Delft Days on Magnetocalorics 2019

November 18-19 2019
Science Center TU Delft, Mijnbouw straat 120
2628 RX Delft

In collaboration with Swiss Blue Energy and RSP Technology

TU Delft

Delft University of Technology

Dear participant,

Welcome to the 5th DDMC being held in Delft, the first Delft Days on Magnetocalorics were initiated as a forum for an informal exchange of ideas in the fast growing field of magnetocaloric materials and devices, bringing together researchers from academia and industries. Such informal contact was thought to be particularly needed, as magnetic refrigeration was to become a game changer.

We intended that commercialisation of magnetic refrigeration would go faster, particularly after the presentation of the first magnetic wine cooler early 2015 (Astronautics, BASF, Haijer) and a refrigerator reaching sub-freezing temperatures the same year (Cooltech). Important progress has been made, but we are still waiting for a magnetic fridge in the domestic appliances store, and probably need to wait a little longer.

Introducing new materials and new technologies, appears to be more complicated than many of us thought. However, we are still persuaded that magnetocaloric technology is the most promising alternative to current compressor-based systems, which are associated with strong greenhouse gases or fire hazards.

This meeting again spans the full range from first principle calculations, new materials development, materials characterization, innovative devices and commercialisation and yet aims at an open dialog between researchers from all over the world. We learned to be patient, but are convinced that in the coming years change will take place.

Enjoy the conference and enjoy Delft.

Ekkes Brück,

Niels van Dijk,

Ilse van der Kraaij-Quick

Program DDMC 2019 – Monday 18 November 2019

9:00 – 9:45 *Registration*

9:45 – 10:00 Opening address

Session 1: Monday 10:00-12:30, Chair: Ch. Bahl

10:00-10:30 F. Cugini, Parma, Italy, *Tuning the magnetic and magnetocaloric properties of austenitic $Ni_{48}Mn_{34}(In,Sn)_{16}$ Heusler compounds*

10:30-11:00 B. Weise, Dresden, Germany, *In-situ investigation of the martensitic transformation in NiMnGa thin films*

11:00-11:30 *Coffee break*

11:30-12:00 M. Fries, TU Darmstadt, Germany, *Making a cool choice: the materials Library of magnetic refrigeration*

12:00-12:30 I. Batashev, TU Delft, The Netherlands, *Ab initio calculations of the magnetocaloric properties of Fe_2P-based alloys*

12:30-14:00 *Lunch break + Posters*

Session 2: Monday 14:00-16:00, Chair: M. LoBue

14:00-14:30 G. Allodi, Parma, Italy

^{55}Mn NMR studies on giant magnetocaloric FeMnPSi alloys

14:30-15:00 N. Maraytta, Jülich, Germany

Direct and indirect magnetocaloric effect of $MnFe_4Si_3$ and Mn_5Ge_3

15:00-15:30 X.F. Miao, Nanjing, China

In-situ TEM studies on the magnetocaloric transition of $(Fe,Mn)_2(P,Si)$

15:30-16:00 F. Guillou, Hohhot, China, *Search for compositional adjustments in Eu_2In*

and complementary studies in FeMn(P,Si)

16:00-16:30 *Coffee break*

Session 3: Monday 16:30-18:30, Chair: L. Caron

16:30-17:00 C. Bahl, DTU, Denmark, *Development of a magnetocaloric heat pump*

towards an innovative multi source heat pump system

17:00-17:30 F. Scheibel, TU Darmstadt, Germany, *Exploiting thermal hysteresis by using a multi-stimuli cooling cycle – concept and possible materials*

17:30-18:00 A. Gràcia-Condal, University of Barcelona, Spain, *Caloric and multicaloric effects in metamagnetic Ni-Mn-In under uniaxial stress and magnetic field*

18:00-18:15 H. Vieyra, Vacuumschmelze, Germany, *Effect of hysteresis on the magnetocaloric properties of LaFeSi alloys for Cryogenic applications*

18:15-18:30 S. Lionte, UbiBlue, Strassbourg, France, *Mechanical and magnetocaloric characterictics of first order LaFeSi-based materials*

19:00 *Dinner*

Program DDMC 2019 – Tuesday 19 November 2019

Session 4: Tuesday 9:00-10:30, Chair: E. Brück

9:00-9:30 D. Dzekan, IFW Dresden, Germany, *Energy harvesting using thermomagnetic generators with magnetocaloric materials*

9:30-9:45 L. Beyer, Dresden, Germany, *Optimizing the fabrication of magnetocaloric composite wires with different magnetocaloric core materials*

9:45-10:00 K. Rajamani, University of Twente, The Netherlands, *Experimental investigation of magnetic pumping for magnetocaloric refrigerator applications*

10:00-10:15 J.A. Lozano, *University of Santa Catarina, Brazil, MagChill: Development of an air conditioner operated by a magnetic refrigeration unit*

10:15-10:30 D. Bessas, ESRF, France, *Inelastic X-ray scattering for Magneto-Caloric Compounds*

10:30-11:00 Coffee break

Session 5: Tuesday 11:00-12:30, Chair: T. Gottschall

11:00-11:30 S. Ahmim, ENS Paris, France, *A La-Fe-Si based thermo-magnetic generator*

11:30-12:00 N. Sun, Shenyang, China, *Microstructure, mechanical and magnetocaloric properties of bulk* $La_{0.9}Ce_{0.1}Fe_{11.7-x}Mn_xSi_{1.3}$ *hydrides*

12:00-12:15 Y. Ouyang, Ningbo, China, *A high throughput study of magnetocaloric materials: gradient solidification applied to La-Fe-Si*

12:15-12:30 C.D. Christiansen, DTU, Denmark, *Freeze-casting of monolithic regenerators with micro-channels and varying Curie temperatures for magneto-caloric compounds*

12:30-14:00 Lunch break + Posters

Session 6: Tuesday 14:00-16:00, Chair: N.H. van Dijk

14:00-14:30 T. Gottschall, Dresden, Germany, *Advanced characterisation of magnetocaloric materials in pulsed magnetic fields*

14:30-15:00 X. You, TU Delft, The Netherlands, *Synchrotron experiments on LaFeSi alloys*

15:00-15:30 L.M. Moreno-Ramirez, University of Sevilla, Spain, *When actual effects look like artifacts: deconvolution of the concurrent transitions in Ni-Mn-In Heusler alloys*

15:30-15:45 R. Skini, Uppsala University, Sweden, *Large magnetocaloric effect at room temperature in* $Pr_{0.64}Sr_{0.36}MnO_3$ *manganite*

15:45-16:00 L. Caron, Bielefeld University, Germany, *Pressure effect on the magneto-structural phase transition in* $Mn_3CuN_{0.75}C_{0.25}$

16:00 Closing remarks

16:00-17:00 Farewell drinks

Posters DDMC 2019 – Monday 18 & Tuesday 19 November 2019

P1 H. Ben Khlifa, F. Ayadi, W. Cheikhrouhou-Koubaa, G. Schmerber,

Screening of the synthesis route on the structural, magnetic and magnetocaloric properties of $La_{0.6}Ca_{0.2}Ba_{0.2}MnO_3$ *manganite: A comparison between solid-solid state process and a combination polyol process and Spark Plasma Sintering*

P2 L. Beyer, T. Gottschall, B. Weise, A. Funk, A. Waske, M. Krautz,

Thermal performance of magnetocaloric composite wires in pulsed magnetic fields

P3 S. Dalvi, M. Shahi,

Numerical analysis of magneto-caloric effect within a circular annulus

P4 F. Erbesdobler, C.R.H. Bahl, R. Bjørk, and K.K. Nielsen,

Spatial and temporal characterization device for magnetocaloric effect and phase transitions

P5 S. Ghorai, R. Skini, S. A. Ivanov, P. Svedlindh,

Tuning the magnetocaloric effect towards room temperature by B-site doping in the perovskite $La_{0.8}Sr_{0.2}MnO_3$

P6 B. Huang, N.H. van Dijk, E. Brück,

A magnetic heat pump prototype for experimental purpose and its multi-layer regenerator bed extension plan

P7 J. Liang, C.D. Christiansen, K. Engelbrecht, K.K. Nielsen, R. Bjørk, C.R.H. Bahl,

Thermodynamic characterization of freeze-cast regenerators

P8 K. Löwe, H. Vieyra, A. Barcza, M. Katter,

Fast measurement of adiabatic temperature changes in LaFeSi-based alloys at cryogenic temperatures

P9 M. Maschek, X. You, N. van Dijk, E. Brück,

Minimization of impurity phases in MnFePSi

P10 K. Navickaitė, J. Liang, C.R.H. Bahl, K. Engelbrecht, S. Wieland,

Experimental performance of passive regenerators with nature-inspired flow structure

P11 K.K. Nielsen, F. Erbesdobler, C.R.H. Bahl, R. Bjørk

Detailed isofield calorimetry of La(Fe,Si,Mn)H revealing localized variation in phase transitions

P12 D. Nguyen Ba, L. Becerra, N. Casaretto, M. Marangolo, M. LoBue,

Growth temperature dependence of phase transformation and of entropy change in gadolinium thick films

P13 A. Pasko, S. Ahmim, D. Nguyen Ba, M. Trassinelli, M. Marangolo, M. Almanza, F. Mazaleyrat, M. LoBue,

Modelling of a $La(Fe,Si)_{13}$*-based magnetocaloric material for a thermomagnetic generator*

P14 I. A. Radulov, D. Yu. Karpenkov, A. Yu. Karpenkov, K. P. Skokov, O. Gutfleisch

