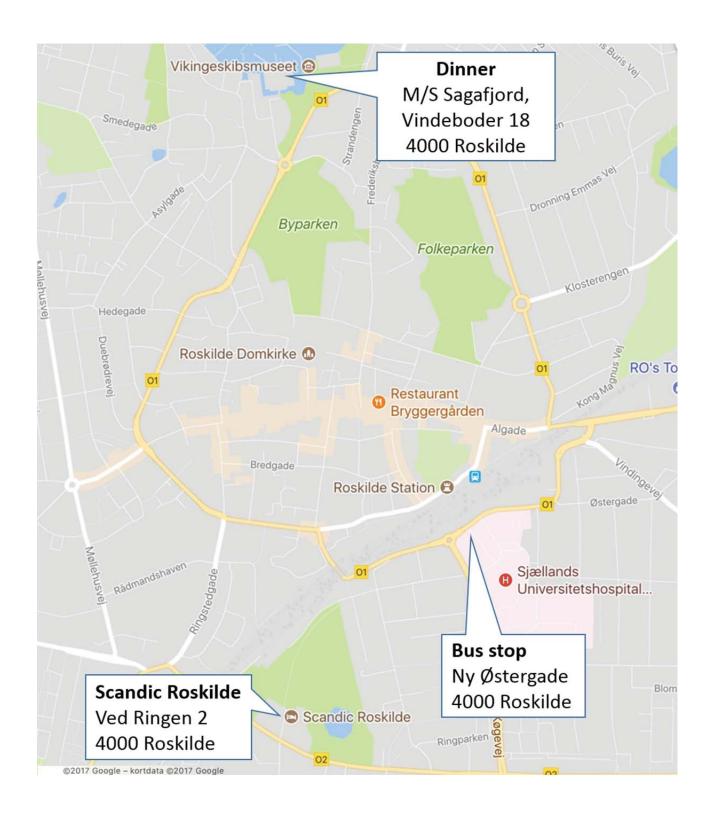
We are delighted with the positive response this has met in the community, and we look forward to two days of insightful talks and discussions with participants from all over the world.

The venue for the meeting this year is the Risø Campus of the Technical University of Denmark (DTU). Risø was inaugurated in 1958 as the Danish national laboratory for the peaceful exploitation of nuclear power, with Niels Bohr playing a key role as the chairman of the Danish Atomic Energy Commission. In the 1970s the focus shifted to sustainable energy, in particular wind power, although Risø National Laboratory continued to operate one of Europe's leading neutron sources for materials research until 2001. In 2007, Risø National Laboratory merged with DTU, and today Risø is one of DTU's three main campuses. The Department of Energy Conversion and Storage (DTU Energy), where the caloric activities at DTU are anchored, was created in 2012.

We wish you a successful and enjoyable meeting.

The local organising Committee

Christian R.H. Bahl Nini Pryds Kaspar K. Nielsen Kurt Engelbrecht Rasmus Bjørk Anders Smith Anita Voss



Practical information

Venue: The meeting will take place in the Niels Bohr auditorium, DTU Risø Campus, Frederiksborgvej 399, DK-4000 Roskilde.

Transportation: There will be busses to Risø Campus Monday and Tuesday morning. They will leave the Scandic hotel at 8.00 and stop at the south side of Roskilde station from where they will leave at 8.20. The map opposite shows the stops of the bus. Please be on time as the busses will leave at the indicated times.

After the closing on Tuesday busses will be going to Roskilde station, leaving Risø Campus at 17.00.

Alternatively, the public bus 600S runs between Roskilde station and the main gate at Risø Campus every 15 minutes. You can buy tickets on the bus, but only with cash (DKK).

WiFi: In each binder there is a personal code for the DTU wireless network. Throughout DTU you can also log on using Eduroam.

Dinner: The dinner will be aboard the ship M/S Sagafjord, which docks at Vindeboder 18, 4000 Roskilde (see the map opposite). There will be busses to Roskilde harbour leaving Risø Campus at 17.30. We will depart Roskilde harbour at 18.30 to sail in Roskilde Fjord while enjoying dinner, returning at about 21.30. From Roskilde harbour, Roskilde station is within walking distance.

Presentations: All oral presentations will be in the Niels Bohr auditorium. Invited presentations are 25 min + 5 min for questions. Other presentations are 12 min + 3 min for questions. Posters will be in the H.H. Koch room, upstairs. Please hang up you poster when you arrive, and leave it until the end of the meeting.

Please upload your presentation to the computer in the auditorium, or check that your laptop will connect properly, before the start of the session. Standard connectors will be available.

Programme

Monday, October 2nd - Morning

Time	Talk
9:00	Opening Session 1.
	Session 1 – Chair: Christian Bahl
9:15 – 9:45	Energy-efficient refrigeration near room temperature with transition metal based
	magnetic refrigerants
	E.H. Brück
	Delft University of Technology, Netherlands
9.45 – 10.00	Hysteresis of MnFePSi spherical powder ensembles studied by magneto-optical
	imaging
	A. Waske
	Leibniz Institute for Solid State and Material Research, Germany
10.00 – 10.15	The magnetocaloric effect across first order magnetostructural transitions: the
	role of the transition broadening
	F. Cugini
	University of Parma, Italy
10.15 – 10.30	How magnetocrystalline anisotropy influences the magnetocaloric effect
	M. Fries
10.00 11.00	Technische Universität Darmstadt, Germany
10:30 - 11.00	Coffee break
11:00 – 11.30	Session 2 – Chair: Kurt Engelbrecht
11:00 – 11.30	Calorics under Pressure
	L. F. Cohen
11.30 – 11.45	Imperial College London, UK
11.30 - 11.45	Shaping of LaFeSi-based alloys via Laser Beam melting and metal powder extrusion
	S. Wieland
	Frauhofer IFAM, Germany
11.45 – 12.00	Shaping magnetocaloric materials for complex regenerator beds
11.45 12.00	M. Krautz
	IFW Dresden, Germany
12.00 – 12.15	Preliminary experimental study on a hybrid cryogenic magnetic refrigerator
12.00 12.13	combined with Gifford-McMahon gas refrigeration
	X. Gao
	Chinese Academy of Sciences, China
12.15 – 12.30	Magnetocaloric heat pump for the residential sector: a promising challenge
	S. Dall'Olio
	Technical University of Denmark, Denmark
12.30 - 13.30	Lunch / Poster session

Monday, October 2nd - Afternoon

Time	Talk
	Session 3 – Chair: Rasmus Bjørk
13.30 - 14.00	Barocaloric materials
	X. Moya
	University of Cambridge, UK
14.00 - 14.15	Frustrated Magnetism and Caloric Effects in Mn-antiperovskite Nitrides: Ab initio
	Theory
	E. Mendive Tapia
	University of Warwick, UK
14.15 – 14.30	Effect of pressure on spin crossover compounds for barocaloric applications
	S. Vallone
	The Graduate Center at the City University of New York, USA
14.30 – 14.45	Active magnetic regenerating performance in cascade arrangements of materials
	with 2 nd -order phase transition
	A. Fujita
	National Institute of Advanced Industrial Science and Technology, Japan
14.45 – 15.00	Optimised layered metal bonded La(FeMnSi) ₁₃ H _x regenerators
	I. A. Radulov
	Technical University of Darmstadt, Germany
15.00 – 15.30	Break
	Session 4 – Chair: Anders Smith
15.30 – 16.00	Stable Operating Points for Active Caloric Regenerators
	A. Rowe
46.00 46.45	University of Victoria, Canada
16.00 – 16.15	"PoloMag": The development of a magnetic wine cooler
	J. A. Lozano
16.45 46.20	Federal University of Santa Catarina, Brazil
16.15 – 16.30	Industrial evolution of magnetocaloric cooling applications
	JB. Chaudron Coaltach Applications France
16.30 – 16.45	Cooltech Applications, France Study of magnetic heat pump using multi-layered magnetic materials
10.30 - 10.45	M. Yoshiki
	Railway Technical Research Institute, Japan
16.45 – 17.00	Modelling of Manganese-Ferrous porous pellets by metal additive manufacturing
10.45 - 17.00	S. Hirano
	Hokkaido Research Organization, Japan
17.00	Leave for dinner in Roskilde
17.00	Leave for diffice in nosking

Tuesday, October 3rd

Time	Talk
	Session 5 – Chair: Nini Pryds
9.00 – 9. 30	Ultralow-fatigue of Elastocaloric NiTICu-based Thin Films
	E. Quandt
	Christian-Albrechts-Universität Kiel, Germany
9.30 - 9.45	Elastocaloric effect and fatigue of Ni-Ti plates under pre-strain conditions
	J. Tušek
	University of Ljubljana, Slovenia
9.45 – 10.00	Long Term Stability of the Electrocaloric Effect
	F. Weyland
10.00 10.15	Technical University of Darmstadt, Germany
10.00 – 10.15	Latent Heat of Metal-Insulator Transition in VO2 Ceramics
	Y. Kinemuchi National Institute of Advanced Industrial Science and Technology, Ignan
10.15 – 10.30	National Institute of Advanced Industrial Science and Technology, Japan
10.15 – 10.50	Integrated design of the magnet-regenerator assembly F. P. Fortkamp
	Federal University of Santa Catarina, Brazil
10.30 - 11.00	Coffee break
20.00 22.00	Session 6 – Chair: Kaspar K. Nielsen
11.00 – 11.30	Finite-time thermodynamics of thermomagnetic generation
	M. Lo Bue
	SATIE, ENS Paris Saclay, France
11.30 - 11.45	A Tesla Type Rotary Thermomagnetic Motor
	L. D. R. Ferreira
	University of São Paulo, Brazil
11.45 – 12.00	Magnetocaloric and magnetovolume effects in static and pulsed magnetic fields
	K. P. Skokov
12.00 12.15	Technical University of Darmstadt, Germany
12.00 – 12.15	Experimental results for caloric energy harvesting
	K. Engelbrecht Technical University of Denmark, Denmark
12.15 – 13.30	Technical University of Denmark, Denmark Lunch / Poster session
12.15 - 15.50	Session 7 – Chair: Christian Bahl
13:30 – 14.00	Industrial development of La-Fe-Si based magnetocaloric alloys
13.30 1.100	A. Barcza
	Vacuumschmelze GmbH & Co. KG, Germany
14.00 – 14.15	Quantifying the magnetocaloric effect from first-principles
	D. Luşan
	Uppsala University, Sweden
14.15 – 14.30	Colossal Barocaloric Effects in Organic Materials
	P. Lloveras
	Universitat Politècnica de Catalunya, Catalonia, Spain.
14.30 – 15.00	CaloriCoolTM: Making a difference in calorics
	V. K. Pecharsky
45.00	Ames Laboratory, USA
15.00	Closing reception and informal lab tour
17.00	Bus to Roskilde station

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Oral presentations

Energy-efficient refrigeration near room temperature with transition metal based magnetic refrigerants

Ekkes Brück, Nguyen Van Thang, Maurits Boeije, Lian Zhang, Xinmin You, Michael Maschek and Niels Van Dijk

Fundamental Aspects of Materials and Energy, Department of Radiation Science and Technology, Faculty of Applied Sciences, Delft University of Technology, Delft, The Netherlands

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An energy-efficient refrigeration cycle can be achieved with magnetic materials that show a large magnetocaloric effect. These materials heat up when a magnetic field is applied. After this heat is transferred to the environment, they cool down on removing the magnetic field and can take up heat from the substance that needs to be cooled. The processes as described are highly reversible and therefore very energy-efficient. Additionally, these magnetic materials are solids that can easily be recycled and do not contribute to the atmospheric greenhouse effect. Thus, this solid-state technology has the potential to strongly reduce the environmental impact of cooling technology.

With the advent of giant magnetocaloric effects (MCE) that occur in conjunction with magneto-elastic or magneto-structural phase transition of first order (FOT), room temperature applications became feasible. In this context the MnFe(P,X) system is of particular interest as it contains earth abundant ingredients that are not toxic. This material family derives from the Fe₂P compound, a prototypical example known since a long time to exhibit a sharp but weak FOT at 210 K (-63 °C).

In this hexagonal system, the Fe atoms occupy two in equivalent atomic positions referred as 3f (in a tetrahedral environment of non-metallic atoms) and 3g (pyramidal). One intriguing aspect is the disappearance of the magnetic moments of iron atoms on the 3f sites when crossing T_C , whereas there is only a limited decrease on the 3g site. This observation has led to a cooperative description of the FOT linking the loss of long range magnetic order at T_C with the loss of local moments on 3f. This mechanism has recently been shown to be at the origin of the G-MCE observed in MnFe(P,Si) [1].

The disappearance of the magnetic moments has been ascribed to a conversion from non-bonding *3f d*-electrons into a distribution with a pronounced hybridization with the surrounding Si/P atoms. Therefore, one can expect to adjust the properties of these compounds by substitutions on the non-metallic site. This solution has been used to optimize the properties of MnFe(P,Si) materials.

References

[1] M.F.J. Boeije et al., "Efficient Room-Temperature Cooling with Magnets", Chem. Mater. 28 (2016) 4901-4905

Hysteresis of MnFePSi spherical powder ensembles studied by magneto-optical imaging

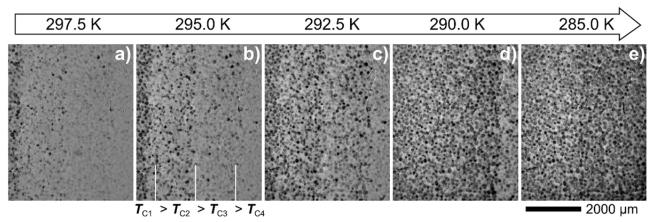
Alexander Funk^{1,2}, Ivan Soldatov^{1,3}, Rudolf Schäfer¹, Michael Zeilinger⁴, Florian Dötz⁴ and Anja Waske¹

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Temperature-dependent magneto-optical imaging is applied to study the thermal hysteresis of magnetocaloric MnFePSi spherical powder packed beds across their magneto-elastic transition (cf. Fig. 1). Cooling and heating imaging series are used to analyze the transition of a statistically relevant number of particles. The magnetization versus temperature behavior reconstructed from those local measurements shows very good agreement with integral measurements of the magnetization of the whole packed bed. Hence, local magneto-optical imaging measurements represent the ensemble behavior well if the number of measurements is large enough. Furthermore, we analyzed the Curie temperature (T_c) distribution of layers with different T_c s and observed that the spread of T_c s within one layer is larger than the spacing between different layers, leading to a gradual switching behavior of the layer ensemble. Additionally, high resolution light microscopy was applied to observe the transition of individual particles, and correlate it to the local magnetic measurements.

This work is supported by BASF New Business and by DFG through SPP 1599 "Ferroic Cooling".



Magneto-optical difference image series of a switching magnetocaloric packed bed with low magnification (Figs. a-e) in the cooling regime. Four layers of T_c are in the field of view (labeled in b).

The magnetocaloric effect across first order magnetostructural transitions: the role of the transition broadening

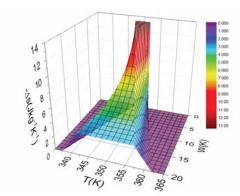
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¹Department of Mathematical, Physical and Computer Sciences, University of Parma, Parco Area delle Scienze 7/A, 43124 Parma, Italia, ² IMEM-CNR Institute, Parco Area delle Scienze 37/A, 43124 Parma, Italia, ³Laboratorio MIST E-R, via P. Gobetti 101, 40129 Bologna, Italia

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The magnetocaloric effect near first-order magnetic transitions is mainly driven by the transformation latent heat, by the magnetization change at the transition and by the correlation between the magnetic and structural degrees of freedom of the material. Besides these three fundamental contributions, the width of the finite temperature span, in which real first-order transitions develop, plays an important role to define the magnetocaloric properties of materials exploitable in magnetic cooling systems.

In this contribution, the negative influence of the transition width on the MCE near first-order transitions will be discussed through a phenomenological model of the transformation, based on geometrical considerations on the entropy-temperature diagram [1]. On the other hand, we will present the effect of the transition width to promote the cyclability of magnetocaloric materials characterized by large thermal hysteresis through the tracing of loops between metastable mixed states. These predictions will be compared to the results of a complete magnetic, calorimetric and magnetocaloric characterization of several (Ni,Mn)-based Heusler alloys near their martensitic transition. A morphological analysis of the sample surface, based on optical microscopy imaging, will be utilized to correlate the broadening of the transformation and the microscopic features of the martensitic transition [2].



Dependence of the isothermal entropy change (ΔS) on the broadening of the transition width (W), obtained through a geometrical model of the transformation.

References

[1] F. Cugini et al., "Influence of the transition width on the magnetocaloric effect across the magnetostructural transition of Heusler alloys", *Phil. Trans. R. Soc. A* 374 (2016) 201503306

[2] F. Cugini et al., "On the broadening of the martensitic transition in Heusler alloys: from microscopic features to magnetocaloric properties", JOM (2017) DOI 10.1007/s11837-017-2373-z

How magnetocrystalline anisotropy influences the magnetocaloric effect

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Since the discovery of the magnetocaloric effect (MCE) many promising material families like LaFeSi- and Fe_2P -based alloys have been extensively studied [1]. It has been found that especially the Fe_2P -type materials show a large magnetocrystalline anisotropy which strongly influences the magnetic properties and therefore could also influence the magnetocaloric properties [2].

The influence of magnetocrystalline anisotropy on the MCE was studied on single crystals of Co_2B and compared to measurements on polycrystalline samples. Large differences in adiabatic temperature change ΔT_{ad} and magnetic entropy change ΔS_M were found along the different crystallographic directions. The MCE differs in the case of ΔS_M by 50% and 35% from each other in field changes of 1 and 1.9 T (see Figure 1), respectively when applying the field along the hard axis and easy plane of magnetization.

This behaviour will be explained by the rotational MCE. It will be shown that especially in the aimed scenario of using magnetocaloric materials in rather small magnetic fields of up to 2 T, achievable by permanent magnets, the effect of magnetocrystalline anisotropy needs to considered [3].

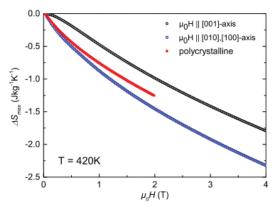


Figure 1: Field dependence of ΔS_{max} for fields applied parallel to [100] (hard-axis), [010],[001] axis (easy plane) and to a polycrystalline sample.

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Calorics under Pressure

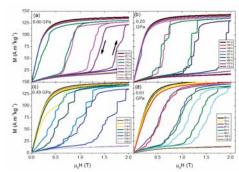
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In this talk will cover aspects of our work using hydrostatic pressure. First I will present an overview of our work on La(FeMnSi)₁₃, our understanding of the nature of the transition as a function of Mn and the addition of hydrogen [1]. I will then discuss how the material changes under the influence of hydrostatic pressure. In the multicaloric cycle the magnetic hysteresis loss can be reduced. Although the additional loss due to the introduction of pressure into the cycle is similar [2], hydrostatic pressure offers some advantages [3]. I will also discuss our recent work examining the barocaloric properties of antiperovskite antiferromagnet Mn₃NiN, in comparison to the previous work reported on the Mn₃GaN system [4]. Finally, I will show our preliminary progress towards realising Mn₃NiN thin films for elastocaloric application [5].



M(H) isotherms of dehydrogenated LaFe_{11.74} $Mn_{0.06}Si_{1.20}$

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Shaping of LaFeSi-based alloys via Laser Beam Melting and Metal Powder Extrusion

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Shaping magnetocaloric materials into thin-walled heat exchanger structures is an important step towards the development of energy efficient magnetic cooling systems. Thin plates or blocks with regular microchannels and structure sizes well below 0.5 mm are favorable to optimize the fluid flow as well as the heat exchange [1]. However, the mass-production and shaping of magnetocaloric materials as La(FeSi)₁₃ remains a major challenge due to the heat treatment necessary to form the magnetocaloric phase, the oxygen sensitivity and the intrinsic brittleness of the material [2].

We report on applying two different shaping technologies to La(FeSi)₁₃-based gas atomized powder: Laser Beam Melting (LBM) and Metal Powder Extrusion. While LBM is an Additive Manufacturing technology that offers a high degree of geometrical flexibility and could be used to test various heat exchanger designs in demonstrators and prototypes, Metal Powder Extrusion is a method capable of high volume series production.

Especially for LBM the particle size and shape of the powder has to be carefully chosen to allow processing. Powders of different size distributions and compositions were processed by laser melting with varied parameters and the produced samples were heat treated to adjust the magnetocaloric properties. For Extrusion the metal powder was mixed with organic components that allow moulding of the respective tool geometry. After shaping the organic materials were removed by chemical and/or thermal debinding and the parts were sintered till sufficient mechanical stability was reached, thereby combining densification, annealing and hydrogenation in one single furnace procedure.

Magnetocaloric heat exchangers with wall thickness 300 μ m have been achieved both by Laser Beam Melting and Metal Powder Extrusion. The density, microstructure, carbon & oxygen content and the magnetocaloric properties of the samples were examined.

This work is in part funded by AWT/ AIF within the BMWi program supporting cooperative industrial research (grant number 18999 N/2)

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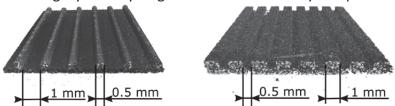
Shaping magnetocaloric materials for complex regenerator beds

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Magnetocaloric cooling has significantly headed towards applicability during the recent years. By now several material families with tuned magnetocaloric properties are on hand as well as prototypes with optimized operation parameters. Apart from theoretical heat transfer considerations defining the lower limit of geometrical boundary, material's shapeability has to be addressed. Different technologies and resulting regenerator bed geometries have already been studied and compared in existing prototypes [1–3]. However, the optimal geometry of such a regenerator bed considering both optimal heat transfer and shapeability has not been concluded yet. In our study, we evaluate the feasibility of two different shaping technologies, tape casting and powder in tube (PIT) processing. By tape casting sheets with a large variety of profiles can be produced and can be stacked as parallel plate bed. Here, two different profiles differing in channel width and channel shape as shown in the figure have been cast. Crucial properties of the stacked sheets, such as pressure drop and temperature change along the bed length have been assessed. Moreover, mechanical integrity after cycling has been evaluated by computed tomography (CT).



Reconstructed CT-Scan of tape cast $La(Fe, Si)_{13}$ -plates with different channel geometries.

PIT processing is another promising technology since brittle materials can be formed into rods with large aspect ratio by means of a surrounding ductile jacket. We show that $La(Fe, Si)_{13}$ -powder packed in a 3 mm steel-tube can be swaged down to 1 mm composite-rods without severely compromising the magnetocaloric properties.

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Preliminary experimental study on a hybrid cryogenic magnetic refrigerator combined with Gifford-McMahon gas refrigeration

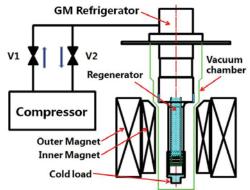
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The Gifford-McMahon(GM) refrigerator is widely used for cryogenic applications because of its easy operation and reliable performance. This refrigerator is based on the expansion of helium gas. In the temperature region below 15 K the big volumetric heat capacity of compressed helium causes a rapid decrease of regenerator efficiency. A possible way to overcome this difficulty is to use in the regenerators the magnetic materials (Er₃Ni, ErNi et al.) instead of lead [1]. Some of these materials have high magnetocaloric effect(MCE) which may be utilized to further improve the efficiency. A cryogenic refrigerator concept combining the GM gas cooling cycle with magnetic cooling cycle has been numerically studied by Yayama et al [2] and a remarkably high refrigeration power was predicted. No experiments at liquid helium temperature has been done.

In this paper, a hybrid cryogenic refrigerator that combines the magnetic refrigeration effect with GM gas refrigeration effect has been experimentally studied. ErNi partly replaced lead in the second (low-temperature) stage regenerator and the second stage regenerator is put in a magnetic field varying from 0 to 1.1 T, which is provided by a Halbach-type rotary permanent magnet assembly. With an optimal phase angle around 60 degree between the gas movement and the changing magnetic field, a lowest no-load temperature of 3.5 K and a maximum refrigeration capacity of 0.87 W at 5.05 K were obtained. Influence of eddy current loss was also analysed.



Schematic diagramof the hybrid refrigerator.

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Magnetocaloric heat pump for the residential sector: a promising challenge

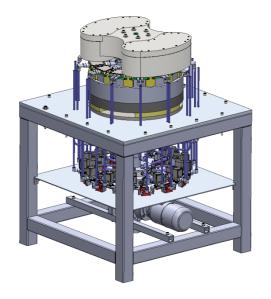
S. Dall'Olio, C. Cibin, K. L. Engelbrecht, A. Insinga, D. Eriksen, R. Bjørk, K. K. Nielsen, T. Lei, H. N. Bez, C. R. H. Bahl

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MagQueen, the prototype heat pump developed at DTU within the ENOVHEAT project, is a magnetocaloric heat pump that aims to concretize the research work and experience of the DTU group. The heat pump is designed to supply the need of a typical Danish house, realizing a COP of at least 5, a heating power of around 1500 W at a temperature span of 25 K.

The main components of MagQueen are: an iron ring with 13 iron teeth equally distributed over the ring, 13 active magnetic regenerators (AMR) placed on the top of the teeth, a centrifugal pump and a permanent magnet designed with the 'virtual magnet' approach developed at DTU [1]. The magnet is made up of two halves, and each of them is encapsulated in the iron yoke. Each half is made up of 28 sintered NdFeB segments, which are glued together. The magnetocaloric material (MCM) used into the regenerators will be packed spherical La(Fe,Mn,Si)₁₃H_z particles.



CAD model of the DTU prototype.

Each of the 13 regenerator beds contains 215 g of MCM, with a porosity of around 0.5. The spheres are bound together by a small amount of epoxy to prevent the breaking apart of the material, due to internal stresses at the phase transition [2]. After the fundamental studies on the magnet and the regenerators, much attention has been devoted to the design of the regenerator housing to reduce the parasitic losses, and to the control of the heat transfer fluid flow. The deep scientific effort in optimizing the components of the machine is the main part of the work, but the goal of the project is broader. The study of the optimum integration of the components within a device and, further on, in a residential heating system, has proven to be an attractive, but promising challenge.

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Barocaloric materials

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Giant barocaloric effects driven by hydrostatic pressure have been suggested for cooling applications, but they have been traditionally seen only in a small range of magnetic materials that are relatively expensive. Here I will describe the fundamentals of barocaloric materials from a historical perspective and present pressure-dependent calorimetry data to demonstrate giant barocaloric effects in non-magnetic materials that are made of cheap abundant elements.

Frustrated Magnetism and Caloric Effects in Mn-antiperovskite Nitrides: *Ab initio* Theory

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A large portion of potential magnetocaloric devices rely on expensive elements such as rare earth based- permanent magnets. The elastocaloric effect offers a solution to this problem but suffers from material fatigue associated with the structural phase transition that is normally necessary to promote large caloric responses¹. Here we propose an alternative route and show how magnetic frustration hosted in Mn-antiperovskite nitrides² enables the generation of large caloric effects associated with pure magnetic transitions driven by mechanical stimuli. We present an *ab initio* Disordered Local Moment theory³ investigation of the temperature effects in Mn₃GaN and its changing magnetism under application of biaxial strain. We present a rich temperature-strain phase diagram with two previously unreported collinear magnetic phases. Both large isothermal entropy change and adiabatic temperature change can be obtained simultaneously by combining second- and first- order transitions between these magnetic structures. Our predictions are linked fundamentally to the magnetic frustration and its rapid release with biaxial strain.

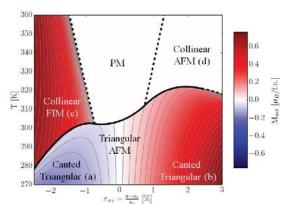


Figure 1: Temperature-strain phase diagram for Mn_3GaN . Thick black lines correspond to first-order transitions while dashed lines denote second-order transitions. The color scheme encodes the size and orientation of the induced net moment. Positive and negative values of ϵ_{xx} correspond to tensile and compressive biaxial strains, respectively.

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Effect of pressure on spin crossover compounds for barocaloric applications

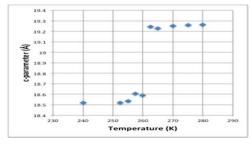
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Spin crossover occurs in compounds where the crystal field splitting of d-orbitals associated with a magnetic moment is of the order of k_BT . The effect is typically most observed in octahedrally coordinated complexes of Fe in e.g. d^5 or d^6 electronic configurations [1]. As a result, a change of state from low spin (LS) to high spin (HS) can occur at the so-called spin crossover temperature, T_{SCO} . Crucially for caloric applications, the change of state from LS to HS can be either continuous or first order, and it can occur at temperatures up to and beyond room temperature. Since SCO compounds are paramagnets, the largest caloric effects will be barocaloric rather than magnetocaloric. This has been proposed from a thermodynamic perspective [2] and verified via a microscopic, Ising-like model [3].

In magnetocaloric materials research, an essential point of comparison has been the caloric output of first order and second order materials. First order materials yield a larger entropic output at a single temperature, but offer a reduced temperature response window, and may possess hysteresis, which is a source of loss in application. Hence there has been interest in (tri)criticality, or tunable magnetoelastic coupling (termed "cooperativity" by the SCO community). In this presentation, we use neutron scattering as well as SQUID measurements to examine the evolution of the structure and transition hysteresis of a first order SCO compound with applied pressures under 1 kbar.



Refined values of the c lattice parameter for ($[Fe(1-bpp)_2][BF_4]_2$) in 200 bar pressure.

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Active magnetic regenerating performance in cascade arrangements of materials with 2nd-order phase transition

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To utilize high-performance magnetic refrigeration, the developments of both the materials and systems are indispensable. Especially, side by side with fundamental analyses from materials science or mechanical modeling, a realistic and pragmatic appreciation of active magnetic regenerator (AMR) mechanism becomes more important. One of the essential issues is the observation of regenerator actions analyses of promising magnetic refrigerants. However, the colossal magnetocaloric effect (MCE) of these materials originate from latent heat of a fist-order transition, while major AMR demonstrations and the accumulation of data from them are mostly based on 2nd order phase transition especially in Gd. Therefore, in demonstrations using various promising MCE materials, a difference in the phase-transition characteristics is positively focused, while other material parameters such as the total heat capacity or the thermal conductivity tend to be left as secondary issue to analyze. To bridge such a gap, in the present study, the phase transition feature in La(Fe,Si)₁₃ was tuned so that the MCE of the compound come close to that of Gd, and the AMR behavior was observed by constructing a cascade arrangement of these materials.

By tuning the Fe and hydrogen concentration [1], the second-order phase transition was observed in La(Fe_{0.85}Si_{0.15})₁₃H_{1.2} (LFSH) and the Curie temperature TC and an isothermal entropy change Δ Sm by magnetic field change of 0-1 T becomes 300 K and 3.6 J/kg, respectively. We construct test module base on the same concept of the previous work [2], and temperature span $\Delta T_{\rm span}$ between both sides of the AMR bed-like Teflon tube, and heat load response were examined. In the Teflon tube, the LFSH and Gd spheres were packed in series and the five kinds of tube with different volume fraction, i.e. LFSH:Gd = 1:0(A), 1/3:2/3 (B), 1/2:1/2 (C), 2/3:1/3 (D), 0:1 (E), were prepared. Typical $\Delta T_{\rm span}$ values for the setting (A) and (D) are 16.5 K and 5.5 K at 300 K, respectively, in our module and conditions. It was found that the variations of $\Delta T_{\rm span}$ and also the heat load response were not proportional to volume fraction, and a certain synergetic behavior was observed especially around 1/2:1/2. Such effect may come from a regenerative feature affected by a large difference in heat capacity between LFSE and Gd.

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Optimised layered metal bonded La(FeMnSi)₁₃H_x regenerators

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Hydrogenated La(Fe,Mn,Si)₁₃ alloys have excellent magnetocaloric properties and belong to the materials considered as most promising for use in active magnetic refrigerators (AMR). However, these alloys have rather poor mechanical and chemical stability. Therefore the La(Fe,Mn,Si)₁₃H_x powder needs additional treatment in order to obtain better machinability, shapeability and corrosion protection. As recently reported in [1], one simple but efficient method is the use of a low melting metal as a coating alloy (binder). First results, obtained on magnetocaloric porous body regenerator produced from metal bonded La(Fe,Mn,Si)₁₃H_x powder, were reported [2].

As presented on Fig. 1 materials with first-order transition have very narrow ΔT_{ad} and ΔS_m peaks, which mean that the regenerator made of such material will have a very narrow thermal span (TS), comparable with the peak width. The TS can be significantly increased by using a multi-layer regenerator of La(Fe,Mn,Si)₁₃H_x alloys with different transition temperatures T_{tr}. Here we present our work on the production of optimized multi-layer regenerator. As evaluation criteria the obtained TS values were used. The optimisation was done by varying the number of the different layers, their thickness and the spacing between the individual T_{tr}.

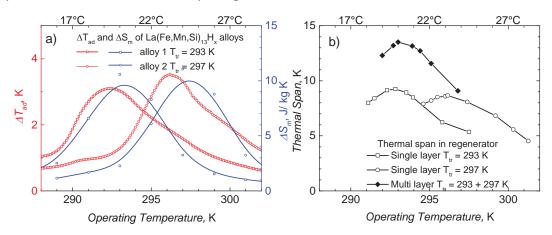


Fig. 1: Performance of two La(Fe,Mn,Si)₁₃H_x alloys as bulk (a) and as single and multilayered regenerator (b).

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Stable Operating Points for Active Caloric Regenerators

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The performance of an active caloric regenerator using many materials is important to understand if first order materials (FOM) are to be used commercially for heating and cooling. However, simpler configurations such as a single FOM, should be well-understood if effective multi-material cascades are to be designed. Magnetocaloric FOMs often exhibit useful effects in a narrow temperature range and history dependent properties. Our experimental results with single and multi-material FOMs in active regenerator cycles show repeatable behaviours that have not been predicted by previous modelling studies suggesting our understanding of FOM performance is lacking.

Here, we compare model results of an active regenerator using FOM material with experimental data using a single material from the MnFe(P,Si) family [1]. With reference to steady-state temperature span at a fixed rejection temperature, for certain operating conditions, multiple points of equilibrium (MPE) are observed. The existence of stable and unstable equilibrium conditions are explained using a one-dimensional, two-phase model [2]. Results indicate that MPEs can exist without hysteresis; however, hysteresis appears to also play a role in the measured experimental data. This phenomenon is observed in single and multi-material regenerator experiments and warrants further study with regards to impact on realized performance.

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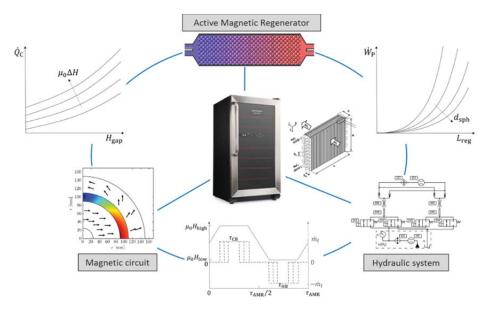
"PoloMag": The development of a magnetic wine cooler

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PoloMag is a research project which aims to develop a domestic wine cooler operated by a compact magnetic refrigeration system with an electric energy consumption similar to that of a conventional wine cooler and that is able to cool up to 30 wine bottles between 5 to 20°C for an ambient temperature of 25°C. This project is managed by a novel methodology based on lean product development using the Toyota Kata approach and the implementation of the Set-Based Concurrent Engineering (SBCE). The main research lines in course for the development of the magnetic wine cooler are: (i) integrated design of the magnet-regenerator assembly; (ii) optimization of multilayer regenerators; (ii) synchronization between magnetic & hydraulic profiles; (iv) commissioning of a low-energy consumption hydraulic system using a manifold of electric valves; (v) thermal design of the cabinet considering the heat exchangers; (vi) commissioning and integration of the main units. This presentation aims to give an overview of the development of the magnetic wine cooler, especially of the main units of the compact magnetic refrigerator and the integration project trade-offs through designer maps for different operating conditions.



Project trade-offs and the integration of the components in the development of a magnetic wine cooler.

Industrial evolution of magnetocaloric cooling applications

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Thanks to engineering efforts, numerous prototypes of magnetocaloric cooling devices have been constructed all over the world [1]. A sustained commitment is kept to transform science into technology and then technology into industrial products [2]. Cooltech Applications has used a Lean start-up approach ("Think it. Build it. Use it.", "Assemble-Measure-Learn-Adjust") to develop different generations of devices with iterative learning and continuous innovation. The technology roadmap, specifications of the used regenerators and performance results will be presented to demonstrate the progress and the steps forward towards industrialization. Some unchallenged research topics and important technical problems will also be shared.

Only few groups have started analysing the economic viability of magnetic cooling devices [3]. Additional industrial insight will be presented here with an actual cost split of the system. Based on the feedback from the market, a better exergy efficiency is an argument [4] but a quick Return Of Investment (ROI) is even more important (CAPEX/OPEX analysis). The choices that led Cooltech Applications to develop a new range of applications for Remote racks in supermarkets will be detailed. After the explanation of the extensive use of modelling and the engineering activities work, the latest built machine will be disclosed with machine design and preliminary testing. To our knowledge, it represents the largest scale machine ever built by the community.



Photo of the operating laboratory prototype for an application of Remote racks to be used in supermarkets

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Study of magnetic heat pump using multi-layered magnetic materials

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Railway Technical Research Institute has been studying a magnetic heat pump for air conditioners of train [1]. A typical air conditioner of the train in Japan has a cooling capacity of 25 kW, an electric consumption of 10 kW and a coefficient of performance of 2.5. Furthermore, it needs that the temperature span is larger than 30 K.