Magnetocaloric heat exchangers

P15 J. Zemen, L. Beran, J. Zázvorka, M. Veis, F. Johnson, D. Boldrin, A. Mihai, B. Zou, L.F. Cohen,

Magneto-Optical Spectra of an elastocaloric Antiferromagnet: Theory and Experiment

P16 F. Zhang, X. You, N. van Dijk, E. Brück,

Magnetocaloric effect in the $(Mn,Fe)_2(P,Si)$ *system: from bulk to nano*

P17 C. Frommen, C. Bahl, E. Delczeg, H. Fjellvåg, B.C. Hauback,

3D printed high entropy alloy micro and nano particles for magnetocaloric energy conversion HI-ENTROPY

P18 L.M. Moreno-Ramírez, J.Y. Law, V. Franco, A. Conde, I.A. Radulov, K.P. Skokov, O. Gutfleisch,

Analysis of the field dependence of magnetocaloric effect of $La(Fe,TM,Si)_{13}$ *(TM = Cr,Ni) alloys*

P19 S. Wieland, C. Breitzke,

Curie-temperature and geometrical variation of $La(FeSi)_{13}$ *heat exchangers produced via laser beam melting*

Oral Presentations

Session 1

Monday 10:00-12:30

Tuning the Magnetic and Magnetocaloric Properties of austenitic $Ni_{48}Mn_{34}(In,Sn)_{16}$ Heusler Compounds

F. Cugini[1,2], G. Cavazzini[1,2], S. Chicco[1], F. Orlandi[3], G. Allodi[1], V. Vezzoni[1], M. Gruner[4], L. Righi[5], S. Fabbrici[2], F. Albertini[2], M. Solzi[1,2]

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The flexible structure of Ni_2MnX Heusler alloys (X= Ga, In, Sn, Sb…) allows, by changing composition, the tuning over a large temperature range of both a second-order and a first-order magnetic transition. The possibility to fine tailoring the critical temperatures and the magnetic states makes this class of compounds very interesting as active elements in energy-conversion thermomagnetic devices.

In this work, we study the $Ni_{48}Mn_{36}In_{16-x}Sn_x$ (x = 0-16) series with the purpose of defining the physical mechanisms that control the saturation magnetization and the Curie temperature of the cubic austenitic phase. All the compounds show a stable austenitic phase with a Curie transition slightly above room temperature, where a large and fully reversible magneto-caloric effect is observed. The replacement of In with the cheaper and less critical Sn brings to a linear reduction of the saturation magnetization and a not monotonous variation of the critical temperature, which decreases with increasing Sn up to 8 at. %, after which it abruptly rises. This unexpected behaviour cannot be easily explained solely by the linear and small contraction of the crystallographic lattice. Magnetometry, neutron diffraction and ^{55}Mn nuclear magnetic resonance experiments combined with first-principles calculations suggest the presence of different physical mechanisms that independently control the saturation magnetization and the critical temperature of the ferromagnetic austenitic phase.

Key Words: thermomagnetic energy conversion, magnetocaloric materials, Heusler compounds, intermetallic compounds, DFT calculations.

References : G. Cavazzini et al. Scripta Mater. 170 (2019) 48–51.

In-situ investigation of the martensitic transformation of NiMnGa thin films

B. Weise [1,2], A. Diestel [1], K. Lünser[1,2], N. Teichert[3], A. Hütten[3], K. Nielsch[1,2], A. Waske[1,4], S. Fähler[1],

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Thin films of NiMnGa can be used as a model system to understand the martensitic phase transition of Heusler alloys in order to improve their performance for ferromagnetic shape memory- or caloric applications. Niemann et al. (1) suggested a model for the nucleation and growth process of martensite in NiMnGa, where two types of shapes called type X and Y appear due to different orientation of the nuclei. However, in recent studies (2,3) it was stated, that these nucleation and growth processes of the magnetic phase are strongly influenced by the surface morphology and surface defects.

In order to investigate this geometrical model of martensite growth, thin films of NiMnGa were studied, using a custom temperature stage for in-situ scanning electron microscopy (SEM). With image analysis the phase fractions where determined and compared to conventional magnetometry. Moreover the growth of the martensitic microstructure is shown and the transformation of type X and Y martensite was investigated seperately. Furthermore the influence of artificial ferromagnetic structures on top of the NiMnGa films were studied: Ferromagnetic FeCo structures were deposited on top of the NiMnGa films in order to understand the influence of mechanical (2,4) and magnetic (4) coupling to the phase transition by in-situ SEM. The deposition quality of the FeCo deposition was tested with cross section TEM. It is shown that the temperature dependent martensite fraction, calculated from in-situ SEM images, is in accordance to the magnetic measurements.

Key Words: (NiMnGa, thin film, in-situ SEM, imaging).

References
(1) R. Niemann, et al. Acta Mater. 132 (2017) 327–334.
(2) R. Niemann, et al. APL Mater. 4 (2016) 064101.
(3) A. Waske, et al. APL Mater. 4 (2016) 106101.
(4) A. Waske, et al. Energy Technol. 6 (2018) 1429–1447.

Making A Cool Choice: The Materials Library of Magnetic Refrigeration

T. Gottschall[1,2], K. P. Skokov[1], M. Fries[1,3], A. Taubel[1], I. Radulov[1], F. Scheibel[1],D. Benke[1,3], S. Riegg[1], O. Gutfleisch[1,3,4]

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The phase-down scenario of conventional refrigerants used in gas–vapor compressors and the demand for environmentally friendly and efficient cooling make the search for alternative technologies more important than ever. Magnetic refrigeration utilizing the magnetocaloric effect of magnetic materials could be that alternative.

However, there are still several challenges to be overcome before having devices that are competitive with those based on the conventional gas–vapor technology. In the presented work a rigorous assessment of the most relevant examples of 14 different magnetocaloric material families is presented and those are compared in terms of their adiabatic temperature and isothermal entropy change under cycling in magnetic-field changes of 1 and 2 T. Furthermore, the study compares criticality aspects and the amount of heat that the materials can transfer per cycle [1].

The work is based on magnetic, direct thermometric, and calorimetric measurements made under similar conditions and in the same devices. Such a wide-ranging comparing study has not been carried out before. This data sets the basis for more advanced modeling and machine learning approaches in the near future

Key Words: Materials Library, Criticality, Magnetocaloric Effect

[1] T. Gottschall et al. Advanced Energy Materials 9 (2019) 1901322.

First-principles Studies of Li-doped Fe_2P compounds.

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Properties of extensively studied $(Fe,Mn)_2(Si,P)$ system, well-known for its promising magnetocaloric qualities are greatly influenced by the crystallographic parameters of this hexagonal system, particularly by *c*/*a* ratio. A change in the unit cell, due to the added element such as N, C, B and Li can induce changes in the Curie temperature and hysteresis. The ability to fine-tune T_c is especially important for practical applications both in case of cooling and energy conversion purposes.

In this work effect of lithiation on magnetization and critical temperature and their connection to structural parameters of Fe_2P have been investigated within the framework of density functional theory. Fe_2P has two magnetic sublattices, one with bigger moment (3g positions) and other with lower (3f positions). Li partially substitutes Fe on the 3g site, with a tendency to form clusters, contrary to usual preference of non-magnetic atoms to replace phosphorus or reside on interstitial positions. We present a study of doping process and for up to 20% Li content.

A steep linear increase of Curie temperature with the rate of ~45 K per Li % was discovered. We show that this is primarily the result of structural changes, the decrease of *c*/*a* ratio in particular.

Key Words: (*ab-initio* calculations, Fe_2P, Curie temperature,).

Oral Presentations

Session 2

Monday 14:00-16:00

^{55}Mn NMR studies on giant magnetocaloric FeMnPSi alloys

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We present an extensive study of a representative set of Fe_2P-based $Mn_{1+x}Fe_{0.95-x}P_ySi_{1-y}$ alloys carried out by ^{55}Mn NMR. [1] The magnetic order parameter is probed locally at the 3*g* and 3*f* sites by the ^{55}Mn spontaneous NMR frequency in zero applied field. The *truncated* (i.e. finite) order parameter curves at T_C demonstrate a first order magnetic transition (FOMT) even at Mn-rich compositions like $Mn_{1.7}Fe_{0.25}P_{0.5}Si_{0.5}$, whose transition was previously classified as second order. The seeming continuous transition of the latter, however, is rather the result of a blurred magnetoelastic transition and a ferromagnetic-paramagnetic phase separation over a broad temperature interval around T_C, and is not driven by critical fluctuations.

The mixed magnetism of these materials is detected as a fractional and more strongly temperature-dependent hyperfine field at the 3*f* than at the 3*g* site. NMR proves that the steeper decrease of the 3*f* ordered moment for T approaching T_C is driven by the drop of the local spin density instead of enhanced spin fluctuations, and that the extinction of the 3*f* spin evolves into a truly nonmagnetic Mn state at temperatures well above T_C. This finding agrees with band-structure calculations and partly disagrees with previous X-ray magnetic circular dichroism experiments, which detected just a partial moment quenching. [2,3]

Besides majority "normal" 3*f* Mn ions undergoing a temperature-driven electronic transition from a magnetic to spinless state, a significant minority Mn fraction with negligible hyperfine couplings, irrespective of temperature, is found in Mn-rich compositions, disproportionated at 3*f* sites. Although the role of such a *diamagnetic* fraction is unclear so far, its presence qualitatively accounts for the reduced average 3f moment previously reported by neutron scattering large Mn concentrations. [4]

Key Words: (MnFeSiP alloys, FOMT, mixed magnetism).