We carried out basic experiments and numerical analyses of the Gd-based multi-layered AMR (Active Magnetic Regenerator) in order to enlarge temperature spans and to design the multi-layered AMR. Figure 1 shows the calculated temperature spans of multi-layered AMRs in dependence on the length of the AMR. The figure has three typical areas. Namely in the area of less than 60 mm of AMR length, there are little difference of temperature spans among 1, 2 and 3 layers AMRs. Between 60 and 200 mm of AMR length, the temperature span of 2 layers AMR changes from the increase tendency to the decrease one, and the temperature span of 3 layers AMR is larger than those of 1 or 2 layers AMRs in the area of longer than 200 mm of AMR length.

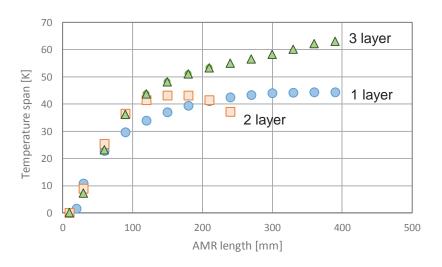


Fig. 1 Calculated temperature span of 1~3 layered AMR

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Modelling of Manganese-Ferrous porous pellets by metal additive manufacturing

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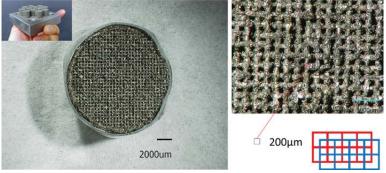
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Basic phenomenon of magnetic refrigeration has discovered by a Weiss and Piccard in 1917 known as a magnetocaloric effect (MCE) [1]. To utilize thermal device such as magnetic heat pump, it is necessary to install magnetocaloric materials (MCMs) which have exothermic/endothermic temperature change when magnetized/demagnetized respectively. And to enhance the temperature difference of the thermal device, Active Magnetic Regenerator (AMR) is essential. When single MCM is embedded in the AMR, efficiency of heat transfer would be smaller as the temperature gradient arises in the AMR.

To recover the disadvantage of the single material AMR, cascade type of AMR has been developing. The cascade AMR retains several MCMs that have different working temperature, and these MCMs are disposed in gradient arrangement. Mn related type of MCMs have giant MCE and is feasible to require the different working temperature such as Curie temperature by control of specific ingredients of the material. [2,3]

This paper presents the modelling of the Mn-Fe MCM porous pellet by non-alloying method using metal additive manufacturing.



Appearance of the fabricated pellet.

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Ultralow-fatigue of Elastocaloric NiTiCu-based Thin Films

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Caloric materials have the potential to serve as an environmentally friendly and more efficient alternative substitute in conventional vapor compression cooling. The principle of ferroic cooling is based on a solid state phase transformation initiated by an external field, in the case of elastocalorics by an external stress field. Combined with thin film processes this technology enables the development of small scale cooling devices required for mobile applications. Up to now, the major obstacle for the implementation of elastocaloric materials in cooling devices is the fatigue of the material. To investigate the underlying microstructural mechanisms TEM and synchrotron analyses of NiTiCu-based thin films are conducted in the pristine state and after superelastic cycling. A strong difference of superelastic degradation for Ti-rich compositions compared to near equiatomic compositions is found. While near equiatomic compositions already degrade severely during the first cycles, Ti-rich compositions are functionally stable for 10 million superelastic cycles [1]. Using stress dependent in situ synchrotron investigations the change of lattice constants of B2 phase and stress induced B19 phase during the superelastic transformation can be quantified. This measurement enables the compatibility calculation of austenite and martensite phases which is known to have a strong influence on the superelastic hysteresis and the thermally induced transformation stability. The microstructural influences of grain size, precipitates and crystallographic compatibility on the functional degradation of NiTiCu-based thin films will be discussed in view of their elastocaloric properties.

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Elastocaloric effect and fatigue of Ni-Ti plates under pre-strain conditions

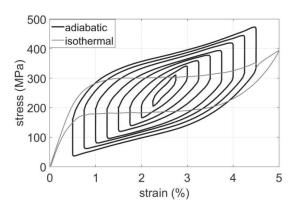
<u>Jaka Tušek</u>¹, Andrej Žerovnik¹, Miha Brojan¹, Matjaž Čebron¹, Borut Žužek², Kurt Engelbrecht³, Andrea Cadelli⁴

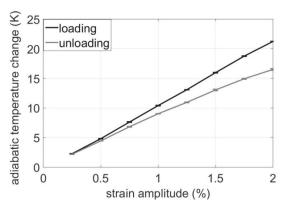
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A recently reported prototype utilizing an elastocaloric regenerator with thin Ni-Ti plates loaded in tension demonstrated high temperature span, high heating and cooling power, and potentially high efficiency [1], but also limited durability with a fatigue life only up to 6.000 cycles [2].

In this work we report a comprehensive analysis of the elastocaloric effect at different mean strains and different strain amplitudes on commercial Ni-Ti plates loaded in tension. Advantages of applying pre-strain conditions for elastocaloric cooling are demonstrated and fatigue life at different strain amplitudes is evaluated. It was shown that properly polished samples can withstand above 10⁵ cycles at a strain amplitude up to 0.5 % without failure, which corresponds to an adiabatic temperature change of 5 K. We further analysed different methods for improving fatigue life also at higher strain amplitudes. Alternative geometries of elastocaloric regenerators, such as tubes loaded in compression (see e.g. [3]) will also be discussed.





Stress-strain behaviour at different applied strain amplitudes and mean strain of 2.5% (left) and associated adiabatic temperature changes (right).

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Long Term Stability of the Electrocaloric Effect

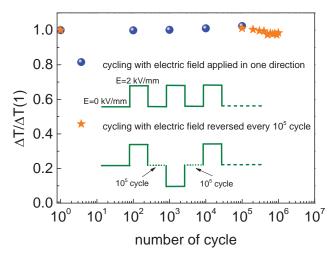
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The electrocaloric effect (ECE) is considered as a key to future on-board cooling of electronic circuits. The temperature change in ferroelectric materials is triggered by the application of an electric field. Therefore, cooling devices based on the ECE are easier to implement in mobile devices then ones based on the magneto- or barocaloric effect. For applications, the long term stability of the achievable temperature change is crucial and not investigated so far in terms of the ECE.

In this study we investigate the EC temperature change over the cycling number in the $Ba(Zr_{0.2}Ti_{0.8})O_3$ system. We observe a cycling stability over 10^5 cycles. Upon further cycling, the material exhibits a degradation which results in enhanced leakage current and additional Joule heating under electric field application. Dielectric measurements and impedance spectroscopy depict the change in defect chemistry during cycling. The degradation mechanism is based on the migration of oxygen vacancies under the electric field. In the figure we show the approach to prevent degradation by changing the polarity of the electric field every 10^5 cycles. By this solution we achieved a long term stability of the ECE in $Ba(Zr_{0.2}Ti_{0.8})O_3$, needed for practical cooling applications.



Electrocaloric temperature change after cycling normalized to temperature change of first measurement. Blue dots denote cycling with electric field applied in the same direction over whole cycling. Orange stars show cycling with change of polarity of electric field every 10⁵ cycles.

Latent Heat of Metal-Insulator Transition in VO₂ Ceramics

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Vanadium dioxide is one of the fascinating materials for caloric applications, possessing a promising latent heat of 240 J/cc [1] when it undergoes metal-insulator transition (MIT) at 340 K. Along with the electronic phase transition, the first order phase transition from monoclinic to tetragonal phase occurs, which contributes to the large latent heat as well. External stimuli such as heat, strain, light, and electric field are known to induce MIT, which offers several coupling effects among them as exemplified in electrocaloric effect [2]. From a technical standpoint, VO_2 in a bulk form is in great demand, particularly for caloric application, however, successful result of the densified ceramics is limited so far. Our preliminary sintering experiments of pellets sealed in quartz ample resulted in porous ceramics with exaggerated grain growth, indicating volume diffusion is somehow limited in this material. Here, we report VO_2 ceramics prepared by high pressure SPS [3], and the impact of the pressure on its latent heat. The new sintering process effectively promoted the densification at relatively low sintering temperature of 500°C, resulting

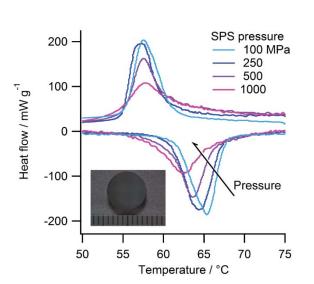


Fig. 1 Broadening of phase transition with process pressure. Inset: densified sample pellet

in ceramics with a relative density higher than 90%. With increase in the process pressure, the phase transition obviously broadened with respect to temperature. (Fig. 1) The systematic reduction in latent heat was also found with the pressure, indicating MIT is impeded by structural factors rather than chemical ones, which is supported by the positive correlation with inhomogeneous strain in the ceramics. The present study indicates the importance of microstructural tuning for the utilization of intrinsic latent heat in Mott insulators.

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Integrated design of the magnet-regenerator assembly

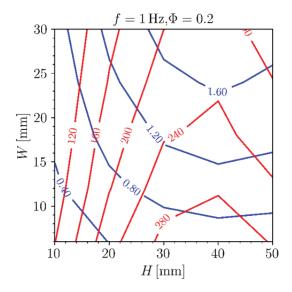
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Modelling can be a powerful tool to design and improve the performance of magnetic refrigerators [1]. However, many works in the literature use separate models and approaches for the design of the magnet and the regenerators, with almost no coupling between them. In this work we present an integrated design methodology for the design of the optimal magnet-regenerator assembly.

The Figure below shows a designer map for the geometry of the regenerator, where the magnet size varies along with the height of the beds. An analytical model for concentric Halbach cylinders [2] is used to dynamically calculate the magnetic profile, and a 1D AMR model [3] is used to calculate the thermal-hydraulic performance of the device. Results are currently being updated with a more realistic model for the magnetic circuit and including other configuration factors such as heat losses through the AMR casing and heat exchangers with finite thermal conductance.



Designer map for the COP (blue) and cooling capacity (red) of an AMR device

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Finite-time thermodynamics of thermomagnetic generation

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Energy harvesting systems based on thermomagnetic generation (TMG) are experiencing a revival, after more than a century since Tesla patent [1] and nearly seventy years since Brillouin and Isjkenderian paper [2]. This is mainly due to the opportunities opened by the properties of new magnetocaloric materials (MCM), to design more efficient energy-conversion devices [3, 4, 5]. So far most of the thermodynamic studies devoted to the thermodynamics of MCM based TMG systems are focused on the achievable efficiencies using different materials as working substance [3, 6]. Curiously enough no much attention has been devoted to the related efficiency at maximum power (EMP). Here we shall discuss TMG thermodynamic cycles using the classical Cruzon-Ahlborn approach [7] where finite-time heat exchanges are considered on an endoreversible engine (i.e. all the other irreversible processes are neglected). The main advantage of this approach is that it allows to define an EMP upper bound based on a very general, nearly universal expression [8]. In this frame we shall discuss our recent results [9] showing the influence of the material equation of state on thermodynamic cycle shapes.

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A Tesla Type Rotary Thermomagnetic Motor

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Thermomagnetic motors (TM) use the temperature dependency of the magnetization of magnetocaloric materials (MCM) in order to perform the conversion of thermal energy into useful mechanical or electrical energy [1]. Most of the recent work in TM is focused on a design in which heat is transferred to the material in a fixed position, while the MCM rotates in a constant manner [2], usually referred to as a Curie Wheel. While this design is capable of providing promising results [3], higher efficiencies might be achieved by the use of a Tesla type TM, in reference to his original patent from 1889 [4].

A Tesla type TM is proposed, as shown in Fig. 1, in which six plates of MCM are fixed to the structure, and two magnets assembly, M_{Ext} and M_{Int} , are mounted to a shaft. By heating 5 of the plates, circulating a hot fluid through them, their magnetization decreases, this causes a high torque to appear in the direction of the colder plate, as indicated in the figure. Once the rotating movement occurs the flow is switched, while the previously cold plate is heated and the next one is cooled. The hot and cold temperatures will depend upon the Curie temperature (T_C) of the selected MCM, in our system the $Gd_{4.7}Nd_{0.3}Si_4$ compound with a T_C of $54^{\circ}C$ is used, converting energy from a heat source at $70^{\circ}C$ and sinking heat to a room temperature source (around $25^{\circ}C$). The proposed design was both built and simulated through finite element methods, using a combination of Magnetostatic Simulation and CFD, the computational model was then validated using the constructed prototype.

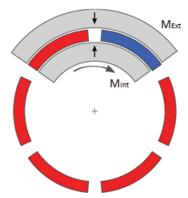


Figure 1 – Schematic view of the Tesla type rotary thermomagnetic motor, the two magnets assembly, M_{Ext} and M_{Int} , are fixed to a shaft and rotate around the center point, while the MCM plates are stationary.

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Magnetocaloric and magnetovolume effects in static and pulsed magnetic fields

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La(Fe,Si)₁₃-based compounds are among the most promising magnetocaloric materials. They show a large magnetocaloric effect at ambient temperature and have been widely studied from perspective of fundamental research and practical applications. The adiabatic temperature change ΔT_{ad} , magnetic entropy change ΔS_m and the Curie temperature T_C of La(Fe,Si)₁₃ alloys can be widely adjusted by small additions of other elements like Co, Mn or H [1,2]. At room temperature, the transition in La(Fe,Si)₁₃-based alloys is accompanied not only by high adiabatic temperature changes ΔT_{ad} (2-3 K/T) and large magnetic entropy changes ΔS_m (10-15 J/kg/K/T), but also by a large volume expansion (0.5-1.3 %). It is essential to understand and control the magnetovolume effect in these materials and aim of this work is an investigation of both magnetocaloric and magnetovolume effects in static (up to 14 T) and pulse (up to 60 T) magnetic fields.

We report on magnetization, adiabatic temperature change and magnetovolume effect of polycrystalline La(FeCoSi)₁₃ and La(FeMnSi)₁₃H_x compounds measured in both quasi-static and pulsed magnetic fields. The adiabatic temperature change and both isothermal and adiabatic magnetostriction were measured in magnetic fields up to 1.93 T and under magnetic field sweep rate up to 1 T/s. Additionally, simultaneous measurements of (i) sample temperature change, (ii) magnetovolume effect and (iii) magnetizations were performed under magnetic field sweep rate up to 0.02 T/s in magnetic field up to 14 T. For the high field experiment, the pulsed magnet produced 60 T in about 7 ms rise time (pulse duration of about 25 ms) was used and magnetization, adiabatic temperature change and magnetostriction were measured under magnetic field change rate of 1000 T/s.

Magnetoelastic interactions in the case of first-order transition, which is accompanied by para-to-ferromagnetic transition, are well described by the phenomenological theory proposed by Bean and Rodbell [3]. Here we were able to quantify the magnetoelastic coupling and, based on that, formulate the criterion distinguishing first- and second-order transitions.

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Experimental results for caloric energy harvesting

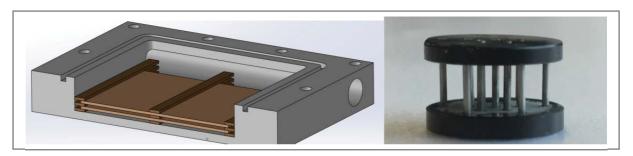
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Caloric effects are generally applied to cooling and heating cycles, but they are also applicable to power generation cycles for waste heat recovery. At the Technical University of Denmark we have built and tested proof of concept devices for both an elastocaloric [1] and a pyroelectric energy harvesters. Both systems rely on the heating and subsequent cooling of the material to give a time-varying electrical power output. The elastocaloric harvester uses the shape memory effect in Ni-Ti wire coupled to a piezoelectric actuator that converts the force actuation from the Ni-Ti into an electrical charge. The pyroelectric harvester uses PZT plates that, when heated, build up a charge on their electrodes due to a change in the polarization of the material, and that charge can be harvested as electricity. An illustration of each caloric device is shown in the figure below.

The elastocaloric device is based on Ni-Ti wires that are 0.8 mm in diameter and arranged in a staggered configuration to the fluid flow. The wires are mechanically constrained at a fixed distance with a prestrain applied. When hot water flows over the wire array, it applies a force on the coupled piezoelectric module. By subjecting the array to an oscillating flow of water that varies between 5 °C and 55 °C, the device can generate approximately 330 μ J per cycle at a potential of approximately 31 V. The pyroelectric device uses 60 mm x 60 mm x 1 mm plates that have a Curie of approximately 205 °C, making them appropriate for low grade waste heat. Heating the plates from 160 °C to 215 °C using silicone oil can give approximately 1 J of energy at a potential of 3.5 kV. For both devices, adequate power densities require relatively high frequency operation which in turn would require high thermal performance in the device.



Design of a two plate pyroelectric generator (left) and construction of the shape memory actuator (right)

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Industrial development of La-Fe-Si based magnetocaloric alloys

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Magnetic refrigeration matured significantly over the last decade demonstrating the ability to overcome many technological hurdles. Devices having a large temperature span [1] or a cooling power greater than 1 kW [2] have been built. This illustrates the various potential areas of application. In order to increase the commercial relevancy of magnetic refrigeration, machines demonstrating efficiencies comparable to current vapour compression refrigerators have to be developed. This remains the biggest challenge to date. Key to reaching this goal lies to a large extent in the intrinsic magnetocaloric performance of the alloys and the possibilities of shaping the alloys into efficient heat exchange structures. La-Fe-Si based alloys combined with production methods used in the field of powder metallurgy offer a way to tackle this challenge [3].

In this work we will present an up to date overview of the pilot production process and magnetocaloric properties of La-Fe-Si alloys. For room temperature applications the La-Fe-Mn-Si-H series reaches adiabatic temperature changes similar to Gadolinium and isothermal entropy changes up to three times that of Gadolinium. We will present production methods allowing feature sizes of less than 400 μ m and a reduced pressure drop compared to irregular particles. Net-shaping of spherical particles as well as the possibility to retain macroscopic structure after hydrogenation will be discussed.



Example structures of La-Fe-Si based alloys. Left: Bonded spherical particles, Middle: Parallel plate structures, Right: Individual plates.

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Quantifying the magnetocaloric effect from first-principles

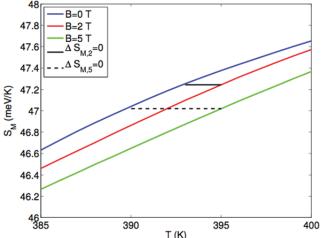
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The magnetocaloric effect may be described in terms of the adiabatic temperature and entropy change during the cooling cycle: ΔT and ΔS . In order to predict theoretically new magnetocaloric materials, or improve upon the existing ones, we need to be able to quantify ΔT and ΔS . In this talk, I will present a way for estimating these quantities from first-principles. Our approach consists in a two-step procedure: The first step is the calculation of the electronic structure and magnetic properties within density functional theory and the mapping of the magnetic interactions onto a magnetic Hamiltonian. This is later used in Monte Carlo simulations at finite temperatures and/or magnetic fields, from which ΔT and ΔS is calculated. The recipe will be exemplified for the Gd, FeRh, Fe₂AlB₂, Fe₂P, and La(Fe,Si)₁₃ systems.



T (K)
The calculated magnetic entropy for Fe2AIB2. The black full (dashed) line indicate the adiabatic cooling when reducing the external magnetic field from H = 2T (5T) for a system initially at room temperature.

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Colossal Barocaloric Effects in Organic Materials

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Environmentally friendly caloric effects near solid-to-solid first-order phase transitions promise to replace current techniques that use harmful gases, but different obstacles hinder the technological implementation of magnetocaloric, electrocaloric and elastocaloric devices, such as large required fields and breakdown. Barocaloric (BC) effects could be an alternative, provided that materials with optimal caloric performances are found. The primary property required for a giant caloric material is a phase transition with large latent heat. Transitions involving orientationally disordered (OD) phases exhibit the largest latent heat among solids, therefore promising extremely large BC effects. Here we use high-pressure calorimetry to demonstrate giant BC effects driven by hydrostatic pressure in an OD compound. The obtained values overcome by one order of magnitude the best caloric materials known so far, suggesting OD compounds as optimal BC candidates that should encourage the development of the first BC cooling prototypes.

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CaloriCool[™]: **Making a difference in calorics**

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Caloric materials encompass reversible thermal effects triggered in solids by magnetic, electric, and/or stress fields. Taken separately or together, caloric effects are in the foundation of transformative solid-state cooling technologies that have the potential to realize substantial energy savings in the United States and worldwide upon adoption and deployment by heating, ventilation, air conditioning, refrigeration, and gas liquefaction industries. In addition, caloric refrigeration offers real environmental benefits. Successful rollout of caloric cooling technologies is, however, inhibited by the unavailability of high-performing caloric solids, lack of effective material-device integration pathways, and unknowns related to scarcity of reliable economic and environmental analyses.

The caloric materials consortium – CaloriCoolTM – is a member of the U.S. DOE Energy Materials Network that aims to dramatically decrease the time-to-market for advanced materials innovations critical to many clean energy technologies. CaloriCoolTM is focused on applied materials genome-based rapid discovery of magnetocaloric, electrocaloric and elastocaloric materials, evaluation of in-device performance and most efficient pathways for material-device integration, processing and scale-up, and initial materials-centric application, economic, and environmental analyses. I will review recent progress by the Consortium in addition to a high level overview of the CaloriCoolTM organization and capabilities, goals and objectives set to be accomplished over the next five years.

CaloricCoolTM is supported by the Advanced Manufacturing Office of the Office of Energy Efficiency & Renewable Energy of the U.S. Department of Energy. Ames Laboratory is supported by the Basic Energy Sciences Programs of the Office of Science of the U.S. Department of Energy under contract No. DE-AC02-07CH11358 with Iowa State University.

Posters

Magnetocaloric effect in Ni-Mn based Heusler alloys

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A large adiabatic temperature (ΔT_{ad}) and magnetic entropy (ΔS_M) change with the application of magnetic field, called magnetocaloric effect (MCE), near the first order phase transition in Ni-Mn based Heusler shape memory alloys make them an important candidate for magnetic cooling applications. The large MCE in these alloys results from a magnetic field induced first order magnetostructural phase transition¹. However, ΔT_{ad} is not reversible upon magnetic field cycling due to the irreversibility of the first order martensite to austenite phase transition. We report here an improved reversible MCE in off-stoichiometric Heusler alloys Ni-Mn-Z (Z=Ga, In) under pulsed magnetic field. As an example figure (1) shows the almost reversible MCE in Ni_{2.2}Mn_{0.8}Ga alloy. The reversible MCE in these alloys is linked with the volume conservation and geometrical compatibility condition of martensite phase transition².

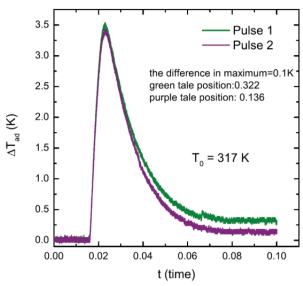


Fig.1. Time dependence of ΔT_{ad} measured at 317 K for a magnetic-field pulse of 6 T in Ni_{2.2}Mn_{0.8}Ga

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Key characteristics of well performing magnetocaloric materials from first principles

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The best performing magnetocaloric (MC) materials in magnetic refrigeration technology have Fe_2P as parent compound [1], that shows easily tunable magnetic and MC properties manifested through a first order magnetic phase transition attributed to the so called metamagnetic transition [2].

Fe₂P crystallizes in a hexagonal crystal structure possessing two inequivalent Fe sublattices, one having high magnetization the other one having low magnetization. We have shown, using density functional theory calculations, that the magnetic properties of Fe₂P are very sensitive to the "a" and "c" lattice parameters [3, 4]. In particular the low moment Fe site may become paramagnetic/non-magnetic changing the in-plane lattice parameter [3]. Similar sensitivity of the ferromagnetic order of the low moment site is found by the decoupling of this sublattice from the other high magnetization Fe site [5]. This sensitivity may lead to a first order magnetic phase transition due to metamagnetism. The highly sensitive interdependence of the magnetic properties and crystal structure as well as of the magnetization of the two sublattices are found not only in the parent system, but they are present in case of Fe₂P based alloys as well [6, 7]. Similar magneto-crystalline coupling has been identified for La(FeSi)₁₃-based compounds [8]. These results allow us to identify the key ingredients of well-performing MC material:

- the different magnetic species occupy different sublattices
- at least one of the magnetic sublattices shows stable magnetism
- at least one of the magnetic sublattices shows unstable magnetism
- substantial interdependence between the magnetism of different sublattices
- strong magneto-structural coupling.

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Optimizing (Mn,Fe)₂(P,Si) compounds for energy conversion in thermomagnetic motors & generators

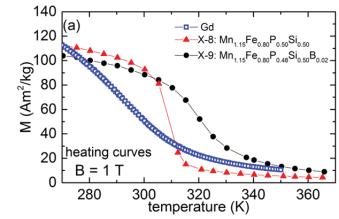
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The conversion of low-temperature waste heat (T < 200 °C) from large-scale facilities into electricity by a thermomagnetic generator (TMG) could effectively lower the total energy consumption of modern-day society and therefore improve the global environment by reducing greenhouse gasses. [1]. The first milestone towards a TMG was achieved by Swiss Blue Energy [2], who successfully developed and tested a first principle demonstrator of a thermomagnetic motor (TMM) utilizing Gadolinium (Gd), which converts the temperature-induced magnetization change into rotational energy.

Our goal is to replace Gd by an abundantly available material, which has magnetocaloric properties optimized for energy conversion resulting in higher TMM efficiencies. Promising candidates are $(Mn,Fe)_2(P,Si)$ compounds [3] typically having tunable Curie temperatures and large magnetization changes (ΔM) . In order to effectively convert waste-heat into energy a large ΔM across the magnetic transition is required. However the latent heat in the system has to be minimized, which is in contrast to magnetic cooling applications. Our study involves tuning $(Mn,Fe)_2(P,Si)$ compounds towards energy conversion applications via changing (Mn,Fe) and (P,Si) ratios, varying heat treatments and additional elements such as boron to find the right balance between a large ΔM and a low latent heat.



Temperature dependent magnetization

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Caloric effects in Heusler metamagnetic shape memory alloys

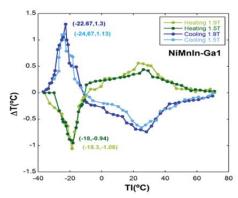
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We have shown that both conventional (MCE) and inverse (IMCE) magnetocaloric effect in the Heusler type MetaMagnetic Shape Memory (MMSMAs) is described by Landau-type theory where the exchange interactions in a system of a two magnetic sublattices have been considered [1]. MCE and IMCE in the thin ribbons of prototype $Ni_{50}Mn_{35}In_{15}$ MMSMA were measured directly by the adiabatic method to be equal to $\Delta T_{ad} = 1.1$ K at 1.9 T, in the vicinity of the martensitic transformation (MT) temperature of 300 K for IMCE, and $\Delta T_{ad} = 2.3$ K for MCE at the Curie temperature $T_{C} = 309$ K [2]. The figure shows results for the bulk $Ni_{50}Mn_{34}In_{16}(Ga)$ exhibiting narrow hysteresis of MT, about 5 K. This alloy demonstrates a cyclic IMCE with $\Delta T_{ad} = 0.75$ K under 1.9 T at 263 K during more than 1000 times.

The conventional and inverse elastocaloric effects (eCE) have been studied for $Ni_{55}Fe_{16}Ga_{29}$ and $Ni_{50}Mn_{40}Sn_{10}$ melt spun ribbons [3]. We have observed that the internal stresses alter the phase diagram of MT leading to the change of sign of stress-induced entropy change.



Magnetocaloric effect in bulk Ni₅₀Mn₃₄In₁₆(Ga) alloy

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Combined caloric effects in a multiferroic alloy with broad working region

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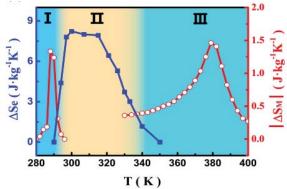
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Solid-state refrigeration based on the caloric effects of ferroic materials has attracted more and more attention. However, the refrigeration temperature regions of most caloric effects are usually in a limited scale, which has been a key drawback for applications. The earlier reports showing limited ability of broadening the refrigeration temperature region indicate that the narrow working temperature region is still a challenge for caloric refrigeration.

Our work combining the magnetocaloric and elastocaloric effects of a directionally solidified multiferroic alloy, Ni_{49.5}Mn₂₈Ga_{22.5} (at. %), achieves a large refrigeration temperature range (280-400 K) under external applying field, which is 1 T for magnetocaloric and 150 MPa for elastocaloric, respectively.

The figure plots the temperature dependence of the combined caloric effects. The obtained magnetocaloric effects showed in region I and III originate from the transformation between ferromagnetic martensite and ferromagnetic austenite and the magnetic transition in the austenite, respectively. Although there is no magnetocaloric effects in the region II from 295 K to 330 K due to the lack of the magnetic phase transition, it is in a ferromagnetic state which can be transformed into martensite by applying the stress. As a result, we obtain an elastocaloric effect in the region II and thereby achieve a broad refrigeration temperature region including room temperature.



Temperature dependence of combined caloric effects for Ni_{49.5}Mn₂₈Ga_{22.5}

The phase diagram of hexagonal Fe₂P-type materials

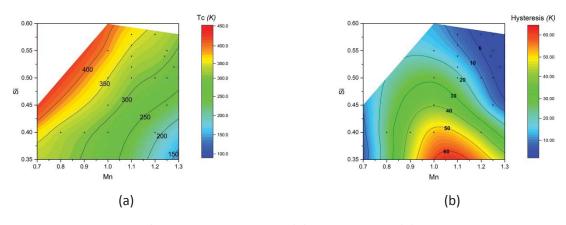
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Magnetocaloric materials (MCMs) are the "energy source" for applications of magnetic refrigeration or thermomagnetic generators (TMGs) [1]. A thermomagnetic motor (TMM) prototype, built by Swiss Blue Energy, shows the possibility of converting low-temperature waste heat to electrical or mechanical energy [2]. In order to get high efficiency, appropriate magnetocaloric materials should be used. Different from the refrigeration application, higher Curie temperature need to be optimized in MCMs for the TMGs.

Materials with matching Curie temperatures and small hysteresis may be found in the quaternary (Mn,Fe)₂(P,Si) system. Based on the phase diagram of Dung et al. [3], we extended the range of compositions towards Fe rich materials with higher T_c . The partial phase diagrams show the Curie temperature and hysteresis of MCMs crystallizing in the hexagonal Fe₂P-type structure.



Contour plots of the Curie temperature (a) and hysteresis (b) in $Mn_xFe_{2-x}P_{1-y}Si_y$ materials. The black points correspond to experimental data.

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Magnetostructural transitions in Fe-substituted $Mn_{1-x}Fe_xNiGe$ and $MnNi_{1-x}Fe_xGe$ (x \leq 0.25) compounds

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MnNiGe belongs to a class of MM'X equiatomic alloys (M, M' = transition metal; X= p-block element) which have received considerable interest in the past few years [1,2]. Here, we report structural, caloric and magnetic data for a series of Fe-substituted MnNiGe compounds prepared by arc-melting the respective elements (purity > 99.99%) followed by post-annealing at 800 °C for 120 hours. The compounds with low Fe-doping level (0 < x < 0.1) adopt the orthorhombic space group Pnma at room temperature, whereas for higher doping levels (x \geq 0.1), a hexagonal structure in space group $P6_3/mmc$ is observed. Differential scanning calorimetry (DSC) shows the presence of two distinct events for x < 0.1: a structural martensitic transformation and a magnetic para-AF/F transformation which are both tuneable over a wide temperature range (see Fig. 1). For higher doping levels (x \geq 0.1) both events overlap and result in a magneto-structural coupling. The low-temperature martensitic phase for Mn_{0.85}Fe_{0.15}NiGe exhibits a complicated magnetic behaviour due to the competition between different magnetic phases (see Fig. 2). The calculated magnetic entropy change ΔS_m for Mn_{0.85}Fe_{0.15}NiGe based on the magnetic isotherms across the magneto-structural transition is 6.46 J/kg·K and 17.06 J/kg·K for H = 2 T and 5 T, respectively.

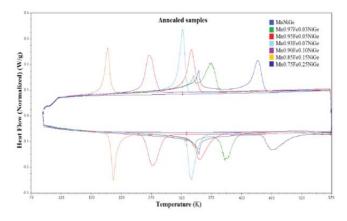


Fig.1: DSC heat flow signals for a series of post-annealed $Mn_{1-x}Fe_xNiGe$ compounds (x \leq 0.25)

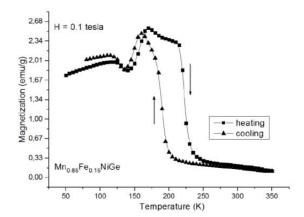


Fig.2: M(T) curves for $Mn_{0.85}Fe_{0.15}NiGe$ in an external field of H = 0.1 T.

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Double corrugated geometry used for active magnetic regenerators

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In order to increase the efficiency of magnetic cooling technologies, the magnetocaloric material (MCM) must have a geometry that enables fast and enhanced heat transfer between solid and fluid [1, 2]. Packed sphere beds and stacked plates are commonly used in various prototypes [3, 2]. Both geometries face their own issues, such as technological limitations in manufacturing plates that are thin enough or spheres that are small enough to obtain a competitive coefficient of performance (COP) [4, 2].

We present a novel active magnetic regenerator geometry based on stacked double corrugated tubes. The double corrugation has been previously described in a reference [5]. CFD simulations showed that tubes with this parametric geometry are more efficient than conventional circular tubes. Figure 1 shows the novel AMR geometry using double corrugated flow channels marked in blue (A-A and B-B cross-sections) and the MCM is marked in grey. Single blow tests are performed to investigate the effect of double corrugated channels on the performance of regenerator to be implemented in an AMR.

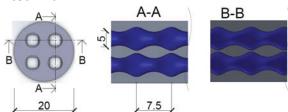


Figure 1. The top and cross-sectional (A-A and B-B) views of the regenerator with double corrugated flow channels.

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High optical quality parallel plate regenerator for heat transfer investigation

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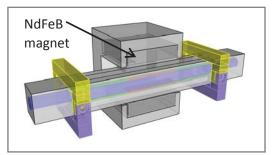
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Due to the high cost of permanent magnet, increasing energy density in present-day magnetic cooling prototypes is realized by a dense packing of magnetocaloric material (MCM). As a consequence, the flow inside the regenerator bed is usually laminar and of small Reynolds number *Re* due to a minimum viscous losses proportional to square of velocity. Thus, the poor heat transfer between the solid state refrigerant and the heat transfer fluid is one major issue limiting the increasing of working frequency of current AMRs.

To study the heat transfer in a simplified AMR, a gadolinium plate is placed in a transparent cuboid glass cell filled with the heat transfer fluid. For the latter an alkaline solution (0.5 M NaOH) was used which provides sufficient electric conductivity with vanishing corrosion of MCM. With the magnetic field as an intrinsic component in any magnetization process, a Lorentz force can be generated by introducing an electric



High optical quality flow channel.

current into the conducting fluid. Within the configuration studied, a rotational force drives a flow in the plane parallel to Gd plate which is accompanied by a toroidal-like secondary flow due to the Ekman boundary condition formed. A heat transfer enhancement in the measurement region of O(10% mA⁻¹) is found in the magnetization process with the configuration studied. It is therefore evident that the application of magnetohydrodynamic convection for heat transfer enhancement is worth to be tested in AMRs.

In order to resolve the temperature field in space and time, a channel of high optical quality is developed which mimics a section of an active magnetic regenerator with a single flat MCM. The horizontal walls of the channel are replaceable by Gadolinium plates of dimension $50\times10\times l_{thick}$ mm³ with l_{thick} 0.5 mm, 1 mm and 2 mm. The internal flow is driven by a vane pump with a maximum flow rate of 100 l/h corresponding to Re = O(3000). Heat transfer investigations are done by placing this setup in a Mach-Zehnder interferometer in conjunction with thermocouples for the temperature distribution inside heat transfer fluid and MCM, respectively.

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Control of Si content in (Mn,Fe)₂(P,Si) Single Crystals

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Magnetocaloric materials that undergo a first-order magnetic phase transition (FOMT) have attracted broad interest since they can be used in magnetic refrigeration (MR), which has potential to replace the vapour compression refrigeration due to its higher cooling efficiency and environmentally friendly features. The rare-earth free (Mn,Fe)₂(P,Si,B) alloys with a hexagonal Fe₂P-type structure have been reported to show a giant magnetocaloric effect with low hysteresis, making them promising candidates for room-temperature MR.

In order to obtain a fundamental understanding of the magnetic and the magnetoelastic coupling of this alloys, several attempts have been made to grow $(Mn,Fe)_2(P,Si)$ single crystals [1,2]. It has been reported that $(Mn,Fe)_2(P,Si)$ single crystals that show a FOMT can be grown by the flux method [1]. However, the stoichiometry of the crystals turns out to be difficult to control, especially keeping the metal:metalloid ratio as 2:1 and a high Si content.

Here, we report different annealing conditions for the flux method, aiming to control the P/Si ratio of the $(Mn,Fe)_2(P,Si)$ single crystals, in order to tune both the strength of the FOMT and the Curie temperature.

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Development of an innovative rotary magnetic heat pump prototype

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Various Researches on room-temperature (RT) magnetocaloric materals (MCM) mainly focus the material properties such as magnetic entropy change (ΔS), Curie temperature (T_c), hysteresis $(\Delta T_{hvs}/\Delta H_{hvs})$, etc. However, to study how these properties affect the actual cooling or heating performance in a realistic environment, complementing innovation has to be made on the experimental devices. Therefore, here we present a RT magnetic heat pump prototype design especially for this purpose. As shown in Fig.1, this prototype is a rotary-type device which is based on the active magnetic regeneration (AMR) cycle. Two symmetrically placed fan-shaped magnetic structures are used to generate an average magnetic field of 0.875 tesla within a volume of 0.71 L. To neutralize the sudden change of the torque when the regenerators entering and exiting the magnetic field, an asymmetric bracket with seven regenerators is applied. With the special designed fluid disperser in the AMR bed, the reciprocating flow is homogeneous distributed perpendicular to the flow direction. The MCM packed bed is fabricated with an original 3D printing assisted mold-casting technology, which ensures not only the fine regularity but also the low pressure drop of the microchannels in the MCM pack structure. The timing of each flow period for different regenerators is controlled by a series of solenoid valves, which ensure the possibility of adapting the system to varying requirement of experiments. Last but not least, a comprehensive performance measurement system is imbedded for data collection.