References

[1] R. Hussain et al. Phys. Rev. B.100 (2019) 104439.
[2] N. H. Dung et al. Adv. Energy Mater. 1 (2011) 1215.
[3] H. Yibole et al. Phys. Rev. B 91 (2015) 014429.
[4] N. H. Dung et al., Phys. Rev. B 86 (2012) 045134.

Direct and Indirect Measurements of Magnetocaloric Effect of $MnFe_4Si_3$ and Mn_5Ge_3

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The magnetocaloric effect forms the basis of magnetocaloric refrigeration, which is a novel energy efficient and environmentally friendly method for cooling that has the potential to replace conventional vapor compression technologies [1]. The MCE is based on entropy changes of magnetic materials in an applied magnetic field, which lead to a change of temperature of the material.

$Mn_{5-x}Fe_xSi_3$ as well as Mn_5Ge_3 compounds have been investigated as promising candidate materials, where hexagonal $MnFe_4Si_3$ and Mn_5Ge_3 are of special interest as they have a transition from the paramagnetic to a ferromagnetically ordered state close to 300 K and they feature a modestly large magnetic entropy change and contain only environmentally unproblematic and abundant elements.

In this contribution, we will present the direct measurements of the adiabatic temperature change (ΔT_{ad}) in pulsed magnetic fields using a home-built experimental set-up in HLD [2]. This technique provides nearly adiabatic conditions during the measurements and the sample is in conditions which are close to the real process used in applications. The results will be compared with the ones obtained from the magnetization and heat capacity measurements in static magnetic fields. For $MnFe_4Si_3$, this will also be combined with the results from neutron depolarization experiments [3] carried out using Cryopad setup at single crystal diffractometer POLI at MLZ [4].

Key Words: (Magnetocaloric effect; $MnFe_4Si_3$; Mn_5Ge_3, Magnetic measurements).

References

[1] K.A. Gschneidner Jr. and V.K. Pecharsky, Intl. J. Refrig. 31(2008), 945 – 961.
[2] M. G. Zavareh et al , Appl. Phys. Lett. 106 (2015).
[3] M. T. Rekveldt, Physica B (1999), 267-268, 60-68.
[4] V. Hutanu et.al., Rev. Scientific Instr. 87(2016),105108.

In-situ TEM Studies on the Magnetoelastic Transition of $(Fe,Mn)_2(P,Si)$

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$(MnFe)_2(P,Si)$-type compounds are, to date, one of the best candidates for magnetic refrigeration and energy conversion applications due to the combination of giant magnetocaloric effect (MCE), tunable working temperature range and low material cost [1]. The giant MCE in the $(Mn,Fe)_2(P,Si)$-type compounds originates from a first-order magnetoelastic transition, where the ferromagnetic-paramagnetic (FM-PM) transition is strongly coupled to discontinuous changes in the lattice parameters without a strcutural transition [2]. Lots of efforts have been made to uncover the characters of the magnetoelastic transition in the $(Mn,Fe)_2(P,Si)$-type compounds. The combination of x-ray absorption experiments and density functional theory calculations indicates the redistribution of electron density and the mixed magnetism behavior in the magnetoelastic transition [3]. (Polarized) neutron diffraction experiments reveal the nuclation and growth processes of the magnetoelastic transition on the atomic and nano scales [4]. However, the structural evolution of the magnetoelastic transition on the micro scale has rarely been studied.

In the present work, we performed in-situ transmission electron microscope (TEM) observations on the $(MnFe)_2(P,Si)$-type compounds. The samples with a first-order and a second transition exhibit distinct phase transition behaviors. The structural origin of hysteresis will be discussed based on the TEM observations. Additionally, the influence of different typies of secondary phases on the phase transition will also be presented.

Key Words: $(Mn,Fe)_2(P,Si)$, Magnetoelastic transition, TEM

References

[1] N.H. Dung et al. Adv. Energy Mater. 1 (2011) 1215.
[2] M.F.J. Boeije et al. Chem. Mater. 28 (2016) 4901.
[3] X.F. Miao et al. Phys. Rev. B. 89 (2014) 174429.
[4] X.F. Miao et al. Phys. Rev. B. 94 (2016) 014426.
[5] X.F. Miao et al. Scr. Mater. 138 (2017) 96.

Search for Compositional Adjustments in Eu_2In and Complementary Studies in MnFe(P,Si)

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Materials presenting first-order magnetoelastic phase transitions are attracting intense interest both for the intriguing fundamental questions they raise and for their potential use in applications, such as for magnetic cooling or other thermomagnetic devices. Isostructural first order transition that do not break the crystal symmetry are rare, only a handful of materials families are known. Here, we present some results obtained very recently at IMNU on two families with such magnetoelastic transitions.

1. Following the discovery of an exceptionally large magnetocaloric effect at the ferromagnetic transition of Eu_2In [F. Guillou et al., Nature Comm. 9, 2925 (2018)], we seek appropriate routes to control the magnetic properties. Different series of materials with rare earth or metalloid substitutions are explored, indicating that the control of the transition temperature in Eu_2In-derivative may turn out challenging.
2. In the $(Mn,Fe)_2(P,Si)$ system, we show that the first crossing of the transition upon cooling in as-synthesized samples is associated with a giant recalescence phenomenon, i.e. an unexpected increase in temperature upon cooling. This study shows that discontinuous magnetic transitions are accompanied by spurious thermal effects, highlighting the need for deeper understanding of the thermodynamic stability of the different phases and the kinetics of the transformations. [F. Guillou et al., Scripta Mater. 160, 81 (2019)]
3. Still in the Fe_2P-type system, we explore the crystal structure and magnetic properties of several series of $(Fe,Co)_2(P,Si)$ and $(Fe,Co)_2(P,B)$ alloys [F. Guillou et al., J. Alloys and Compds. 800 (2019) 403]. A detailed study of the magnetocrystalline anisotropy reveals that this materials family can combine relatively high Curie temperature and magnetic anisotropy, which opens some perspectives for applications in the field of permanent magnet, in addition to their magnetocaloric properties.

Key Words: magnetocaloric materials, rare earth intermetallics, iron-phosphides, magnetic anisotropy.

Oral Presentations

Session 3

Monday 16:30-18:30

Development of a Magnetocaloric Heat Pump for an Innovative Multi Source Heat Pump System

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In the RES4Build H2020 project, we will implement a magnetocaloric heat pump, called the MagQueen[1,2], into an innovative multi source heat pump system targeted at residential buildings. The MagQueen prototype is a rotary active magnetic regenerator (AMR) system, where the permanent magnet (B_{max} = 1.46 T) is rotating and 13 AMRs are mounted on a solid iron ring. In the project, it will be coupled to lower-temperature vapor compression heat pump and will provide heating to a building that also includes PV power, concentrated solar heating, and borehole thermal energy storage. In summer operation, the MagQueen will operate in reverse to provide cooling to the building.

However, the operation of the current magnetocaloric heat pump design is hampered by eddy currents that are induced inside the solid iron ring at higher frequencies. As a result, the input work is increased, the iron ring is heated, and the efficiency is significantly reduced. To prevent excessive power loss and overheating of the existing ring, a new iron ring design is needed.

In the present work, a new ring was designed and constructed made of soft iron laminations, which are electrically isolated from one another by a thin layer of epoxy. As these laminations are relatively thin, they restrict the size of the eddy currents. Additionally, improved magnetocaloric materials and improved cycle configurations will be tested to make the MagQueen more efficient, aiming at a COP above 5 for both cooling and heating modes.

Key Words: Magnetic refrigeration, active magnetic regenerator; heat pump

References:

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Exploiting thermal hysteresis by using a multi-stimuli cooling cycle – Concept and possible materials

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The rising demand for cooling increases also the energy demand and the associated CO_2 emission. The development of new energy-efficient cooling concepts is therefore unavoidable. In recent years, research has been intensified on caloric cooling - magnetocaloric, elastocaloric and electro-caloric. In the field of magnetocaloric cooling, it has been shown that materials with a magneto-structural phase transition exhibit a giant magneto-caloric effect (MCE). However, the thermal hysteresis associated with the first-order phase transition reduces the MCE in cyclic operation and the minimization of hysteresis is still a current research topic.

We would like to present an alternative possibility to obtain a giant, reversible MCE: the concept of the multi-stimuli cooling cycle. Figure 1 shows the six-step cooling cycle that uses the thermal hysteresis and enables a fully reversible magneto-structural transition by using an external magnetic and a stress field. The thermal hysteresis prevents therefore a retransformation when the external field is removed.

We will present our recent results on Ni(Co)Mn-based Heusler alloys. Especially alloys with larger thermal hysteresis are now potential candidates for the new multi-stimuli cooling cycle.

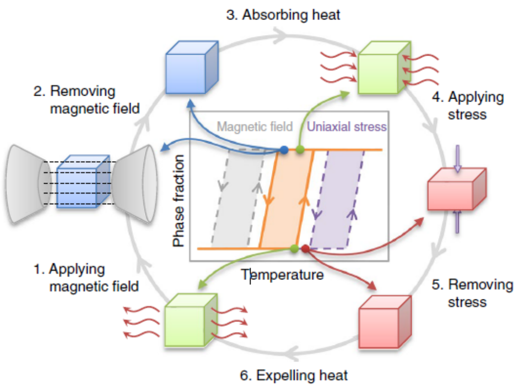

Fig.1 Schematic of a mutli-stimuli cooling cycle[1].

Key Words: magnetocaloric, elastocaloric, multicaloric cooling cycle, exploiting thermal hysteresis.

References

[1] T. Gottschall et al. Nature Mater. 17 (2018) 929-934.