Fig 1. The overview of the prototype

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A numerical analysis of an active magnetic regenerator

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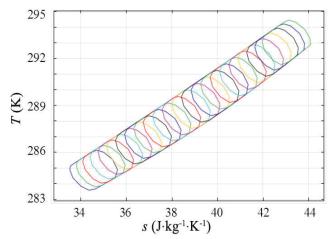
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To achieve a temperature span comparable to conventional refrigeration, active magnetic regenerator (AMR) is widely used in room-temperature magnetic refrigerator. In this study, a two-dimensional transient model of an AMR has been established. The model's geometry is in the form of parallel plates. Gadolinium and water have been used as refrigerant and heat transfer fluid respectively. The basic governing equations [1, 2] in the numerical model include mass and momentum conservations of heat transfer fluid and energy conservations of fluid and magnetic refrigerant. Magnetocaloric effect (MCE) has been taken into account as an internal heat source in the energy conservation equation.

The model simulates the working process of AMR and evaluates the performance in the terms of COP, temperature span, cooling load and pressure drop for different parameters of parallel plates. By tracing particles at different position in the AMR, a more realistic T-s diagram of magnetic refrigeration cycle is obtained.



T-s diagram of a realistic magnetic refrigeration cycle with AMR

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Experimental performance of different gadolinium-based active magnetic regenerators

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Room temperature magnetic refrigeration is a newly-developed and environmental-friendly refrigeration technology [1], which is widely known as one of the alternative technology. Although many prototypes have been constructed and studied recently, it is still very necessary to do further research on geometric configurations in the active magnetic regenerator.

The paper compared the operating performance of active magnetic regenerators (AMRs) respectively filled with magnetic refrigerants in four different geometric characteristics, including parallel plate, wire-cutting bulk, powder and sphere. A compact rotary type room temperature magnetic refrigerator was used as the testing apparatus [2]. It mainly consisted of a rotating Halbach permanent magnet array with 1.3 T maximum magnetic field and a static AMR with 184 mm maximum filling length. Using four kinds of gadolinium as the refrigerant and NaOH solution as the heat transfer fluid, no-load temperature spans of AMRs are acquired at different operating frequencies and utilization factors. The results show that AMR with Gd spheres (0.50-0.80mm) generated a maximum temperature span of 13.3 K at 0.6 Hz operation frequency. A cooling power of 20 W was obtained when the temperature span was 2.1 K at 0.4 Hz operation frequency and 0.49 utilization factor.



Photograph of four Gd-based active magnetic regenerators

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Numerical analysis of the influence of flow maldistribution on both ends of active magnetic regenerator

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Active magnetic regenerator refrigeration (AMRR), which is based on magnetocaloric effect (MCE), is a promising alternative to gas compression refrigeration because of its eco-friendliness and high efficiency. As summarized by Nielsen et al. [1], a number of researchers numerically studied the performance and the operation of magnetic refrigeration. Among these numerical researches, to improve performance of magnetic refrigeration, many factors such as flow maldistribution and demagnetization effect have been considered and studied [2]. Flow maldistribution may seriously deteriorate the effectiveness of magnetocaloric material. Therefore, the flow in regenerator must be as uniform as possible.

This work focuses on studying the phenomenon of uneven flow at the both ends of the regenerator. A two-dimensional transient model of magnetic refrigerator including the active magnetic regenerator, cold and hot heat exchanger has been developed with Comsol 5.2. Two cases were considered. The diameter ratio of the regenerator to heat exchanger was 6. Case 1 did not include transitional area at both ends of regenerator while case 2 included. Compared with case 1, the flow was more uniform in case 2, which, consequently, resulted in an increased no-load temperature span by 19 percent (Fig. 1).

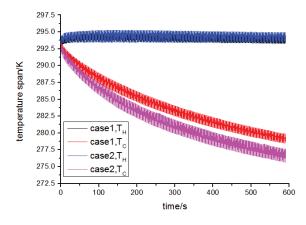


Fig. 1. Time evolution of the temperature span at no cooling load obtained by the two cases.

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Modelling Thermal Waves Propagation in Static Cascade Electrocaloric Based Cooling Device

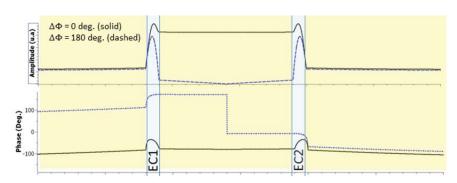
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Due to the increasing energy demand and the related environmental issues, a large activity of research is carried out for allowing the exploitation of physical phenomena for cooling applications, in replacement of refrigerant fluid based devices. The magnetocaloric effect is probably one of the most known and studied so far. More recently, electrocaloric effect (ECE) has attracted attention after the discovering of a large ECE [1] making this effect useable for cooling application. This last has many advantages compared to magnetocaloric effect for instance, as the control of electric field is much easier than for the magnetic field. Few concepts have been proposed for ECE based cooling devices. Among them, the "cascade principle" looks like very promising [2]. It makes use of a series of stacked electrocaloric materials sandwiched between thermal conductor or active thermal switches.

In this work, we have developed a semi-analytical model based on the Rosencwaig-Gersho theory developed for thermal waves modelling in photothermal application [3]. It allows the study of the temperature oscillation dependence (amplitude, phase) as a function of the thermal (diffusivity, effusivity) and geometrical (thickness) properties of the layers. It is also possible to change ECE intensity (power density) of each EC material layers as well as the polarization phase delay between them, which is of most importance in static cascade concept [2]. We believe that this tool will help for the design of performant static cascade based cooling device.



Amplitude et phase of temperature oscillations in a 5 layers system with two EC layers.

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Simulation of a Magnetocaloric Heat Pump in Building Technology

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Increased quality of building envelope in the last decades leads to decreased heating demands of new buildings and therefore heating devices with lower heating powers are needed. There is a lack of suitable solutions in the heating market in the small power range, which can cover small heating loads decentral without distribution losses. In the presented study, the potential of magnetocaloric heating is investigated. Apart from the advantage that no climate-relevant gases are used compared to commonly used compression heat pumps, this technology is suitable for covering low heating requirements. A cornerstone of the investigation is the development of a program for simulating the behaviour of a building-integrated magnetocaloric heat pump. Target is to determine the effect of the change in basic properties such as the nature of the magnetocaloric material, the magnetic flux density, the working frequency, etc., but also to determine the influence of building parameters on the overall efficiency of the heating system. In order to validate the simulation results, the integration of a magnetocaloric heat pump prototype into the heat pump test bench of the University of Applied Sciences Pinkafeld [1] is intended for the future. This test bench with a focus on electrically driven heat pumps and chillers can be used to simulate realistic conditions like part load behaviour, stand-by-losses, on/off behaviour or user/weather conditions by using different kind of building models and will allow the effective optimisation of the simulation program.



Heat pump test bench of the University of Applied Sciences Pinkafeld.

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Towards a scale bridging understanding of transformation hysteresis in magnetocaloric Heusler alloys

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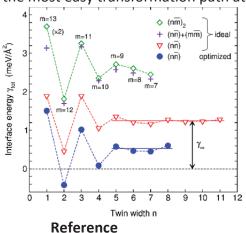
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Ferroic phase transitions driven by external magnetic, electric or stress fields promise more energy efficient solid state refrigeration. A key step towards this environmentally friendly technology was the use of first instead of second order phase transitions, which substantially increased the associated entropy change. However, a drawback of first order materials is the transformation hysteresis, which heats up the material and thus reduces or even eliminates the efficiency of a solid state cooling device. Here the structural and microstructural origin of hysteresis exemplarily for Heusler alloys will be analyzed. Starting point is the transient coexistence of both phases, which requires the formation of interfaces between both phases. As these interfaces disappear when the complete sample has transformed, the associated interface energy contributes to the hysteresis loss. In case that the transformation is associated with a reduction of crystal symmetry, the formation of a nanotwinned microstructure minimizes the interface energy. We will show that ordering of nanotwins contributes to about half of the hysteresis losses [1]. In addition the elastic energy from the volume change at the transformation is dissipated twice during a cooling cycle. These contributions to hysteresis will be used to sketch the microstructural features formed during the transformation. The hierarchical microstructure reflects that the system tries to find the most easy transformation path at all length scales.



Oscillating interface energy of nanotwin boundaries γ separated by n martensitic building blocks calculated by DFT. Independent of the particular arrangement (ideal, symmetric, asymmetric, optimized) a pronounced minimum of interaction energy is observed for n=2. Thus this twin width is energetically favoured, which explains why all observed modulations contain this particular spacing. As minimization of total twin boundary energy occurs during ordering, part of the interaction energy is dissipated during a martensitic transformation, which explains a significant contributes to hysteresis losses..

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Profile-matching optimization of the remanence directions of a magnetic circuit

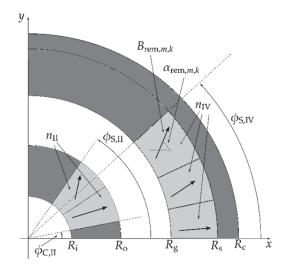
Fábio P. Fortkamp, Jaime A. Lozano, Jader R. Barbosa Jr.

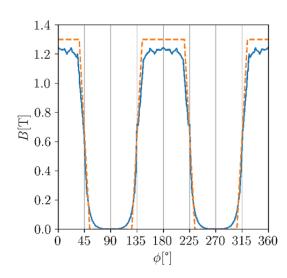
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The canonical thermodynamic cycle for active magnetic regenerators (AMR) is the Brayton cycle, which has shown to maximize the cooling power of AMR devices [1]. However, it can be challenging for permanent magnet-based magnetic circuits to yield the required magnetic profile of having large intensities of magnetic fields followed by almost no-field regions. In this work, we present a parametric model for a magnetic circuit composed by segments of iron and NdFeB, as that shown in the left Figure below, and an optimization procedure for the remanence direction of the magnet segments ($\alpha_{\text{rem},m,k}$) with the objective of matching the resulting magnetic profile to a target profile.

Using a linear model, the principle of superposition can be applied [2] and only a minimum number of finite element simulations are necessary. Results for a sample combination of parameters are shown in the right Figure below.





Left: Model for the magnet design; Right: Results for the optimal magnetic profile

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Magnetocaloric test-bench with an optimized Halbach permanent magnet made from recycled Nd-Fe-B

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The fundamental magnetocaloric properties of most materials are well known. Nevertheless, there is a lack of knowledge on how these properties translate into a performance in a realistic environment. However, this knowledge is crucial to identify the bottlenecks that are hindering magnetocaloric cooling from further progress. In order to assess the cooling performance of different materials under realistic application-near conditions, we built a demonstrator for magnetocaloric materials (see figure 1). This work will show the thermal span in the demonstrator with stacks of materials with properly arranged transition temperatures. These materials include La-Fe-Si-type compounds produced with new shaping and bonding techniques [1].

At the same time, we improved the ecological footprint of the demonstrator by using recycled Nd-Fe-B for the permanent magnet source. This step is necessary to be able to compete with conventional cooling [2] and shows the performance of recycled Nd-Fe-B.



Figure 2: Photo of the demonstrator at TU Darmstadt

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Dynamics at the metamagnetic transition in La(Fe,Mn,Si)₁₃ magnetocaloric compounds

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Magnetocaloric material systems for environmentally friendly and energy-efficient solid-state magnetic cooling require a magnetic phase transition which can be induced by relatively small magnetic fields (<0.5 T: within the range of cheap permanent magnets) concurrent with a large magnetic entropy change and a large adiabatic temperature change. Those exhibiting a phase transition of first-order type have the potential to fulfil these criteria, such as La(Fe,Si)₁₃-based compounds which are promising contenders due to the wide tunability of their working temperatures in response to compositional variations, and small intrinsic hysteresis which results in reduced energy losses in a cooling cycle [1].

In a working cooling device, the high cycling frequencies necessary in order to compete with existing technologies require the timescales for the transition, heat exchange with the exchange fluid/gas and cyclic movement of this fluid to all be on the order of tens of milliseconds. The transition of La(Fe,Si)₁₃ is known to demonstrate dynamic growth characteristics on the timescale of seconds to minutes, both as a time dependent response to driven field and by relaxation [2]. Additionally, so-called "avalanche" periods of accelerated growth between metastable mixed states have been observed indicative of a complicated free energy landscape on the local scale [3]. Understanding the mechanisms responsible for these slow dynamic effects is very important as a step towards achieving these fast timescales. We study both the microscale and macroscale dynamic behaviour of compounds of Mn-doped La(Fe,Si)₁₃ using magnetometry and a calorimetric method which can separate the contributions from heat capacity and latent heat. A field rate independent microscale dynamic signature of separate transition events is observed in the latent heat, which progresses faster with improved thermal coupling to the surroundings and which we show has no impact on the intrinsic heat release, but becomes rate dependent as we move towards the macroscale. We explore this dynamic aspect in terms of thermal linkage, microstructure and the strength of first-order character.

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Small-scale production of CALORIVAC® spherical granules

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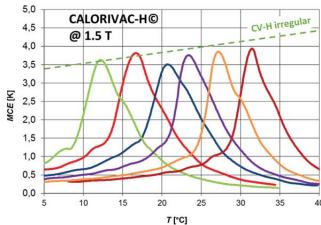
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The overall efficiency of a cooling device based on the magnetocaloric effect relies on the individual performance of its components. In the case of the refrigerant material, not only its magnetocaloric properties but also its shape strongly influences the performance of the device. The demand for cooling aggregates with defined structures, which reduce the losses due to pressure drop while ensuring an efficient heat exchange, is one of the main current challenges in the field of magnetic cooling.

Spherical granules are perhaps the best compromise between performance, losses and costs up to date. VAC's response to the increasing demand for spherical shapes is the development and production of granules of the LaFeSi-based high-performing grade CALORIVAC- H^{\otimes} , which until recently has only been available as irregular particles.

In this work a comparison between two processes for the production of CALORIVAC-H $^{\odot}$ granules is presented. The fluidized bed granulation and the extrusion/spheronisation processes are described and their results compared. The extrusion/spheronisation technique has been further developed for the small-scale production of granules with diameter ranging from 400 to 1200 μ m, depending on the dies used. Even though organic additives are used during shaping, the produced granules show low impurity levels (O<0.5 wt.%, C<0.05 wt.%) and therefore good magnetocaloric properties comparable to irregular CALORIVAC-H $^{\odot}$ particles. Heat treatment including hydrogenation does not affect the form of the granules yielding quasi-spherical particles with good mechanical stability.





Left: CALORIVAC-H© granules produced at VAC. Right: Typical adiabatic temperature change of the produced spherical particles

Magnetism, Ferroelectricity and Caloric Effects in SrMnO₃

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Recently, immense research efforts have been aimed at finding ferroic materials with large magnetocaloric or electrocaloric effects for cooling technology [1]. Meanwhile, magnetoelectric multiferroics, exhibiting coexistence of magnetism and ferroelectricity, have attracted much attention within fundamental and applied research. Caloric effects in ferroic materials tend to be large near the critical temperature of the phase transition [1]. Consequently, in a multiferroic material with similar critical temperatures for the magnetic and ferroelectric phase transitions, interesting and novel phenomena resulting from the interplay between magnetocaloric and electrocaloric (multicaloric) effects can be expected [2]. Computational work [3], with experimental corroboration [4], suggested that epitaxial strain can produce ferroelectricity, and possibly also ferromagnetism, in the otherwise paraelectric antiferromagnet SrMnO₃, making it a potentially interesting candidate material to explore such effects.

In this work, the strain-induced ferroic phase diagrams in SrMnO₃ are explored using computational methods based on density functional theory (DFT), in combination with classical Monte Carlo (MC) and molecular dynamics (MD) [5]. This allows the identification of a region in the strain-temperature space that is promising for exploring multicaloric effects. Furthermore, the coupling between magnetism and ferroelectric structural distortions are studied, aiming at a realistic description of multicaloric effects, starting from first principles calculations.

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Structural and magnetic phase transformations and magnetocaloric effect of Cu substituted MnCoGe compounds

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Structural and magnetic phase transformations and magnetocaloric effect of Mn and Co substitutions by Cu in MnCoGe compound have been investigated using X-ray diffraction, differential scanning calorimetry and magnetization measurements. Increase in Cu concentration rapidly reduces the martensitic structural (T_{str}) magnetic (T_C) phase transition temperatures [1, 2]. However, nearly a double amount of Co substitution is required as compared to that of Mn for an equivalent change in the T_{str} and T_C . A giant magnetocaloric effect ($-\Delta S_m^{(max)}$) > 40 $J.kg^{-1}K^{-1}$ for $\Delta B = 5$ T), resulting from the coupling of the concomitant structural and magnetic transformations, near room temperature has been obtained for around 10 at.% of Mn substitution by Cu. Fine tuning of Cu concentration (20 at.%) in case of Co substitution also resulted in concurrent structural and magnetic transitions at around 260 K. However, the absence of magnetostructural coupling led to a peak entropy change of less than 3 $J.kg^{-1}K^{-1}$. Samples with the Co-substitution of 15 at.% or higher showed complex magnetic behavior, indicating a completion between antiferromagnetic and ferromagnetic interaction [3]. A comparative study of the various phase transitions and the magnetocaloric effect in the Co- and Mn-substituted samples will be presented and discussed.

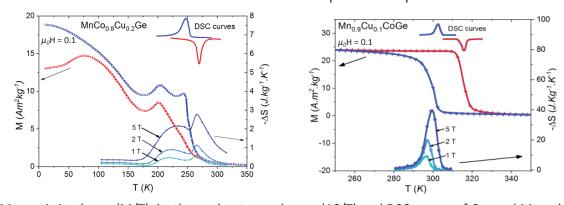


Fig. 1: Magnetic isotherm (M/T), isothermal entropy change (Δ S/T) and DSC curves of Co- and Mn-substituted MnCoGe samples.

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Danish Days on Caloric Materials and Devices Technical University of Denmark, Risø Campus, 2-3 October 2017

Design of a compact rotating magnetic refrigerator

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The design of a magnetocaloric effect (MCE) refrigerator is a challenging problem. The task turns out a lot more demanding if the target includes a wide temperature span, a compact design and including a modular graded active magnetic regenerator (AMR) that allows using different magnetocaloric material (MCM) combinations.

A modular, graded AMR has been designed to allow the use of shorter AMR stacks, lowering in this way the pressure loss. The AMR consists of eight beds covering 45° each, with alternative activation in groups of four. The magnet is rotated by means of a slewing ring gear and the core, the AMR and, therefore, the fluid distribution system are static; no fluid rotary valves are needed.