Caloric and Multicaloric effects in Metamagnetic Ni-Mn-In under uniaxial stress and magnetic field

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Despite all the achievements of the last decades in diverse caloric effects, there are still a series of bottlenecks to overcome in order to make them a feasible alternative cooling technology. On the one hand, large external fields are needed to obtain giant caloric effects. On the other hand, the hysteresis associated with the phase transition reduces the efficiency and the reversibility of the caloric effects.

In many caloric materials there is a strong coupling between different degrees of freedom which leads to a cross-response of the ferroic order parameter to different external fields. Therefore, the simultaneous or sequential application of different external fields gives rise to multicaloric effects. Multicaloric materials exhibit significant advantages with respect to caloric materials, but still few materials have been experimentally studied up to date.

In this talk we will present the results of a thorough study on the multicaloric response of a prototype Ni-Mn-In metamagnetic shape memory alloy subjected to the combined action of magnetic field and uniaxial compressive stress, by using two different bespoke experimental setups. The first setup is a differential scanning calorimeter (DSC) which enables the application of magnetic field and uniaxial compressive stress. A second device has enabled us to perform direct measurements of the adiabatic temperature changes resulting from the application and removal of magnetic field under constant applied uniaxial compressive stress. The whole set of data provides a complete characterization of the multicaloric response of a metamagnetic shape memory alloy in terms of isothermal entropy and adiabatic temperature changes.

Key Words: magnetocaloric, elastocaloric, multicaloric, shape memory effect

Effect of Hysteresis on the Magnetocaloric Properties of LaFeSi alloys for Cryogenic Applications

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The commercially available LaFeSi-based CALORIVAC® alloys are one of most developed refrigerants for magnetic cooling applications around room temperature. Their operation span is, however, not limited to this temperature range. It can potentially be extended for cryogenic applications such as gas liquefaction or for medical applications.

In this work, LaFeSi-based alloys have been studied aiming for an optimization of the magnetocaloric properties down to -100°C. As a starting point, the effect of Cer substitution on a ternary LaFeSi material has been studied. With the rare earth substitution a 100% increase in the isothermal entropy change, ΔS_T, has been observed [1] . However, the improvement in ΔS_T is not reflected in the adiabatic temperature change, ΔT_{ad}, which in turn decreases.

The correlation between ΔS_T and ΔT_{ad} is further explored for different compositions and the role of hysteresis is studied to account for the observed effects. A better understanding of the hysteresis mechanism in LaFeSi can be used to minimize the reduction of ΔT_{ad} due to hysteresis effects in CALORIVAC alloys at cryogenic temperatures.

The authors acknowledge the financial support by the Federal Ministry for Economic Affairs and Energy of Germany (BMWi) in the project MagMed (03ET1478C).

Key Words: Hysteresis, LaFeSi

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Mechanical and magnetocaloric characterictics of first order LaFeSi-based materials

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We present here several types of experimental results of a LaFeSi-based magnetocaloric material. Firstly, the mechanical characteristics of several samples have been tested during an endurance test composed of two types of solicitations on a specific benchmark. Secondly, the magnetocaloric behaviour of several layerings with different Curie temperatures of this material has been analysed with a R&D rotating prototype. The obtained results are promising and show that the LaFeSi-based alloys have the potential to increase the cooling power and to reduce the cost of magnetocaloric units due to reduced raw material costs. This is one of the important factors which will lead to making the technology more accessible for a large-scale production.

Key Words: Magnetocaloric materials, experimental results, LaFeSi, FOPT

Oral Presentations

Session 4

Tuesday 9:00-10:30

Energy harvesting using thermomagnetic generators with magnetocaloric materials

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4. Technische Universität Hamburg, Hamburg, Germany

To date, there are only very few technologies available for the conversion of low temperature waste heat to electricity. More than a century ago, thermomagnetic generators were proposed, which are based on a change of magnetization with temperature, switching a magnetic flux, which according to Faraday's law induces a voltage. In this talk, we first describe the principle of thermomagnetic generators. Then we focus on the impact of topology of the magnetic circuit within thermomagnetic generators. We demonstrate that the key operational parameters strongly depend on the genus, i.e. the number of holes within the magnetic circuit. A pretzel-like topology of the magnetic circuit with genus =3 improves the performance of thermomagnetic generators by orders of magnitude. By a combination of experiments and simulations, we show that this topology results in sign reversal of the magnetic flux, avoids hysteresis as well as magnetic stray fields, and allows for versatile device design. Our demonstrator illustrates that this solid state energy conversion technology is on its way to become competitive with thermoelectrics for energy harvesting near room temperature. For all parameters, i.e. induced voltage, electrical output power, optimum frequency, and ratio between experiment and theory, a logarithmic scale is necessary to cover the orders of magnitude in improvement when using a topology with genus = 3. [1] In the next part of this talk we focus on the active magnetic materials used within a thermomagnetic generator. We present experiments using a thermomagnetic material close to a first-order type transition (La-Fe-Co-Si) in comparison to second-order type Gadolinium. We analyze the impact of the width of the magnetic transition and hysteresis on the conversion of thermal to electrical energy. Similarly to magnetocaloric materials [2], thermomagnetic materials must meet several requirements besides excellent magnetic properties, and we will review them and point out differences between optimum magnetocaloric and thermomagnetic materials.

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Optmizing the fabrication of magnetocaloric composite wires with different magnetocaloric core materials

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For magnetic refrigeration near room-temperature, LaFeSi- and Fe_2P-based alloys are considered as promising material classes due to their low-cost elements and tunable magnetocaloric properties [1]. Forming these materials into regenerator geometries is challenging because of their mechanical brittleness and structural changes during the magnetic phase transition. In order to evaluate the potential of different materials as refrigerants in cooling devices near room temperature, it is necessary to develop shaping technologies that allow the production of filigrane regenerator geometries to ensure optimal heat transfer.
A way to fabricate suitable regenerator geometries is presented in [2], through the application of the powder-in-tube process to produce magnetocaloric composite wires with a LaFeCoSi-based alloy. Therefore, magnetocaloric powder was filled into a seamless, 6 mm austenitic steel tube and gradually deformed to a diameter of 1 mm, resulting in a fraction of the core of about 58 vol.% and a wall thickness of the surrounding steel of about 100 µm. Heat treatment after swaging led to magnetocaloric properties comparable to those of reference material [2].
In this work we show the progress of this fabrication method towards thinner wires with 0.5 mm diameter at below 100 µm wall thickness. These favour the filling factor in regenerators and the heat exchange.
Moreover, we show the variation of magnetocaloric core material cladded in steel, including Gd and a LaFeSiMn alloy. After comparing these different composites, the results serve as basis for further studies and experiments, e.g. applying pulsed magnetic fields to evaluate the achievable adiabatic temperature change.

Key Words: composite, regenerator, powder-in-tube, shaping

References :

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Experimental Investigation of Magnetic Pumping for Magnetocaloric Refrigerator Application

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A suspension of micro/nano particles of magneto-caloric material in a heat transfer fluid in combination with the use of Magnetic Pumping (MP) enable the operation of a magnetocaloric refrigerator with no moving parts (see fig. 1). The present study utilizes space and time varying magnetic fields (in the order of 50 mT) to realize MP in ferrofluids, for the Reynolds number up to 10. Different spatial and temporal profiles of current, along with its intensity and frequencies less than 100 Hz are used to characterize the performance of MP. For example, a flow rate of ~ 0.2 g/s at 20 mT is obtained over a height difference of 2.5 mm (fig. 2). The usage of higher frequencies is restricted due to heating effect caused by viscous dissipation between micro/nano particles and the suspended fluid, which is detrimental to the cooling effect produced by the magneto-caloric effect. In the range of frequencies investigated, the optimal pumping was obtained for frequencies less than 1 Hz, at which the heating effects are almost eliminated.

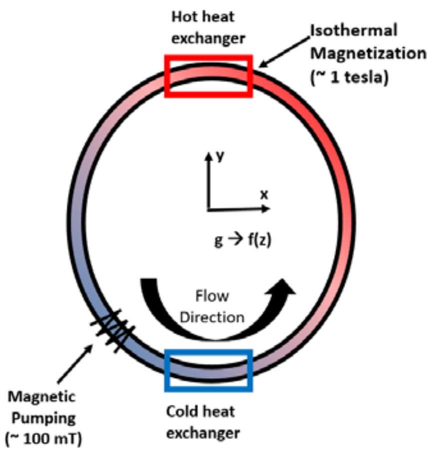

Figure 1 – Illustration of the proposed magneto-caloric refrigerator.

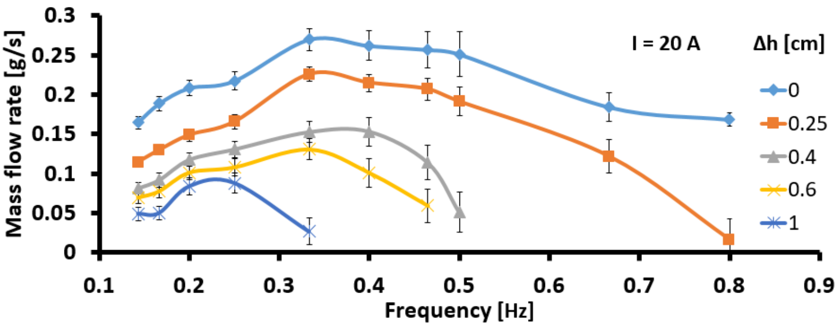

Figure 2 - Mass flow rate dependence on current frequency for different pumping height for a current intensity of 20 A.

Key Words: Magnetic pumping, Magnetocaloric heat pump.