Fluid flow is controlled by means of high speed solenoid valves, which allow the control of the fluid flow sequence by means of software. These valves have a response time of about 20 ms and allow flows of 0.2 I/s at a pressure of 8 bar. The working cycle includes four steps: magnetization with blow, static heat balancing, demagnetization with opposite blow, and static heat balancing. The fluid flow is unidirectional, with no dead volumes. The global flow is constant, but the alternative use of half of the beds, allows the static heat balancing steps. The eight AMR beds work in parallel pairs connected in series with another pair, with the cold spot in between. The cold spot consists of a block of four soldered copper circuits that allow good thermal contact but no fluid mix. Most of the fluid circuit's elements remain on the hot side to further reduce thermal losses in the cold side.

The magnet design follows the general configuration described in [1]. It has been optimized in angular width and direction of each NdFeB sector's magnetization, resulting in B_{max} =1.86 T, B_{min} =0.003 T and, for each 45° sector of the AMR, $\langle B_{max} \rangle$ =1.71 T and $\langle B_{min} \rangle$ =0.015 T.

Small spheres of MCM with first and second order transitions are used and they have been modelled to carry out simulations using a modified version of the procedure described in [2].

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Reversibility of minor hysteresis loops in magnetocaloric Heusler alloys

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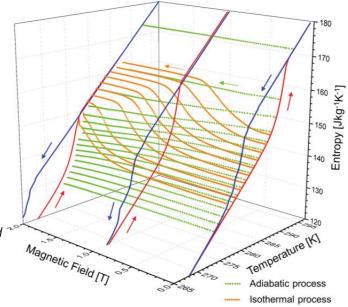
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Common magnetocaloric materials like Gadolinium warm up when magnetized due to the partial alignment of the magnetic moments which is called conventional magnetocaloric effect. Larger effects are observed when the character of the magnetic state change is accompanied by a structural conversion which is referred to as a magnetostructural transition [1]. However, the unavoidable existence of thermal hysteresis in magnetocaloric materials with a first-order phase transition is one of the central problems limiting their implementation in cooling devices. Using minor loops, allows to achieve significant cyclic effects even in materials with relatively large hysteresis [2]. Here, we compare calorimetric measurements of the isothermal entropy change ΔS_T [3] and thermometric measurements of the adiabatic temperature change ΔT_{ad} [4] when moving in minor hysteresis loops driven by magnetic fields. Under cycling in 2 T, the Ni-Mn-In-Co Heusler material provides a reversible magnetocaloric effect of $\Delta S_T^{\text{rev}} = 10.5 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{ad}^{\text{rev}} = 3.0 \text{ K}$. Even though the thermodynamic conditions and time scales are very different in adiabatic

and isothermal minor loops, it turns out that after a suitable scaling, a self-consistent reversibility region in the entropy diagram is found. This region is larger than expected from basic thermodynamic considerations based on isofield measurements alone which opens new opportunities in application.

3D plot of the S(T,H) diagram. The red and blue curves indicate the entropy in 0, 1 and 2 T under heating and cooling. The green and orange dotted lines are the transition paths under adiabatic and isothermal conditions.



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First-principles-based investigation of the electro-caloric effect

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The electro-caloric effect (ECE), i.e., a temperature change observed in certain materials under application or removal of an electric field, provides a very attractive prospect for future solid state cooling devices. Here, we use molecular dynamics simulations based on an effective Hamiltonian derived from first principles, to study the ECE in the prototypical ferroelectric material BaTiO3 (BTO) [1]. Our studies allow to gain a better understanding of the underlying mechanisms and to identify routes for optimizing the electro-caloric response towards future device applications.

We analyze the ECE in the vicinity of all three ferroelectric transitions in BTO, and we discuss in particular the origin of an inverse ECE (i.e., decreasing temperature under application of an electric field) that occurs for certain orientations of the applied field [2]. We also discuss effects of irreversibility that results from the first order character of the ferroelectric transitions.

Furthermore, we explore ways to optimize the caloric response through epitaxial strain in thin films of BTO [3]. We show that strain can be used to shift the largest caloric response to both higher and lower temperatures, depending both on the type of strain (compressive or tensile) and on the orientation of the applied field. Furthermore, our results indicate an enhanced caloric response due to strain-induced multi-domain formation.

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Hysteresis on the magnetic phase diagram of Ni-Mn-In Heusler alloys near room temperature

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A well known technological issue for an efficient room temperature magnetocaloric effect (MCE) is to obtain materials which, cycled in magnetic fields below 2 T, have large isothermal entropy changes (ΔS_{iso}) and a thermo magnetic hysteresis not limiting the adiabatic temperature change (ΔT_{ad}). The Ni-Mn-In based Heusler alloys can be designed to have large MC properties by exploiting their magneto structural phase transition from a low temperature and low magnetization martensitic phase (MT) to a high temperature ferromagnetic austenitic phase (AU), which results in a inverse MCE near 294 K. However, in the martensitic transition, due its first order nature, the hysteresis always exists [1]. We perform a study on off stoichiometric compositions close to the Ni₅₀Mn₃₅ln₁₅ [2] having the MT to AU structural phase transitions gradually nearing the Curie temperature of the austenitic phase ($T^{AU}_{c} \approx 312$ K). By following the thermal and magnetic hysteresis of the transitions we show how the hysteresis is affected by the magnetic field and by the composition, i.e. increases as function of the distance from T^{AU}_{c} . In this context, in field calorimetry and direct adiabatic temperature change measurements are performed to reveal the reversible and irreversible contributions to the MCE.

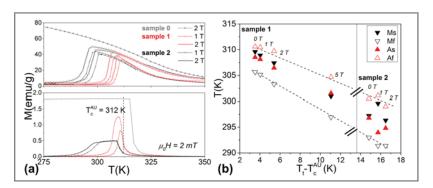


Figure: a) In field magnetization curves of $Ni_{50}Mn_{35}In_{15}$ based alloys with slight changes in the three elements (sample 0 shows only the austenitic phase, sample 1 and 2 have the MT close to T^{AU}_{c} . b)

Transition temperatures as a function of the distance from T^{AU}_{c} .

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Characterization and modelling of the first-order magnetoelastic transition in a Mn-Fe-P-Si magnetocaloric material

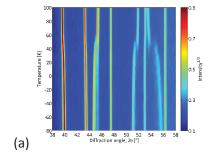
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The Mn-Fe-P-Si system is considered as a promising candidate for solid-state cooling and thermomagnetic energy conversion. Simulation of the related thermodynamic cycles needs reliable models of the active materials [1]. As we showed earlier [2], the magnetoelastic isostructural phase transition can be described by a simple Landau model. In this presentation the experimental results and corresponding model parameters obtained for the $Mn_{1.24}Fe_{0.71}P_{0.46}Si_{0.54}$ compound suitable for thermomagnetic applications (above room temperature) are reported.

Magnetocaloric powder was prepared using ball milling followed by heat treatment. Physical properties of the obtained single-phase material were examined in the temperature range of the first-order transition by X-ray diffraction (XRD, Co K α radiation), differential scanning calorimetry (DSC) and vibrating sample magnetometry (VSM). Figure (a) shows the XRD patterns of the Mn-Fe-P-Si powder (mixed with reference silicon to improve accuracy) versus temperature on heating. Figure (b) presents the magnetization as a function of temperature in different fields.



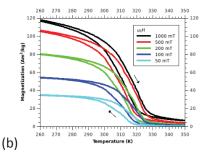


Figure: (a) Temperature-dependent XRD patterns; (b) magnetization versus temperature for different fields.

The Rietveld refinement of the diffraction profiles was used to determine the evolution of the crystal lattice parameters with temperature and the volume fractions of the paramagnetic and ferromagnetic phases. Then, an equation of state of taking into account hysteresis was derived from the thermal and magnetic measurements. The thermodynamic description of the first-order phase transition in Mn-Fe-P-Si is given in terms of the Landau model with magnetoelastic coupling, the procedure of fitting the phenomenological parameters to the experimental data is explained.

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Electron-phonon coupling in LaFe_{13-x}Si_xH_v

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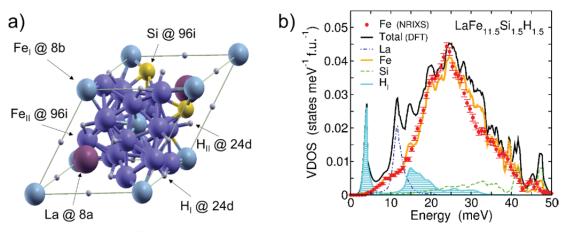
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Fully hydrogenated La-Fe-Si is one of the most interesting candidates for room temperature magnetic refrigeration. The first order nature of the magnetic transition is connected to its itinerant electron metamagnetism, which relates to a particular coupling between the microscopic degrees of freedom. By combining first principles calculations in the framework of density functional theory (DFT) and nuclear resonant inelastic X-ray scattering (NRIXS) we investigate the interplay of electronic structure, magnetism and vibrational degrees of freedom in fully hydrogenated La-Fe-Si. We demonstrate that the adiabatic electron-phonon coupling which leads to a cooperative contribution of magnetic, electronic and vibrational degrees of freedom to the entropy change in the non-hydrogenated La-Fe-Si [1] and is thus responsible for the superior magnetocaloric properties, is again important for the hydrogenated compound. Since full loading with hydrogen involves the occupation of only a part of the available 24d sites, we also discuss the site-occupation of hydrogen based on total energy calculations and by comparing vibrational density of states from DFT involving different distributions of hydrogen with the NRIXS measurements.

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a) Primitive cell with different hydrogen sites. b) Element-resolved vibrational density of states of hydrogenated La-Fe-Si in the ferromagnetic phase from NRIXS (Fe-partial) and DFT (all contributions).

On the interactions of single La(Fe,Mn,Si)₁₃H particles

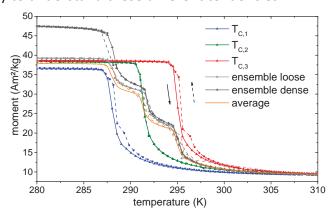
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Beds of layered working temperatures are considered to increase the working temperature span of magnetocaloric regenerators [1]. Both packed beds and stacked plates are suggested as regenerator geometries, in these cases there will be interactions of areas with different working temperature, either on the interfaces of layers or within one layer, e.g. due to inhomogeneous chemical composition.

In this work the interaction between regions of different chemical composition and therefore a variation of the Curie temperature T_C are analyzed in idealized experiments: The magnetic transition behaviour of three nearly spherical particles of La(Fe,Mn,Si)₁₃H (CALORIVAC H supplied by Vacuumschmelze) are studied by magnetometry. There are two series of particles, with a T_C distribution of ± 3.5 K and ± 1 K, respectively. In order to investigate their influence among each other, the distance between the particle ensemble has been varied. It is known that single particles have a higher adiabatic Temperature change compared to powder [2]. On the other hand it is reported, that a collaborative behaviour of particles in a so called interlocked state appears [3]. With this work we try to understand these different tendencies.



Temperature dependent magnetisation of 600 μ m particles with three different Curie temperatures ($T_{C,1-3}$), the calculated average, both the loose and the dense packed particles. Cooling curves are indicated dashed, heating with full lines. The magnetic field was $\mu_0 H = 0.1 T$.

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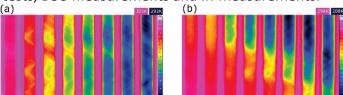
Cobalt gradient evolution in sputtered TiNiCuCo films for elastocaloric cooling

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DC magnetron sputtered Ti-rich TiNiCuCo films show a high functional stability for more than 10' cycles and adiabatic temperature changes larger than 10 K [1-2]. To be on a competitive level with conventional vapour compression technology, temperature spans ~ 30 K are needed. The principle of active regeneration allows exceeding the intrinsic adiabatic temperature change of the material, as recently shown by Tušek et al. in a device using NiTi shape memory alloys. A temperature span of 15.3 K was measured between the hot and cold side of the demonstrator [3]. According to the Clausius Clapeyron equation, a temperature gradient leads to a change in the thermomechanical response along the regenerator bed and in case of TiNiCu to an additional stress of approximately 300 MPa for a ΔT =30 K. This in turn will lower the efficiency and increase the risk of failure due to structural and functional fatigue. To solve these issues a transformation temperature gradient along the flow direction of the cooling liquid in the regenerator is needed. Chluba et al. showed that by adding Cobalt to TiNiCu it is possible to lower the transformation temperature by 21 K at.%⁻¹ Co [2] without influencing the functional stability. Multilayer dc magnetron sputtering of TiNiCu and Co can be used to a create transformation gradient along a SMA film. By adjusting the process parameter a transformation gradient of 0.3 K mm⁻¹ can be established. The influence on the mechanical properties and the elastocaloric properties will be discussed using tensile tests, DSC-measurements and IR-measurements.



IR images showing the reverse martensitic transformation in a TiNiCuCo film without (a) and with (b) transformation gradient.

Acknowledgements: Funding by the DFG priority program SPP1599 ferroic cooling is gratefully acknowledged. **References**

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Application of Ni-Mn-In Heusler alloys second order transitions to room temperature magneto-cooling

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An efficient room temperature magneto-cooling device requires materials with large isothermal entropy (ΔS_{iso}) and adiabatic temperature (ΔT_{ad}) changes at T \approx 293 K and null (or negligible) thermo-magnetic hysteresis when cycled in a magnetic field below 2 T. With this in mind, we focused our studies on Ni₂MnIn based Heusler alloys with a direct MCE at the second order Curie transition [1]. The starting composition, i.e. Ni₄₈Mn₃₆In₁₆, has the austenite ground state and the highest saturation magnetization among the off stoichiometric compositions based on Ni-Mn-In (125 emu/g at 80 K)[2]. This composition is further optimized for room temperature operation by substituting iron and copper at Mn sites, which, respectively, enhance the magnetization values and lower the Curie temperatures. The direct MCE across a series of Ni₄₈Mn_{36-x-y}InCu_xFe_y can be tuned in a broad temperature range around room temperature (figure 1) and the ΔT_{ad} can be optimized by improving the microstructure and composition homogeneity to around 1 K in 1 T. The experimental ΔT_{ad} curves are used in simulations based on the finite differences method to evaluate the refrigeration capacity of a magneto-cooling prototype based on a rotating MC disk.

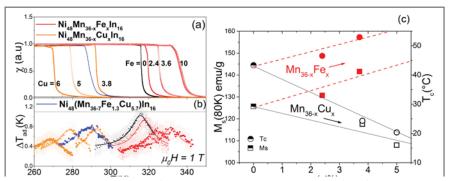


Figure 1: a) Magnetic susceptibilty and b) adiabatic temperature changes of quaternary and quinary alloys based on $Ni_{48}Mn_{36}In_{16}$. c) Saturation magnetization and T_c as a function of Fe and Cu substitution vs Mn sites.

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Structural and magnetic proprieties of magnetocaloric Ni₁₋ _xZn_xFe₂O₄ (0≤x≤1) ferrite synthesized by co-precipitation method

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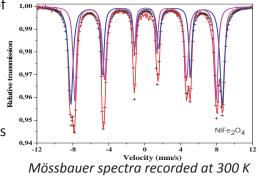
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Spinel ferrites nickel zinc are among the most widely used magnetic materials because of their low cost, high electrical resistivity, high magnetic permeability, high saturation magnetization, chemical stability and their magnetocaloric effect.

In this work we present the effect of Zn substitution on the structural and magnetic properties of Ni ferrites. The $Ni_{1-x}Zn_xFe_2O_4$ ferrites nanoparticles, with x=0, 0.2, 0.4, 0.6, 0.8 and 1, were synthesized using co-precipitation method. The powder samples calcined at the suitable temperature were characterized by X-ray diffraction, transmission electron microscopy and transmission Mössbauer spectrometry. The X-ray diffraction patterns results reveal the formation of single phase spinel. The average crystallite size, calculated using Scherrer's formula, was found to be ranging from 20 to 26 nm. These values are in good agreement with those deduced for transmission electron microscopy observations. The lattice parameters were found to increase from 8.33 to 8.43Å with increasing zinc content which can be attributed to the larger ionic radius of zinc. The cubic structure with space group Fd3m was confirmed by the refinement of the X-ray diffraction patterns using Rietveld method.

The Mössbauer spectra recorded at room temperature, of the powders, show that ZnFe₂O₄ and Ni_{0.2}Zn_{0.8}Fe₂O₄ phases exhibit a paramagnetic behavior and their spectra consist only of a central doublet. For the other contents of Zn, the Mössbauer spectra are adjusted by superposition of two sextets, with different areas, due to Fe³⁺ at tetrahedral and octahedral sites. Fig.1 shows a typical spectrum for this series. All the hyperfine parameters are determined for each spectrum. The work will be completed with magnetic measurements recorded at different temperatures, using SQUID, in order to study the magnetocaloric effect of our samples.



of NiFe₂O₄ calcined at 1000 ° C

Magnetocaloric behavior in perovskite manganites $Y_{0,8}Fe_{0,2}MnO_3$

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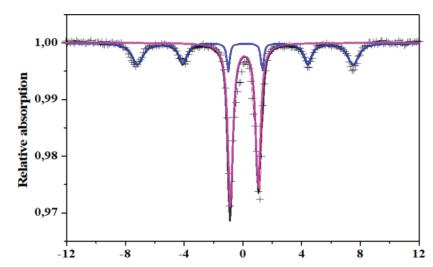
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This work concerns the study of new manganite materials of perovskite structure which can have a large magnetocaloric effect under low applied field and around room temperature. $Y_{1-x}Fe_xMnO_3$ is attracting great attention due to their higher chemical stability, high resistivity and more importantly the ability to tailor their magnetic transitions temperatures close to room temperature. These properties suggest that this system maybe a possible candidate for low temperature magnetic refrigeration. The $Y_{1-x}Fe_xMnO_3$ —nanomaterials were carried out by the combustion reaction process and the synthesized products were finally annealed in air for 2h at different temperatures in the range 1100 - 1300°C. The crystalline phase of the as-prepared materials was identified by powder X-ray diffraction technique. These analyzes were completed by scanning electron microscopy observations. Magnetic measurements were performed by Transmission Mössbauer Spectrometry and Superconducting Quantum Interference Device.

The result that we present here concern the sample $Y_{0,8}Fe_{0,2}MnO_3$ annealed at 1200°C. So, the X-ray diffraction measurements showed the formation of single phased and the diffraction peaks have been easily indexed according to hexagonal structure. The Mössbauer spectrum collected at

temperature room is the superposition of two components (Fig.1). One sextet of low weight and paramagnetic quadruple doublet corresponding to Fe³⁺ ion. The results will be completed by **SQUID** measurements. magnetocaloric effect will be studied-in terms of isothermal magnetic entropy change.