"*MagChill*": Development of an air conditioner operated by a magnetic refrigeration unit

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POLO – Research Laboratories for Emerging Technologies in Cooling and Thermophysics, Department of Mechanical Engineering, Federal University of Santa Catarina, Florianópolis, SC – Brazil.
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MagChill is a research project which aims to develop an air conditioner with a cooling capacity of 9000 Btu/h (~2.6 kW) operated by a magnetic refrigeration unit (MRU) for internal and external reservoir temperatures of 22 and 35 ºC, respectively. The MRU consists of a magnetic circuit of Nd-Fe-B permanent magnets and solid refrigerants based on La-based alloys.

The development of a magnetic refrigeration system is a multidisciplinary task that requires the simultaneous and integrated design of several components. Not only the optimization of every single component but also the integration between them is fundamental for the design of a compact and efficient system. For that, a lean product development using the Toyota kata approach and Set-Based Concurrent Engineering strategy is applied to the system design. The project of the magnetic air conditioning system has been developed in five major research fronts: (1) magnetic circuit, (2) active magnetic regenerator, (3) heat exchangers, (4) hydraulic management system and (5) integration and optimization.

The target of this work is to give a summary of the overall advances on the design of the magnetic air conditioner. The design strategies proposed for every one of the components, as well as the integrated optimization methods used to achieve the minimum power consumption and mass of the system will be discussed. The expected thermodynamic performance, power consumption and mass breakdown of the system will be presented and evaluated.

Key Words: Magnetic refrigeration, air conditioning system, integrated design.

Inelastic X-ray Scattering for Magneto-Caloric Compounds

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The giant magnetocaloric effect, associated with a first-order magnetic transition, makes near room-temperature magnetic refrigeration [1] and energy harvesting [2] attractive as a highly efficient and environmentally-benign technology [3]. In magneto-caloric applications, for example an isothermal magnetic entropy change, ΔS, is followed by an adiabatic temperature change, ΔT, upon magnetic field variations resulting in either heating or cooling [4].
The quest for materials suitable for magnetocaloric applications close to room temperature resulted in systems beyond the archetypal Gd metal. One of the most promising system in this respect is $(Mn,Fe)_2(P,Si)$-based compounds because not only they comprise of cheap and environmental friendly elements but also because in such compounds the magnetic properties can be tuned over a wide range of temperatures, between 210 and 430 K, by varying the Mn/Fe and P/Si ratios [5].
A complete and comprehensive lattice dynamics characterization using nuclear inelastic scattering and inelastic X-ray scattering will be presented across the magnetic transition in $(Mn,Fe)_2(P,Si)$. The Fe specific and the total density of phonon states will be shown across the magnetic transition.
In an attempt to have a better understanding in the lattice dynamics of magnetocaloric compounds, preliminary inelastic X-ray scattering under externally applied magnetic field in the archetypal Gd metal will be also discussed.

Key Words: Inelastic scattering, thermodynamic characterization.

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Oral Presentations

Session 5

Tuesday 11:00-12:30

A La-Fe-Si Based Thermo-Magnetic Generator

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Low-grade heat from industrial processes and residential buildings represents a huge and cheap energy source. Development of new technologies to convert waste heat into electricity is today considered a major objective. The new generation of magnetocaloric materials (MCM) for refrigeration applications is offering some fresh opportunities to energy harvesting technologies. In cooling applications, the magnetocaloric effect is used to pump heat through the entropy change of the MCM associated to application/removal of a field. Thermomagnetic generators (TMG) use the pyromagnetic effect, namely the variation of magnetization as a function of the temperature, to perform thermodynamic cycles under varying field and eventually convert the magnetic energy into electrical one. Several thermo-generation prototypes using MCM have been proposed relying on different conversion chains. Here we have developed a new prototype based on a three steps conversion: Thermal/Magnetic, Magnetic/Mechanical and finally Mechanical/Electrical. The geometry is similar to the one studied in [1] with three main differences: the magnetic field lines are spatially confined by the use of a Halbach array improving the magnetic force and the field inside the magnetocaloric material [2]; the active substance is a first order $La(Fe,Si)_{13}$ from Vacuumschmelze; the mechanical displacement of the MCM is eventually converted to electrical energy using piezoelectric material. All the energy conversion chain steps have been studied through direct measurements performed on the working prototype. Notably the total energy efficiency of the device is worked out experimentally using the prototype as a characterization bench.

This work benefited from the financial support of the project HiPerTherMag (ANR-18-CE05-0019) managed by the French National Research Agency.

Key Words: Magnetocaloric materials, magnetocaloric effect, thermomagnetic generator, electrical energy.

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Microstructure, mechanical and magnetocaloric properties of bulk $La_{0.9}Ce_{0.1}Fe_{11.7-x}Mn_xSi_{1.3}$ hydrides

Naikun Sun,[1,] Yang Zhang,[1] Xinguo Zhao,[2,] Jie Guo, [1] Juan Cheng,[3] Jiaohong Huang,[3]

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ABSTRACT

La(Fe, Si)$_{13}$ hydride is regarded as one of the most promising room-temperature refrigerants. However, to use the alloys in an active magnetic regenerator machine, it is vital to prepare thin refrigerants. In this work, a high H_2 gas pressure of 40-50 MPa was employed to suppress the desorption of hydrogen atoms during the sintering process of plate-shaped La(Fe, Si)$_{13}$ hydrides. Fully hydrogenated $La_{0.9}Ce_{0.1}Fe_{11.7-x}Mn_xSi_{1.3}$ bulk hydrides with Curie temperature T_C around room temperature were prepared by high-hydrogen-pressure sintering. High-resolution X-ray microtomography has been employed to analyze the morphology, size and distribution of the micropores in the sintered bulk sample. The analysis result shows that most of the micropores have the size of several micrometers with the porosity of 0.22 %. A thin plate of $La_{0.9}Ce_{0.1}Fe_{11.35}Mn_{0.35}Si_{1.3}H_{2.0}$ exhibits a magnetic-entropy change ΔS_m of 7.5 J/kg·K at 290 K and a hysteresis loss of 0.5 J/kg for a magnetic-field change from 0 to 2 T. As the sintering pressure increases from 40 to 50 MPa, more α-Fe (~20 wt %) precipitates from the 1:13 phase, which causes a reduction of ΔS_m to 6.2 J/kg·K for a field change from 0 to 2 T at 297 K and a remarkable enhancement of the compressive strength from 46 to 421 MPa.

Key Words: high-pressure sintering; micropores; mechanical properties; magnetocaloric effect

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A High-throughput Study of Magnetocaloric Materials: Gradient Solidification Applied to La-Fe-Si

Yi Ouyang [1,2], Mingxiao Zhang [1], Jun Li [3], Aru Yan [1,2], Jian Liu [1,2,*]

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[3] School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
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Magnetocaloric properties of rare-earth-based materials often highly rely on the solidification microstructure. In this work, we employ the wedge-mold solidification technique as a high-throughput method to investigate the cooling rate-dependent microstructural evolution and magnetocaloric effect in single La-Fe-Si samples. Finite element simulations indicate that the cooling rate continuously varies in a large range of 270-3000 K/s along the axial direction of the sample. The non-stoichiometric $La_{1.7}Fe_{11.6}Si_{1.4}$ keeps $NaZn_{13}$-type $La(Fe,Si)_{13}$ functional phase of about 80 vol.% by cooling in 500-3000 K/s and subsequently annealing at 1323 K for just 5 min. This suggests that fast cooling brings about quick atomic diffusion and shortened annealing time. With the maximum cooling rate up to 3000 K/s, a large magnetic entropy change of 14 J/kg K at 2 T field has been achieved. In addition, by analyzing the elemental distribution in the same position, a needle-like phase was found to act as the diffusion channel of Si atoms for fast phase reaction. From this work, we have demonstrated the wedge mold casting technique as a simple and efficient method to study the microstructural dependency of magnetocaloric properties in cooling-rate sensitive materials.

Key Words: High-throughput method; La-Fe-Si alloys; Magnetocaloric effect; Cooling rate

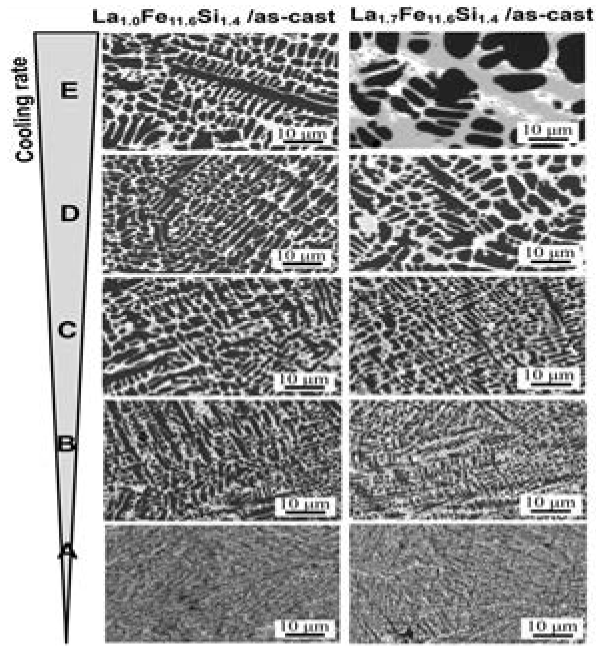

Fig. 1. SEM backscattered electron images of as-cast $La_{1.0}Fe_{11.6}Si_{1.4}$ and $La_{1.7}Fe_{11.6}Si_{1.4}$ alloys at selected wedge-shaped sample positions with different cooling rates.

Freeze-casting of monolithic regenerators with micro-channels and varying Curie temperatures

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We present the engineering of monolithic active magnetic regenerator (AMR) geometries of lamellar micro-channels by freeze-casting. Freeze-casting is a versatile templating technique based on the anisotropic growth of ice crystals that when applied on for example $La_{0.66}Ca_{0.33-x}Sr_xMn_{1.05}O_3$ (LCSM) magnetocaloric ceramics results in rigid ceramic structures with homogenous and low tortuosity micro-channels of ~5 to ~50 µm in width and with ~70% porosities (Christiansen *et al.* 2019). For the application of LCSM ceramics as AMR, a larger operational temperature span using this material can be achieved by a layering of LCSMs with various Curie temperatures (Bahl *et al.* 2012), i.e. various Sr-doping. Here, we show that layering of LCSM in a combined freeze-cast structure can be achieved by altering freezing conditions and by changing suspension properties by the addition of various organic additives. This allows multiple suspensions to be freeze-cast together, with distinct interfaces between LCSM layers as illustrated in Figure 1. These interfaces can easily be made to be continuous for the microchannels.

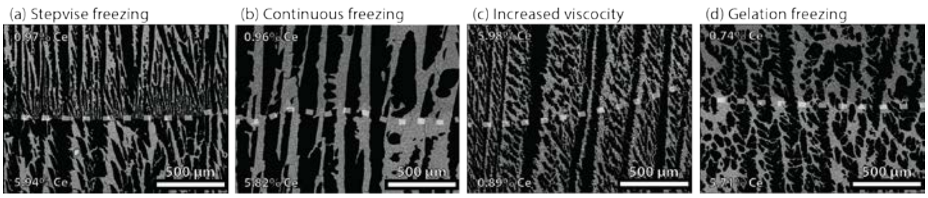

Figure 1: SEM micrographs showing the interface between LCSM layers of freeze-cast ceramics frozen under various conditions. Images are obtained at cross sections parallel to the freezing, i.e. channel, direction, where black areas are channels and grey areas are ceramic walls. The dashed lines indicate the interfaces.

Key Words: Freeze-casting, micro-channels, layered regenerators

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Oral Presentations

Session 6

Tuesday 14:00-16:00

Advanced characterization of magnetocaloric materials in pulsed magnetic fields

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The direct determination of the adiabatic temperature change, ΔT_{ad}, as a function of the magnetic field and the starting temperature is of central importance for a profound characterization of magnetocaloric materials [1]. Recently, a technique was developed to measure the temperature change in pulsed magnetic fields by using ultra-thin thermocouples attached to the sample [2]. This enables the investigation of different phenoma, such as the scaling behavior of the magnetocaloric effect in magnetic fields ranging from 2 up to 62 T [3], the dynamics of first-order phase transitions in dependence of the sweeping rate [2], thermal transport properties of composite structures, and more.

In this work, we give an overview of the most recent results that have been obtained in pulsed magnetic fields at the Dresden High Magnetic Field Laboratory. It could be shown on the basis of gadolinium that the usual $H^{2/3}$ power law of the magnetocaloric effect fails in fields beyond 10 T. For that reason, the position of the maximum ΔT_{ad} shifts towards higher temperatures.

First investigations on multicaloric materials demonstrated that the strain of the sample parallel and perpendicular to the magnetic field can be measured at the same time as the temperature change with good resolution. This shows the great potential of pulsed-field experiments for their comprehensive characterization.

Key Words: Adiabatic temperature change.

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Synchrotron X-ray diffraction on the charge distribution in $La(Fe,Si,Co)_{13}$ compounds

Xinmin You[1], Michael Maschek[1], M.F.J. Boeijie[1], Alexander Barcza[2], D. Chernyshov[3], Niels van Dijk[1], Ekkes Brück[1]

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$La(Fe,Si)_{13}$ compounds are magnetocaloric materials that show a negative thermal expansion [1]. In the $La(Fe, Si)_{13}$ system, Co substitution increases T_C and can be used to tune the system to make it suitable for room temperature applications. A series of $La(Fe,Si,Co)_{13}$ samples was prepared by Vacuumschmelze for the present study.

Temperature-dependent high-resolution X-ray powder diffraction and magnetization measurements are used to investigate the lattice structure and the magnetic and electronic degrees of freedom across the magnetic phase transition. The magnetic properties for the $La(Fe,Si,Co)_{13}$ samples show that an increasing Co content leads to an increase in T_C and tunes the material from a first-order magnetic phase transition (FOMT) material to second-order magnetic phase transition (SOMT), while the thermal hysteresis remains neglectable. The most significant change in lattice parameter across the transition appears in the FOMT sample with the lowest Co content. Surprisingly, the transition is accompanied with an angular change for the orientation of the cage within the lattice. The electron density is obtained from the high resolution X-ray diffraction. The evolution in electron density across the transition and for increasing Co contents is monitored by electron density maps [2].

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When actual effects look like artifacts: Deconvolution of the concurrent transitions in Ni-Mn-In Heusler alloys.

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Nowadays, magnetic materials with first-order phase transitions have been the focus of magnetocaloric research. Among them, Heusler-type alloys exhibit magneto-structural transformation other than the Curie transitions of their martensite and austenite. It has been considered that its total entropy change can be improved when structural and magnetic phase transition coincide. Such tuning can be made possible as the transition temperatures are composition-dependent, having the largest tunability in Ni-Mn-In among the Ni-Mn-based Heusler alloys. In this work, the MCE of $Ni_{49+x}Mn_{36-x}In_{15}$ (x=0-2) was studied [1]. With increasing electron per atom ratio (e/a), their martensitic transitions shift to higher temperatures and the overlap of martensitic transition and Curie transition of austenite becomes tighter. In particular, the sample with e/a=7.874 shows resemblance of an experimental artifact but actually arises due to the concurrent phase transitions: one positive ΔS_{iso} amidst the region of conventional MCE. Using field dependence of AC susceptibility, the concurrence of phase transitions was characterized, leading to their deconvolution. The magnetic field stabilizes the austenitic ferromagnetic phase and shifts the martensitic transition to lower temperatures, thus demonstrating that the observed spike is due to the martensitic transition of the sample. In this case, the concurrence of magneto-structural and Curie phase transitions in e/a=7.874 is not optimal for improving the magnetocaloric response as the inverse MCE is compensated by the conventional MCE.

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Key Words: Ni-Mn-In Heusler alloys, thermomagnetic phase transitions, magnetocaloric effect.

References [1] J. Y. Law et al. Acta Mater. 166 (2019) 459

Large Magnetocaloric Effect At Room Temperature In $Pr_{0.64}Sr_{0.36}MnO_3$ Manganite

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The structural, magnetic and magnetocaloric properties of the perovskite $Pr_{0.64}Sr_{0.36}MnO_3$ manganite have been investigated. The single phase of the investigating compound has been confirmed by Rietveld refinement of X-ray powder diffraction patterns. From the magnetic measurement, a second-order magnetic phase transition from paramagnetic to ferromagnetic state was noticed near the room temperature. Besides, the magnetocaloric effect (MCE) as well as the Relative Cooling Power (RCP) has been estimated. The obtained results have confirmed that the proposed sample has a quite high magnetic entropy change and relative cooling power around room temperature, which makes it potentially used as magnetic refrigerants in magnetic refrigeration.

Key Words: Perovskite, Magnetocaloric effect; Relative Cooling Power.

Pressure Effect on the Magneto-structural Phase Transition in $Mn_3CuN_{0.75}C_{0.25}$

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Recently, antiperovskite manganese nitrides of the form Mn_3AN, where A is a metal or semiconductor element, have been studied due to several useful properties such as giant negative thermal expansion, Hall effect, near zero temperature coefficient of resistance and magnetocaloric effects. Mn_3CuN undergoes a first order phase transition from a low temperature tetragonal ferrimagnetic phase to a high temperature cubic paramagnetic phase at 143 K. The volume of the cell is nearly conserved at the transition, resulting in low thermal hysteresis and a moderate giant MCE of 13.52 J/kgK ($\Delta B = 5$ T) [1].

We have recently reported on the magnetic and structural properties of Mn_3CuN-based compounds with N substituted by C[2] as well as Cu partially replaced by Ag and Ni and simultaneous substitution of N by C[3]. Moderate tuning is achieved between 130 and 165 K and entropy changes as high as 12 J/kgK ($\Delta B = 2$ T) were observed in $Mn_3CuN_{0.75}C_{0.25}$. However, we have observed that tuning the transition by substitution is limited to this very narrow temperature interval and that the sensitivity of the transition temperature to the applied magnetic field is very weak. These characteristics point to a weak magneto-structural coupling. In order to test this hypothesis we have applied hydrostatic pressure to the $Mn_3CuN_{0.75}C_{0.25}$ compound. Hydrostatic pressure does not suffer from parasitic effects originating in the substitution itself and allows a clean probing of the magneto-structural coupling. We observed that both chemical and physical pressures have similar effects on the transition, and that just as substitutions have a limited effect on the transition temperature a low dT_C/dP is also observed.