Room temperature Mössbauer spectra of $Y_{0,8}Fe_{0,2}MnO_3$ annealed at 1200°C

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Performance evaluation of AMRs using different casings

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In past years, the number of studies that investigated Active Magnetic Regenerator (AMR) performance and losses has significantly increased. Among those losses, the heat transfer between the AMR and the external environment presents itself as one of the main responsible for AMR performance decay [1-2]. To reduce this effect, in this work, we numerically evaluated the performance of AMRs with different casing materials and values of wall thickness. The size of the air gap between the casing mounted concentrically in the magnetic circuit, which acts as a thermal insulator of the AMR [3], was also evaluated numerically. Moreover, an experimental validation was carried out in the AMR bench of [2] and recently updated by [4] using electric valves. In order to achieve high temperature spans, up to 40 K, the critical scenario for this situation, theoretical magnetic profiles were assumed, with peaks up to 2 T. Numerical results for AMRs with different casing materials and thicknesses are presented in Figure 1. Results for cooling capacity have shown that there is an optimum value for the air layer between the AMR and the magnetic circuit, while the optimum points for casing thickness were obtained with the thinnest ones. COP results presented the same trend in terms of casing thickness, but thicker air layers exhibited higher COP values. Therefore, the air layer should provide sufficient thermal insulation to the AMR, while the casing should be designed to contain the mechanical stress in the AMR.

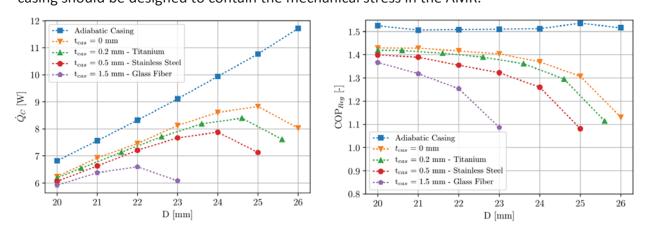


Figure 1 - Cooling Capacity and COP for selected casing materials and geometries

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Danish Days on Caloric Materials and Devices Technical University of Denmark, Risø Campus, 2-3 October 2017

Mn_{3-x}Fe_xSn system materials with Curie temperature tuneable by Fe composition for application in thermomagnetic motors and magnetic refrigeration

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This research presents a new, cheap, and easy to prepare rare earth free material, with good saturation magnetization and Curie temperature tuneable by Fe content for application in thermomagnetic motors and magnetic refrigeration. Alloys from the $Mn_{3-x}Fe_xSn$ system with x in $0.00 \le x \le 3.00$ range and $\Delta x = 0.25$ were characterized and analysed structural and magnetically.

The magnetic results revealed a linear behaviour for the Curie temperature with a large temperature range between the hot and cold sources, $\Delta TC = 604$ K, allowing the immediate application of the material in thermomagnetic motors working in cascade. According Egolf *et al.*, [1] and Solomon [2], an arrangement of cascaded thermomagnetic motors working with ferromagnetic material thermally cycled around its Curie temperature was reported as the manner to work with the maximum energy efficiency. However, a wide temperature range between the hot and cold sources is required. This material fits perfectly for this purpose. Furthermore, SOMT Mn-Fe-Sn system materials were also reported with advantages that make alloys of the Mn_{3-x}Fe_xSn system, $(0.88 \le x \le 1.20)$, applicable in magnetic refrigeration.

Typical ferromagnetic behaviour was found for the alloys with $x \ge 1.00$ and the saturation magnetization was not observed in $0.00 \le x \le 0.50$ range even in the high applied field of - 13 T up to + 13 T.

The main structural results indicated biphasic samples formed by the hexagonal Mn_3Sn and Mn_2Sn phases with Fe added to its structure. The results of the refinements by the Rietveld method indicated a decrease in the lattice parameters values of these two phases with the increase of the Fe content.

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The demagnetizing factor effect in thermomagnetic motors

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The application of thermomagnetic motors (TMM) in energy conversion is currently being proposed for both high [1] and very low [2] power outputs. These devices present a high relative efficiency to Carnot ratio (η_{rel}) for small temperature differences around the Curie temperature of the magnetocaloric material (MCM). One important parameter, that is usually overlooked in the design of the TMM, is the demagnetizing factor (N_d) of the MCM part, which can modify considerably the η_{rel} for the proposed TMM, as shown in Fig .1(a), in which the properties of Gd [3] are considered, with an applied field change ($\mu_0\Delta H$) of 1.35 T, for different heat source temperatures (T_{Hot}).

The use of geometries that increase the N_d cause the reduction of the η_{rel} , this happens because the increase of the N_d implies in a reduction of the internal magnetic field in the magnetocaloric material, a process analogous to the reduction of the $\mu_0\Delta H$ for the same temperature conditions, as shown in Fig. 1(b) for N_d of 1/3. Therefore, the material geometry must be designed adequately to the applied field distribution, reducing N_d as much as possible.

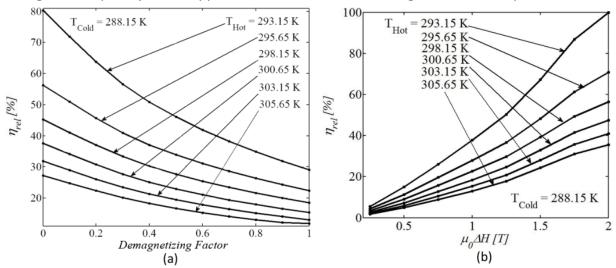


Figure 1 – The η_{rel} for a TMM using Gd as a magnetocaloric material (a) η_{rel} for different demagnetizing factors with $\mu_0 \Delta H = 1.35$ T. (b) The η_{rel} for different $\mu_0 \Delta H$ when $N_d = 1/3$ – factor of a cube shaped material in which the magnetic field is perpendicular to one face.

- [1] P. S. Coray, "Fully Operational Prototype of a 1kW Thermo-Magnetic Motor for Generating Electricity from < 80°C Heat", Abstract for the Delft Days on Magneto Calorics, DDMC (2015)
- [2] C. Chen *el al.* "A Miniature Magnetic-Piezoelectric Thermal Energy Harvester", IEEE Transactions on Magnetics, Vol. 51, Issue 7 (2015)
- [3] M. Risser *et al.*, "Construction of consistent magnetocaloric materials data for modeling magnetic refrigerators", Int. J. Refrig. 35 (2012) 459-467

On the relevance of hysteresis in thermomagnetic motors

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Thermal hysteresis (TH) is usually considered a problem in the application of materials with first order transition into magnetocaloric refrigeration (MR) systems, this behavior will introduce losses and in a worst case scenario can even nullify the magnetocaloric effect (MCE), hindering the application of materials with a high TH [1]. However, the same is not true for thermomagnetic motors (TMM), which, opposite to MR, have their operational temperature imposed by the heat sink and heat source and not by the temperature variation obtained through the MCE. As long as the temperature differences are high enough to surpass the TH the application of the material will not be compromised. With that, the use of magnetocaloric materials with a high TH, e.g. MnAs [2], opens the possibility of applying higher temperature differences between the heat sink and heat source (ΔT) in the TMM, while keeping a high relative efficiency to Carnot (η/η_{Carnot}), and also presenting high specific works when compared to materials with a low TH, as the compounds MnFePSi [3] and La(FeMnSi)₁₃H [4], and also to second order transition materials like the Gd [5], as shown in Fig.1. These characteristics can make the application of materials with high TH desirable in TMM, obtaining higher energy densities and allowing the use of a higher ΔT .

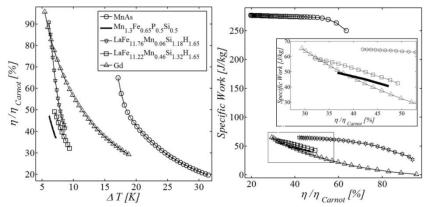


Figure 1 – Characteristic behavior of thermomagnetic motors in a Brayton cicle for different materials in their optimum condition of relative efficiency, for an applied field of 1.5T.

- [1] L. V. Moos *et al.*, "Experimental investigation of the effect of thermal hysteresis in first order material MnFe(P,As) applied in an AMR device", Int. J. Refrig. 37, p. 303-306, (2014)
- [2] S. Gama *et al.*, "A general approach to first order phase transitions and the anomalous behavior of coexisting phases in the magnetic case", Advanced Functional Materials, vol. 19, issue 6, p. 942-949, (2009)
- [3] A. Bartok *et al.*, "Influence of particle size on the magnetocaloric properties of Mn_{1.3}Fe_{0.65}P_{0.5}Si_{0.5} powders", Refrigeration Science and Technology Proceedings Thermag VII, p. 119-122, (2016)
- [4] V. Basso *et al.*, "Specific heat and entropy change at the first order phase transition of La(Fe-Mn-Si)13-H compounds", J. Appl. Phys. 118, 053907 (2015)
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On the optimization of the ball-milling preparation conditions of (Mn-Fe)₂(P-Si) compounds

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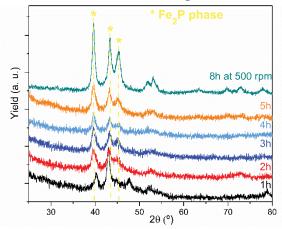
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Among the more competitive magnetocaloric materials reported so far, Mn-Fe-Si-P is highlighted due inexpensive and non-toxic constituent elements, tunable Tc and high magnetocaloric effect [1]. Nevertheless, the production of these alloys involves a two-step process (mechanical alloying plus solid state sintering) that is time-consuming and expensive, therefore with room to improve in terms of large-scale industrial production optimization, by lowering the energy and time consumption in processing. Recently, Thang et al. have demonstrated a processing time reduction by water quenching [2]. Nevertheless, to our knowledge, no thorough study devoted to the influence of the mechanical alloying parameters (frequency, time, ...) has been presented.

Here, we have studied the influence of temperature controlled, high-energy/frequency ball-milling (1500 rpm) mechanical alloying of the pure Mn, Fe₂P, P and Si powders on the (Mn-Fe)₂(P-Si) production. Such high-energy BM promotes significant structural and particle size changes after 1h. The BM effect is stabilized after two hours, leading to a nanometric particle size that is only slightly reduced up to 6 BM hours. The obtained XRD spectra for 2 BM hours is found to be similar to the ones obtained for lower energy BM (500 rpm) for 8 hours, which constitutes a 4-time reduction. Furthermore it is expected that the smaller particle size, induced by the high-energy BM, promotes faster atomic inter-diffusion leading to quicker sintering (2nd processing step). In fact, the next step of this work will be to assess the effect of shorter sintering.

Figure 1. X-ray diffraction spectra of pure Mn, Fe2P, P and Si powders mixed and mechanically alloyed at 1500 rpm Ball-Milled for different times (hours) and for 8h at 500 rpm.



- [1] Dung *et al* "From first-order magneto-elastic to magneto-structural transition in (Mn,Fe)1.95P0.50Si0.50 compounds" Applied Physics Letters (2011), 99, 092511;
- [2] Thang *et al* "Effect of heat treatment conditions on MnFe(P,Si,B) compounds for room-temperature magnetic refrigeration", JALCOM (2017), 699, 633-637;

Influence of substitutions, hydrostatic pressure and magnetic field on the MnNiGe system

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Solid-state cooling technology based on the magnetocaloric effect (MCE) offers a more efficient and environmentally friendly alternative to conventional gas compression cooling devices [1]. The MM'X material systems of Mn-Co-Ge and Mn-Ni-Ge recently attract a significant interest because of their sharp and precisely tunable martensitic phase transition from a high temperature hexagonal (P6₃/mmc) phase to a low temperature orthorhombic (Pnma) phase resulting in high magnetocaloric effects [2,3]. Challenges are the reduction or elimination of the resource critical element Ge and also the large volume changes (~3%) during the structural phase transition.

In our work, we give a comprehensive overview on the technique of isostructural alloying that has been introduced for this material system [3]. It provides an efficient tool to tune the magnetic properties as well as the structural phase transition. Consequently, the amount of critical Ge can be reduced and the transition temperature can be tuned precisely in a broad range by the substitution of Fe on the Mn site and Si for Ge. Furthermore, the magnetocaloric properties can be enhanced significantly.

The volume change of the phase transition also leads to a high sensitivity towards pressure and gives the opportunity of a pressure tuned magnetocaloric effect (see Fig. 1). This influence of pressure is evaluated as well as various amounts of substitutions on the magnetic and structural properties of the versatile $Mn_{1-x}Fe_xNiGe_{1-y}Si_y$ substitutional system.

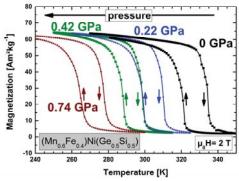


Figure 1: Influence of pressure on the phase transition of Mn_{0.6}Fe_{0.4}NiGe_{0.5}Si_{0.5}.

- [1] O. Gutfleisch et al., Adv. Mater. 23, 821-842 (2011)
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Test stand for a Tesla type thermomagnetic motor

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Thermomagnetic motors in which the heat transfer between the magnetocaloric material (MCM) and the thermal reservoirs, and the production of work occur in distinct moments is denominated Tesla type thermomagnetic motors (TTMM), in reference to his patent from 1889 [1]. These devices are usually described through a Brayton cycle, as a reverse magnetocaloric refrigerator [2]. Searching to verify the real cycle developed by a TTMM, a test stand was built as shown in Fig. 1a, using Gd [2] as a reference MCM.

A Hall effect sensor measured the applied magnetic field distribution. Measuring the temperatures in the motor (Fig.1b) and the position of the moving MCM it is possible to describe the operational cycle of the TTMM in the MH diagram (Fig.1c) and also the TS diagram taking into account the demagnetizing factor of the sample. The magnetization process of the MCM sample does not occur in a perfectly adiabatic manner, causing the system not perform a Brayton cycle, but rather a cycle intermediate between the Brayton and Ericsson cycles.

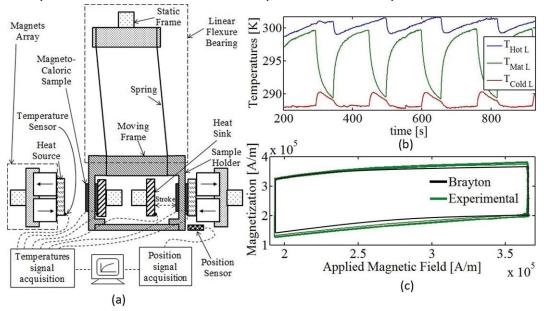


Figure 1 – (a) Schematic diagram of the TTMM test stand built. (b) Temperatures of the hot $(T_{Hot \, L})$ and cold $(T_{Cold \, L})$ sources, and the sample of MCM $(T_{Mat \, L})$ on the left side of the TTMM. (c) Theoretical Brayton cycle and the measured cycle in the M-H diagram in the TTMM.

- [1] N. Tesla. "Thermo-Magnetic Motor", US Patent US396121, (1889).
- [2] A. Morgan *et al.*, "First vs second order magnetocaloric material for thermomagnetic energy conversion", IEEE Transactions on Magnetics, (2017), future issue
- [3] M. Risser *et al.*, "Construction of consistent magnetocaloric materials data for modeling magnetic refrigerators", Int. J. Refrig. 35 (2012) 459-467

Ni₅₀Mn₂₈Ga₂₂ alloy processed by Selective Laser Melting

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Ni-based Heusler alloys exhibiting magnetocaloric properties, are very promising class of materials for Active Magnetic Regenerators (AMR) in magnetic cooling. However, they are very hard to machine. Pulverized alloy with Ni50Mn28Ga22 nominal composition was 3D printed using Selective Laser Melting (SLM). Various laser parameters and scanning strategies were applied.

SEM observations of the obtained samples were performed to reveal the microstructure and porosity. They revealed spontaneous martensitic bands formation in the melt pools and, sometimes, across them (Fig. 1). EDS tests carried out to examine the chemical composition showed uniform elements distribution in every melt pool and revealed no segregation in subsequent layers of the powder melted with the laser beam.

Magnetic measurements revealed the martensite to austenite transformation at around 320 K. Adiabatic temperature change, measured at room temperature, was ~0,1K.

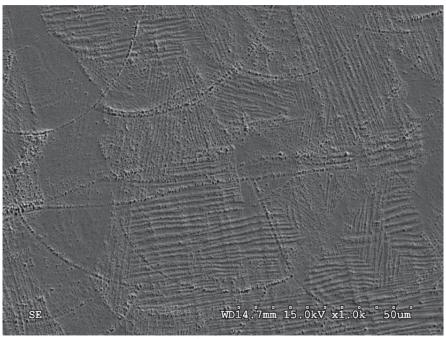


Fig. 1. Microstructure of laser melted $Ni_{50}Mn_{28}Ga_{22}$ alloy .

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Tailoring the magnetocaloric effect of La₂NiMnO₆ −based thin films

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In search for materials with significant magnetocaloric effect over an extended temperature range, we focus on double perovskites such as La_2NiMnO_6 [1, 2] which are ferromagnetic insulators with Curie temperatures approaching room temperature and exhibiting a large spin-phonon coupling [3]. A natural phase competition/segregation during the growth of double perovskites between the ordered La_2NiMnO_6 phase and a disordered perovskite phase of formula $LaNi_{0.5}Mn_{0.5}O_3$ leads to two-phases samples with proportions that can be controlled by the growth conditions. A series of La_2NiMnO_6 -based thin films was investigated to explore the impact of this phase competition on their magnetic and magnetocaloric properties. In particular, we demonstrate that the magnetocaloric effect of La_2NiMnO_6 thin films can be easily tailored by changing their growth conditions. We find that a large magnetocaloric working temperature range can be covered while keeping a nearly constant entropy change using only a La_2NiMnO_6 compound. This is of great interest from a practical point of view since the active magnetic refrigeration can be achieved without needing layered regenerators [4].

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- [4] M. Balli et *al.*, "Advanced materials for magnetic cooling: Fundamentals and practical aspects", Applied Physics Reviews 4 (2017) 021305.

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Heat flux in electrocaloric multilayer capacitors

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The electrocaloric community has recently been more and more involved in the development of prototypes in order to demonstrate that electrocaloric effect (ECE) can be used for new kinds of cooling devices. In this study, we have considered commercial multilayer capacitors (MLCs) playing the role of active cooling element. In this context, information concerning the thermal behaviour of MLCs is crucial in order to integrate them into any refrigerator prototype and to determine what operating limit could be imposed by MLCs themselves. Some papers have reported prediction of MLCs thermal behaviour by modelling their peculiar structure or by measuring their surface heat flux. The cooling power of commercial MLCs has been estimated between 0.3 kW.m⁻² and 1 kW.m⁻² [1-3].

In this study, we propose to directly observe by IR thermography the heat exchange between an MLC and the environment by looking at the temperature change of the whole MLC as a function of time for different types of heat exchange configuration (see figure). Our work permits to explore two different heat transfer regimes, one limited by the external heat exchange and the other one limited by the thermal conductivity of the MLC itself. In the latter regime, the maximum heat exchange power reaches 6 kW.m⁻². Finally, meticulous comparison between the different configurations allows us to define some design rules regarding prototyping.

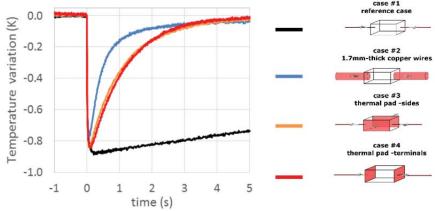


Figure 3: Average MLC temperature as a function of time just after electric field has been removed according to the four different heat conduction configurations depicted in the right part of the figure (in red the preferential heat exchange paths).