Key Words: magnetocaloric effect, hydrostatic pressure, antiperovskite, magneto-structural phase transition

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Posters

Screening of the synthesis route on the structural, magnetic and magnetocaloric properties of $La_{0.6}Ca_{0.2}Ba_{0.2}MnO_3$ manganite: A comparison between solid-solid state process and a combination polyol process and Spark Plasma Sintering

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a b s t r a c t

$La_{0.6}Ca_{0.2}Ba_{0.2}MnO_3$ ceramics are prepared by an original route, combining soft chemistry and Spark Plasma Sintering, within a few minutes at 700 °C and by the solid-state reaction at high temperatureswith an annealing temperature of 1200 °C. We have studied the leverage of the powder synthesismethod on the structural, morphological, magnetic and magnetocaloric properties of the samples. X-ray diffraction analysis using Rietveld refinement revealed that our materials crystallize in the rhombohedral system with R3-c space group for the sample prepared by the Polyol-Spark Plasma Sintering method and in the orthorhombic structure with Pbnm space group for the sample synthesized by the solid-state reaction. Magnetization measurements versus temperature under magnetic applied field of 0.05 T show a paramagnetic-ferromagnetic phase transition for both samples. The Arrott plots reveal that ours materials undergo a second-order phase transition. The maximum values of the magnetic entropy change ($-\Delta S^{max}_M$) under the magnetic field change of 5 T are 2.4 and 4.7 J/kg K for $La_{0.6}Ca_{0.2}Ba_{0.2}MnO_3$ synthesized by using solid-state reaction and Polyol-Spark Plasma Sintering methods respectively. The highest value of the relative cooling power RCP is found to be 244 J/kg for the Polyol-Spark Plasma Sintering sample under 5 T. These results are interesting enough and suggest that the Polyol-Spark Plasma Sintering synthesis method is a feasible route to prepare high quality perovskite material for magnetic cooling application.

Keywords:
Manganites
Preparation methods
Magnetization
Magnetocaloric effect

Thermal performance of magnetocaloric composite wires in pulsed magnetic fields

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Apart from the benchmark Gadolinium, LaFeSi- and Fe_2P-based alloys are considered as promising candidates as refrigerants in cooling devices near room temperature [1]. However, due to their mechanical brittleness and the accompanied structural change during the magnetic phase transition, shaping these materials into effective regenerator geometries is difficult. Complex geometries have been achieved for example by extrusion [2] or additive manufacturing [3]. As a post heat treatment is required after these processes, the mechanical durability of such geometries still is reduced. In [4], we presented the successful application of the powder-in-tube technology on a LaFeCoSi-based alloy. The magnetocaloric powder was cladded in a seamless steel tube and successively deformed down to a diameter of 1 mm with only only about 100 µm thickness of the surrounding steel. After a short heat treatment the composite wires showed the same magnetocaloric properties as the reference alloy.
However, the influence of the steel jacket on the achievable thermal span in a cooling device remains unclear. In this work, we assessed the evolution of the temperature change in dynamic operation conditions by applying pulsed fields of 2 T, 5 T and 10 T within. The temperature change of the core and the surrounding steel was monitored by thermocouples simultaneously. These results served as a basis for further numerical simulations, revealing the influence of operation frequency, thermal properties of the jacket material and interfacial resistance between core and jacket on the effectively achievable temperature change in the composite wires.

Key Words: composite, regenerator, powder-in-tube, shaping process

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Numerical Analysis of Magneto-Caloric Effect within a Circular Annulus

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In the past few years, a lot of experimental and numerical studies are done to use Magneto-Caloric Effect for operating automated energy transport devices [1-3]. In context with that work, an unsteady CFD investigation is carried out to explore the effect of size and different locations of permanent magnet on Magnetocaloric Effect. A circular annulus of fixed L/D ratio of 0.125 is observed for kerosene-based Gadolinium (*Gd*) nanoparticles. Maxwell's Equations of Magnetostatics are solved in addition to continuity, momentum and energy equation for incompressible, newtonian fluid in COMSOL environment. A validation is carried out to ensure the accuracy of numerical results. Also, grid independence and a time independence analysis is performed to minimize possible discretisation errors.

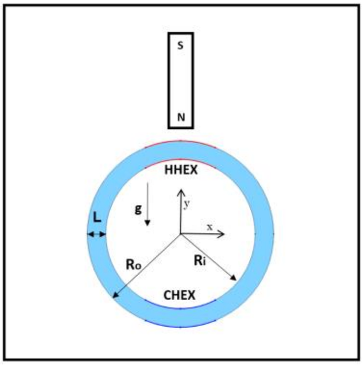

Figure 1: Geometrical Details

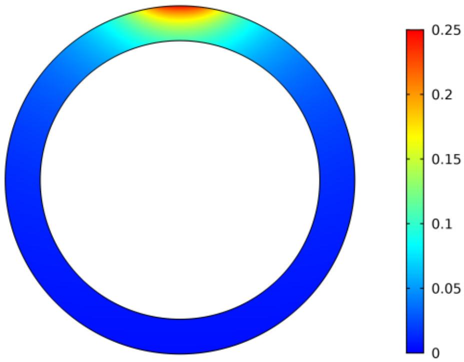

Figure 2 : ***H'*** distribution within annulus

The geometrical description for the present analysis is shown in Figure 1. The non-dimensionalised magnetic field ($\boldsymbol{H'} = \mu_0 H/B_r$, here B_r represents Remanant Flux Density) produced by a permanent magnet is also shown in Figure 2. To achieve the maximum adiabatic temperature rise, the initial temperature for present analysis is taken as Curie Temperature (*Tc*) of *Gd*.The surface averaged Nusselt Number (Nu_{avg}) is also plotted along with velocity and temperature contours.

Key Words: Magnetocaloric Effect, Magnetocaloric nanofluid, Permanent Magnet, Heat Transfer

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Spatial and Temporal Characterization Device for Magnetocaloric Effect and Phase Transitions

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We present a device capable of measuring the magnetocaloric effect and phase transitions of magnetocaloric materials by means of infra-red (IR) thermography. Thereby, both the temporal and spatial temperature response upon change in applied field is investigated at a frequency up to 170 Hz and with 320x256 pixels, each pixel corresponding to 20x20 μm^2.

The temperature of the sample is controlled by a Peltier element and can be set from 260 to 330 K. A ~10 cm long temperature control Cu-finger is required to fit into the central, cylindrical opening of a concentric Halbach array of permanent magnets, which allows the application of a magnetic field in the range from zero to one tesla across the sample. In order to simultaneously apply high vacuum, the Cu-finger is encapsulated by an Aluminium cylinder, with an IR transparent ZnSn window (1 mm thick). A FLIR SC5200 IR Camera, with thermal resolution down to 20 mK, is positioned directly above the Halbach cylinder on an XYZ stage. The applied field is measured inside the vacuum chamber in-plane of the sample surface by a hall probe sensor. Additionally, a Pt100 sensor measures the temperature near the sample holder.

In order to explore the functionality of the device we present measurements of Gadolinium and La(Fe,Si,Mn)H with stoichiometry variation to gain different transition temperatures. We compare the results with literature and point out the crucial role of the sample holder, since its thermal conductivity needs to adapt with the temporal resolution of the IR Camera.

Key Words: spatial, characterization, phase, transition.

Tuning the Magnetocaloric Effect towards Room Temperature by B-site Doping in the perovskite $La_{0.8}Sr_{0.2}MnO_3$

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The influence of Cu^{2+} B-site doping on the magnetic properties in the perovskite $La_{0.8}Sr_{0.2}MnO_3$ prepared by solid-state reaction method has been investigated. The single phase of the investigating compounds has been confirmed by Rietveld refinement of X-ray powder diffraction patterns. Cu^{2+} doping in the B-site affects the Mn-O-Mn bond angle, which plays a major role to determine the Curie temperature of perovskite-manganites. The experimental results show a 16 K change of the Curie temperature for only 5% of Cu doping. Using the Banerjee criterion, second order phase transitions have been verified for both the parent and doped compounds. The value of the isothermal entropy change was observed 3.83 J/Kg-K ($\Delta H = 5$T) for the $La_{0.8}Sr_{0.2}MnO_3$ compound, which also increases by 4% in the doped $La_{0.8}Sr_{0.2}Mn_{0.95}Cu_{0.05}O_3$ compound, makes this doping process significantly important for room temperature magnetic refrigeration applications.

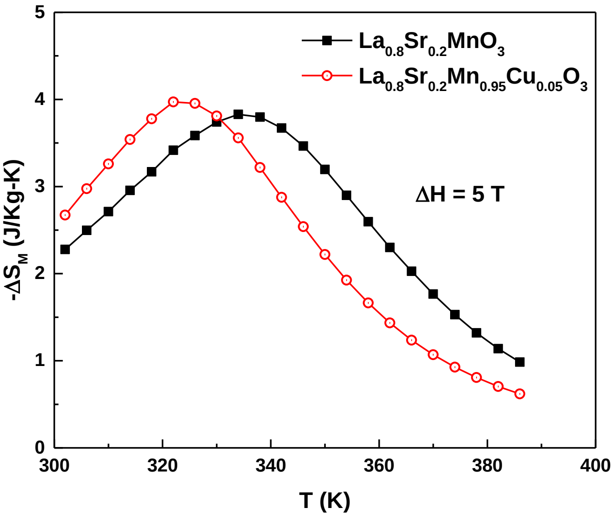

Figure 1. Temperature variation of the isothermal entropy change for $\Delta H = 5$T.

A Magnetic Heat Pump Prototype for Experimental Purpose and its Multi-layer regenerator bed extension plan

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With this, we present a room temperature magnetic heat pump prototype designed especially for studying how the properties of magnetocaloric material (MCM) correlated to heating or cooling performance in a realistic environment. This prototype is a rotary-type device which is based on the active magnetic regeneration (AMR) cycle. This prototype utilizes only simple magnetic field source with a field density of 0.875 T. However, performance is gained from other structural designs, such as the asymmetric regenerator bed layout and flow disperser in all regenerator beds. The MCM packed bed is fabricated with epoxy-bonded gadolinium spheres and ensures good packing density while the pressure drop across the regenerators remains moderate. The timing and synchronizing are achieved with a real-time control system and a closed-loop coupling between encoder and solenoid valves. Under the condition of AMR frequency of 1.7 Hz and utilization of 0.25, a result of maximum zero power temperature span 11.6 K, the maximum zero-span cooling power 162.4 W, and COP of 1.59 has been achieved with a hot end temperature of 295K; Under a condition of AMR frequency 1.2 Hz, utilization of 0.10, the maximum heating temperature span 16.1 K is observed with cold end temperature of 286.7 K. Besides, to further extend this prototype with multi-layer MCMs, a numerical system model is applied for predicting the performance of the given MCM layer configuration. The influence of layer thickness and spacing of Curie temperature is explored with the preliminary result.