^[1] S. Crossley et al., "Finite-element optimisation of electrocaloric multilayer capacitors," APL, 104,(2014), 082909 [2] S. Kar-Narayan and N. D. Mathur, "Predicted cooling powers for multilayer capacitors based on various

electrocaloric and electrode materials," APL, 95,(2009), 242903.

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Study of the Giant MCE across the Ni₂Mn_{1-x}Cu_xGa_{0.8}Al_{0.2} alloys

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Among the materials studied for magnetic refrigeration, Heusler alloys have attracted considerable attention due to some interesting properties, such as their martensitic transition[1] and shape memory effect[2]. Physical properties in these materials are sensitive to chemical composition, which facilitates the coupling of the second order magnetic transition with the first order structural transition, therefore maximizing MCE[3].

Here we present an investigation in the series of polycrystalline compounds $Ni_2Mn_{1-x}Cu_xGa_{0.8}Al_{0.2}$ prepared by arc-melting. Room temperature x-ray diffraction patterns show a $L2_1$ cubic structure for x=0.00, 0.10, 0.20, 0.30 and 0.31, and a martensitic structure for x=0.35 and 0.40. In order to study their properties and examine the structural transition we performed temperature dependent magnetization, heat flow and x-ray diffraction measurements. Our results show a giant MCE near room temperature and lower thermal hysteresis for x=0.30 and 0.31.

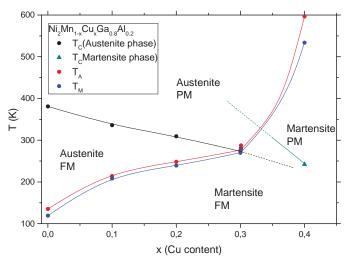


Figure 1: Phase diagram showing both structural and magnetic transitions.

- [1] Antoni Planes, et al., "Magnetocaloric effect and its relation to shape-memory properties in ferromagnetic Heusler alloys", J. Phys.: Condens. Matter 21 (2009) 233201
- [2] P.J. Brown, et al., "Magnetic shape memory behaviour", J. Magn. Magn. Mater. 310 (2007) 2755–2760
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Magnetic plates compacted and epoxy bonded

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The recent development of magnetocaloric refrigeration around room temperature and thermomagnetic motors has prompted a very active search for new and improved magnetic materials (MM) [1]. Although some challenges still have to be overcome in order for these promising technologies to achieve the market [2], one of these challenges is obtaining MM that can be easily produced and machined, or that can be in any other form practically used.

Most promising materials are brittle intermetallic compounds, as the MnAs [3] or the $Gd_{4.7}Nd_{0.3}Si_4$ compounds, which can be more easily obtained in a powder form than in a machinable stock form. One alternative is to bond the MM powder with epoxy or other resin, then using a pressure die to compact a mixture of MM powder with a low mass percentage (< 5% weight) of a high temperature curing epoxy, the part is then cured at 140°C for 24 hours. By the use of an adequate die design, intricate forms can be obtained, as shown in Fig. 1, where a MM-epoxy plate with internal square channels is presented, to be used in a rotating thermomagnetic motor. This technique is capable of producing plates with good mechanical and magnetic properties while maintaining a high relation of MM to epoxy, opposed to previous works that have reported percentages of epoxy of 45% [4].

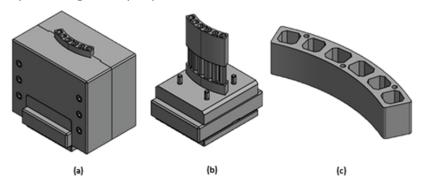


Figure 1-a) The die used to compress the aggregate of magnetocaloric material and epoxy; b) The die without the external cover, showing the complex pin structure; c) The form of the finished compressed piece, with internal channels allowing the fluid flow.

- [1] A.M. Tishin, et al, "A review and new perspectives for the magnetocaloric effect: New materials and local heating and cooling inside the human body", International Journal of Refrigeration, v. 68, p. 177–186, (2016).
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Magneto-caloric effect and electronic topological transition driven by hydrostatic pressure in hexagonal compounds

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Multi-caloric effects are drawing increasing attention to the field of solid-state refrigeration very recently [1,2]. As one of the potential caloric materials, the hexagonal MM'X compounds show both giant MCEs and giant volume change [3,4], which enables the high possibility of tuning the MCEs by hydrostatic pressure on these materials.

Here I will show our recent study on hydrostatic pressure effect on the magnetostructural transitions of hexagonal compound (MnFe)Ni(GeSi). The magnetostructural transition was postponed to low temperatures with increasing pressure, with a rate of 66 K/GPa. The large MCE of about 30 J/kgK can be tuned over a temperature range of 70 K by up to 1.034 GPa, across the room temperature. Meanwhile, the saturation magnetization decreases, non-linearly, with the increasing pressure (Fig. 1). A sudden decrease in the magnetization happened around 0.6 GPa. The first-principles calculations revealed an electronic topological transition occurring at this pressure, resulting in remarkable decreases in both *c* axis and spin polarization of the compounds.

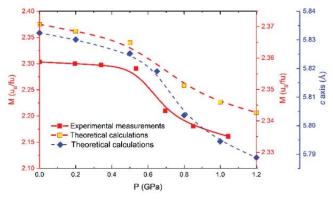


Fig. 1 Pressure dependence of measured, calculated magnetization and calculated c axis.

- [1] X. Moya, S. Kar-Narayan, N. D. Mathur, "Caloric materials near ferroic phase transitions", *Nat Mater* 13 (2014) 439-50 [2] L. Mañosa and A. Planes, "Materials with giant mechanocaloric effects: Cooling by strength", *Adv Mater* 29 (2017) 1603607
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- [4] Z. Y. Wei et al., "Unprecedentedly wide Curie-temperature windows as phase-transition design platform for tunable magneto-multifunctional materials", Adv Electron Mater 1 (2015) 1500076

Comparison between thermomagnetic and thermoelectric generators

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So far, thermal energy harvesting of low-grade heat has been mainly associated to thermoelectric generator (TEG) technology. However, recent advances on magnetocaloric materials (MCM) aimed to applications in room temperature magnetic refrigeration, could pave the way for a new generation of thermomagnetic generators (TMG). We propose to compare the efficiencies and the power density of TMG and TEG at maximum power. The performance will be discussed as a function of the temperature difference ΔT between the hot reservoir and the heat sink and for different non-ideal heat exchangers.

Our model of TMG [1-2] uses a finite-time approach on an endoreversible engine with Brayton cycles whereas the TEG model uses force-flux formalism [3]. Using this simple thermogenerator model (Fig. 1) a first efficiency, power density comparison has been possible (Fig. 2). Here we shall adjust the geometries of the systems in order to optimize the power density. Limitations due to design specific to the two technologies will be discussed.

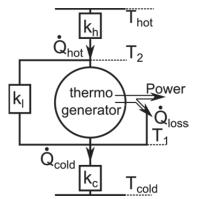


Figure 4 Simple model of thermogenerator

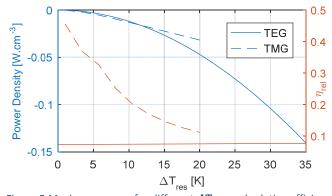


Figure 5 Maximum power for different ΔT_{res} and relative efficiency for TEG with the heat exchanger (solid lines) and TMG with 1st order MCM (dashed lines).

- [1] M. Almanza, A. Pasko, F. Mazaleyrat, and M. LoBue, "First vs second order magnetocaloric material for thermomagnetic energy conversion," *IEEE Trans. Magn.*, 2017.
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Optimal segmentation of three-dimensional permanent magnet assemblies

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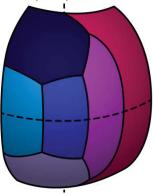
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Permanent magnet assemblies are found in many different scientific and technological fields, such as electromechanical energy conversion, magnetocaloric applications, and accelerator physics.

These assemblies are realized by combining several permanent magnet blocks each of which is characterized by a constant direction of magnetization. The shape and magnetization direction of each magnet segment can be optimized with respect to a suitable objective functional which expresses the purpose of the magnetic assembly. It has been shown [1] that the optimization of two-dimensional magnetic systems can be performed employing an analytical framework, as long as the optimization problem is expressed by an objective functional which is linear with respect to the magnetic field. The analytical optimization approach relies on the reciprocity theorem and guarantees global optimality of the solution with respect to the objective. However, the segmentation of three-dimensional magnetic systems presents additional challenges and has to be carried out using a different approach.

In this study we introduce a heuristic optimization method which is also based on the reciprocity theorem, and can be applied to three-dimensional systems. Our method has been implemented into a fast and effective algorithm which can be applied to different magnetic systems, as demonstrated by the various examples presented here.



One quarter of a structure optimized to generate a uniform transversal field in the central cylindrical cavity which is accessible from the top and bottom sides.

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Numerical routine for magnetic heat pump cascading

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Heat pumps use low-temperature heat absorbed from the energy source to create temperature gradient (TG) across the energy sink. Magnetic heat pumps (MHP) can perform this function through operating active magnetic regeneration (AMR) cycle. For building heating, TGs of up to a few K might be necessary, which is hardly achievable with a single MHP and such techniques as cascading are required. Series and parallel cascading increase the AMR span and heating power, respectively, but do not change TG. Therefore, the intermediate type of cascading

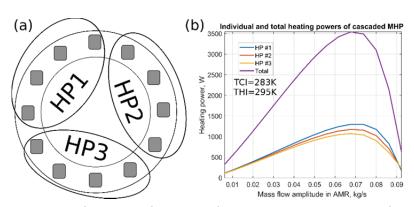


Figure 1. The original MHP with 12 AMRs is reconnected to give (a) a 3 MHP with (b) their individual heating powers summing up to the total system heating power.

was proposed with individual MHPs separately connected at their cold and hot sides [1, 2]. In these works, a single MHP is separated into smaller cascaded MHPs with the same total mass. This kind of mass redistribution is hard to implement experimentally since several prototypes with different AMR number and sizes should be constructed. In this theoretical study, instead of changing individual AMR sizes, we

rearranged parallel-connected AMRs in separate blocks (HP1, HP2 and HP3 in Fig. 1(a)) and connected the cold (hot) outlet of one block to the cold (hot) inlet of the next block giving a cascading configuration. Thus, not only the total mass but also the total number of AMRs remain constant, making this configuration easier to implement. A MATLAB routine for cascading simulation from a single AMR data was implemented. Calculated heating power for configuration in Fig. 1(a) is plotted in Fig. 1(b) and the cold- and hot-side TGs are around 2 K and 3 K. Changing the number of MHPs, we optimized input parameters to achieve maximum heating powers. We have found that both maximum heating power and COP decrease together with number of heat pumps, but the TGs and the temperature span can be largely

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Danish Days on Caloric Materials and Devices Technical University of Denmark, Risø Campus, 2-3 October 2017

Fast and efficient heat transfer via check valves in a magnetocaloric heat pump

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Several magnetocaloric heat pumps based on the "Active Magnetic Regenerator" (AMR)-concept were built in the last years [1,2]. The basic principle is to actively pump a heat transfer fluid through the magnetocaloric regenerator to achieve a heat flux in one direction. Cooling systems based on magnetocaloric materials have the potential to surpass the efficiencies of conventional compressor-based cooling systems. However, a higher efficiency than shown by compressor-based systems has not been measured yet. Furthermore, cost analyses indicate a lack of competitiveness compared to conventional systems even due to large costs of the magnetic material [3].

In this work, a new concept for a magnetocaloric heat pump is presented which enables fast and efficient heat transfer. This concept combines latent heat transfer and thermal diodes. Based on the condensation and evaporation of a non-hazardous working fluid the concept has the potential to achieve heat transfer rates, which are several orders of magnitude larger than in conventional AMR-systems. In order to set a certain temperature span a number of segments are stacked into a thermosiphon-like container. Each segment contains magnetocaloric material and a check valve enabling a passive transport of the working fluid from magnetocaloric material to a heat exchanger.

In this work experiments show the proof of concept. A single stage segment is built up and characterised.

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Danish Days on Caloric Materials and Devices Technical University of Denmark, Risø Campus, 2-3 October 2017

Quasi-direct measurements of barocaloric materials

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Giant barocaloric materials show nominally reversible thermal changes near non-isochoric first-order phase transitions, and have been recently suggested as promising alternative to vapour-compression cooling technologies [1]. The barocaloric response of these materials is typically evaluated via quasi-direct measurements [1], where temperature dependence of heat-flow is recorded at different pressures, instead of pressure-dependent heat-flow at different temperatures. However, the presence of hysteresis in first-order barocaloric materials can lead to artefacts in their calculated barocaloric response. Here I will describe how to avoid these artefacts in order to obtain reversible barocaloric effects from quasi-direct measurements, and I will apply this method to a number of giant barocaloric materials with hysteresis of various magnitude.

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Direct measurements of electrocaloric PbSc_{0.5}Ta_{0.5}O₃ ceramics

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Direct electrocaloric measurements are challenging, and so the majority of electrocaloric studies are instead performed using indirect methods. I will present direct measurements of isothermal heat Q and adiabatic temperature change ΔT using a bespoke calorimeter and an ultrafast infrared camera in the well-known electrocaloric material PbSc_{0.5}Ta_{0.5}O₃ (PST). We find room-temperature values of $Q \sim 850 \, \text{J kg}^{-1}$ and $\Delta T \sim 1.8 \, \text{K}$, for changes in electric field of 13.4 kVcm⁻¹. The values of Q and ΔT determined using these two independent techniques are in excellent agreement with each other, via values of specific heat measured at zero electric field. Separately, I will discuss the fatigue behaviour of PST under sustained electrical operation, which is an important but overlooked aspect from the device perspective.

Topology optimization of heat exchangers and heat sinks

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Efficient heat transfer is critical for the overall performance of caloric devices. Topology optimization [1] is concerned with optimizing a material distribution within a design domain under given constraints. In contrast to size and shape optimization, topology optimization does not rely on an initial design parametrization which can lead to reduced development time and identification of unintuitive and unanticipated designs. Topology optimization of thermofluid systems has for example been treated in [2] for forced convection problems and [3] for natural convection problems.

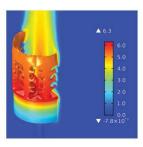
Work within our group deals with density-based topology optimization of heat exchangers and heat sinks as well as fabrication and experimental validation of these devices. Figure 1 shows a heat sink design generated using a thermofluid natural convection topology optimization model and the corresponding prototype fabricated by investment casting of Britannia alloy. Moreover, the temperature span over the heat sink predicted by simulation and experimentally measured with an IR camera is depicted.



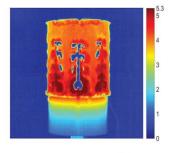
Optimized design



Prototype (investment casting)



Temperature span [K] (simulation)



Temperature span [K] (experiment)

Fig. 1: Optimized heat sink design, fabricated prototype, and simulation and experiment based validation results.

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Finite heat transfer modelling of spatially resolved magnetocaloric materials with a first order transition

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Here we focus on the numerical modelling of magnetocaloric materials with a first order transition. We present a model, which is able to simulate the time-dependent heat transfer in these materials. This is a continuation of our recently published time-independent model [1]. The basic model building block is the well-known Bean-Rodbell model [2]. A model sample is made up of a number of small elements (rectangular prisms) that each can have different properties, e.g. Curie temperature. The model then solves the unsteady heat transfer equation in time and includes hysteresis and magnetic self-interaction. As we model first order materials, the sharp transitions of key properties like the specific heat make the numerical calculations non-trivial. However, with appropriate approximations the model is able to predict the spatial distribution of magnetic field, temperature, magnetisation, entropy, and all the other parameters of interest as a function of time. We will present how the model works, give some details about the numerical implementation and discuss the first results that we have obtained. The program is of interest because it will allow us to model experimental measurements on materials, and try new kind of experiments that could be difficult to set up in the laboratory. We focus on LaFeSi-type materials for the moment, but the model can be used for any kind of first order magnetocaloric materials.

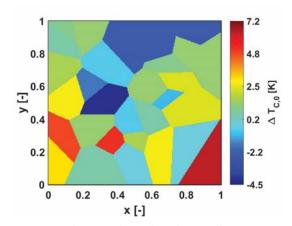


Figure 1. A discretized sample with spatially varying Curie temperature given as the difference compared to a mean value.

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Flow profiles in a rotary multi-bed AMR

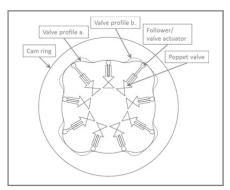
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Controlling the flow of heat transfer fluid is crucial to the performance of AMRs. As the magnetic field in a regenerator varies during the cycle, how and when to optimally apply the flow are non-trivial questions. A recent experimental study at the Federal University of Santa Catarina, Brazil investigates the effects of varying the flow fraction, i.e. the time fraction of the cycle which is used for flow, in their single regenerator machine [1]. Their results indicate that there might be a trade-off between COP and cooling power.

At the Technical University of Denmark we are investigating the same issues with MAGGIE, our rotary multi-bed prototype [2]. This regenerator consists of 11 circumferentially arranged beds that are subsequently magnetized and demagnetized by a rotating magnet array. In this type of device, the situation is further complicated by the fact that the magnetic field in each bed is non-homogeneous during the entire cycle. In the design phase, 2D AMR simulations capturing the spatial field variations in the beds were used to support the initial choice of flow fraction as a compromise between COP and cooling power. Furthermore, concepts on how to vary this flow fraction in operando were developed [3]. Here we present initial experimental results with different flow fractions by simply replacing the cam rings actuating the poppet valves controlling the flow in the beds.



Variable cam concept for controlling fluid flow profile of a multi-bed AMR device.

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Redesigning the regenerators of a rotary prototype

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Our magnetic refrigeration prototype (Fig.1) was presented earlier by Monfared & Palm[1] with some technical problems necessitating redesigning the regenerators. The main problems were pulverization and corrosion of La(Fe,Mn,Si)₁₃H_z particles used as refrigerant.

The tool used for redesigning the regenerators is a simulation model consisting of three parts: a detailed model of magnetic field in which the effect of presence of magnetocaloric materials in the magnetic circuit is considered; a 3D model of parasitic heat transfer from the warm end to the cold end and from the ambient to the regenerators; a 1D model of active magnetic regeneration. The simulation is validated against experimental measurements using gadolinium as refrigerant.

For validating the simulation model, the regenerators are emptied and two of them, out of 12, are filled by gadolinium particles. The reason for using gadolinium at this step is its well-known properties and high mechanical strength. Different parameters such as cooling load, heat transfer fluid flow, and operation frequency are varied in the tests. Comparison between the experimental results and the simulated ones showed the validity of the simulation results.

Then the validated model is used to redesigning the number of layers, particles size, and choice of transition temperatures with epoxy-bonded $La(Fe,Mn,Si)_{13}H_z$ particles. In this study the effect of epoxy layer on the pressure drop and heat transfer rate between the particles and the heat transfer fluid are taken into account. In addition, the effect of varying different parameters on the performance of the prototype are investigated and analysed.

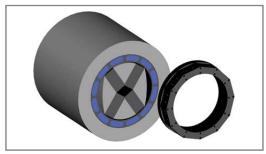


Fig.1: Prototype with rotating magnet and 12 regenerators. Header is removed to show details.

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