Thermodynamic Characterization of Freeze-cast Regenerators

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The efficiency of the magnetic refrigeration cycle strongly depends on the design and heat transfer performance of the regenerator. One of the technical challenges is improving the heat transfer performance in a regenerator made from magnetocaloric material in a porous geometry. A packed bed as a classical porous geometry has been successfully demonstrated. Small hydraulic diameter design, ~100 microns, is a potential way to achieve improved heat transfer performance for a regenerator. Derived by the successful engineering of lamellar micro-channel structures fabricated by freeze-casting (Christiansen et al. 2019), we characterized the freeze-cast regenerators made from the ceramic $La_{0.66}Ca_{0.27}Sr_{0.06}Mn_{1.05}O_3$ (LCSM). By means of three freeze-cast regenerators characterized by different pore widths (Figure 1), heat transfer performance and friction factor are experimentally analyzed for passive regenerator operation. Stability of the regenerators is validated by a long time experiment running on combined passive and active experiments. This study aims to improve the design parameters for developing freeze-cast regenerators.

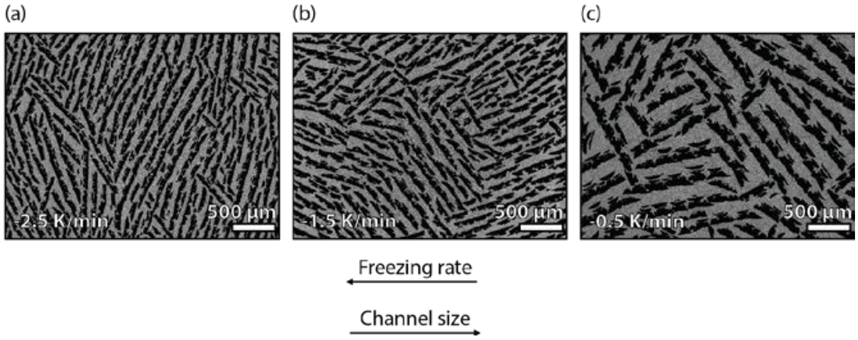

Figure 1 SEM images of the channel cross section in the freeze-cast regenerators with different pore widths: (a) 37.7 µm, (b) 45.5 µm and (c) 62.1 µm, respectively.

Key Words: Magnetic regeneration; Thermal regenerator; Freeze-casting; Lamellar microchannel; Thermodynamic characterization

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Fast Measurement of Adiabatic Temperature Changes in LaFeSi-based Alloys at Cryogenic Temperatures

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LaFeSi-based alloys are well-suited for applications which cool down to -90°C and below. Besides the alloys, the appropriate measurement technology must be developed for this purpose. In this contribution the conception, development and validation of a test stand for the measurement of adiabatic temperature change (ΔT_{ad}) of materials with peak temperatures down to -90°C shall be presented.

Over the years, Vacuumschmelze has gathered experience in the field of measuring magnetocaloric quantities and has set up a ΔT_{ad} measuring system for room temperature, which is already in use for testing materials. The test stand presented here is a modification of this established technique.

The test stand consists of a sample holder placed inside of the air gap of a rotating permanent magnet assembly. A cryogenic gas flows through the sample holder, which is also connected to an electric heater and a temperature control unit. With the help of this construction it is possible to ensure a continuous heating rate of the sample. The sample temperature is continuously measured using a thermocouple attached to the sample. The adiabatic temperature change is the temperature difference between the temperatutre measured when the sample is in a high magnetic field region and the temperature when the sample is the the zero-field region.

In our contribution it will be shown that the ΔT_{ad} measuring station enables a fast and direct measurement of the adiabatic temperature change of a LaFeSi-based samples, at cryogenic temperatures.

The authors acknowledge the financial support by the Federal Ministry for Economic Affairs and Energy of Germany (BMWi) in the project MagMed (03ET1478C).

Key Words: Measurement technique, Adiabatic temperature change, Cryogenic

Minimization of impurity phases in MnFePSi

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The conversion of low temperature waste heat into power by thermogmagnetic motors has the potential to supplement renewable energy sources [1]. Suitable materials for power generation are MnFePSi based compounds [2], which have a tunable temperature range and show large magnetization changes.
The MnFePSi compounds were produced by melt spinning, which is also suitable technique for mass production.
In order to optimize production on lab-scale and industrial scale, the impurities have to be minimized by optimization of the stoichiometry. X-ray diffraction has been used to identify impurities and determine the impurity phase contents.

Key Words: Melt spinning, X-ray diffraction, Wast heat to power generation, thermomagnetic motor

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Experimental Performance of Passive Regenerators With Nature-Inspired Flow Structure

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Recent developments in additive manufacturing have enabled production of active magnetic regenerators (AMR) with unconventional flow structures (Moore *et al. 2013;* Trevizoli, *et al. 2019)*. In this study, experimental heat transfer characterisation of a nature-inspired regenerator geometry is presented. Previosuly, the potential of this geometry as an AMR was evaluated numerically using a 1D numerical AMR model (Navickaitė, *et al. 2019)*. Based on the numerical results, two regenerators with corrugated flow paterns and one reference regenerator with cylindrical micro-channel matrix were manufactured using Laser Beam Melting (LBM) technique in $AlSi_7Mg_{0.6}$ powder at Fraunhofer IFAM (Figure 1). The regenerators were tested in the oscillating-flow passive regenerator setup developed at DTU. The hydrauluic diameter of the regenerators flow channels was 0.35 mm and wall thickness 0.30 mm. The height and internal diameter of the regenerators was around 46.8 mm and 28.3 mm, respectively.

(a) (b) (c)

Figure 1. The regenerators manufactured using LBM technique with (a) straight flow channels, and double corrugated flow channels with (b) constant cross section area and (c) constant hydraulic diameter.

Key Words: (Biomimetics, selective laser melting, magnetic cooling, AMRs flow geometry).

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Detailed Isofield Calorimetry of La(Fe,Si,Mn)H Revealing Localized Variation In Phase Transitions

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We present detailed calorimetric measurements on La(Fe,Si,Mn)H around 305 K at applied fields from zero to one tesla. At low ramp rates (0.05 K/min) we observe distinct peaks as a function of temperature within a single sample in accordance with previous results [1]. Upon analyzing the peaks' behavior as a function of applied field we find for finite fields above approximately 0.15 T that the peaks move to higher temperatures as a function of field at different rates.

We show that the different slopes of the peak positions as a function of field are consistent with a narrow spread in the Bean-Rodbell parameter, η. We furthermore show that the individual peak transition temperatures do not follow this behavior, i.e. the localized transition temperature T_0 is at best weakly coupled to η. This is contradictory to the overall behavior of η as a function of T_0; η is expected to decrease linearly with increasing T_0 in accordance with softening of the phase transition at higher temperatures.

We propose this local decoupling of η and T_0 to be caused by one or more effects: i) subtle details regarding local variation in stoichiometry only relevant in the vicinity of the nominal composition, ii) conjugate effects due to inhomogeneity of the internal field thus causing internal stresses that modulate the local phase diagram [2].

Key Words: Calorimetry, Bean-Rodbell,

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Growth temperature dependence of phase transformation and of entropy change in Gadolinium thick films

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Bulk Gadolinium (Gd) is commonly used as a benchmark material to evaluate other magnetocaloric materials. It has also been the first and most used active substance in magnetic refrigerator prototypes. Up to now, while there is a number of studies focusing on Gd bulk and thin film in the nanometer range, a systematic study of Gd thick film in the micrometer range is lacking. Recently the interest in caloric materials based energy harvesting applications is growing, with a particular focus toward small high frequency devices. In this field Gd thick films can play once more a reference role. However, although a micrometer sized film can be reasonably expected to show properties similar to bulk Gd, a study on the role of the growth conditions is in order. Here we focus on growth temperature effect on magnetic properties of 3 µm Gd thick films prepared by DC sputtering. Growth temperature was varied from room temperature (RT) up to 550^{o}C. Microstructure was characterized by a scanning electron microscope and a high precision diffractometer. Magnetic properties were measured using VSM-PPMS and a SQUID magnetometer. Results show that the growth temperature strongly impacts the properties of thick films. Notably, RT deposited samples show an increase of lattice parameters *a* and *c*, a decrease of Curie temperature T_C as compared with the bulk values. Increasing growth temperature leads to reduce lattice parameters and increase T_C as well as in-plane magnetization. It also sharpens the phase transformation curve. Entropy change as a function of temperature with application of in-plane magnetic field, an important parameter to evaluate the magnetocaloric performance, also increases with an increase of growth temperature.

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Key Words: Gadolinium, magnetocaloric effect, thermo-magnetic power generation, magnetic refrigeration

Modelling of a La(Fe,Si)$_{13}$-based magnetocaloric material for a thermomagnetic generator

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The present work has been performed as a part of a project aiming to develop an efficient thermomagnetic micro-generator [1]. The design process includes thermodynamic simulations of a self-oscillating heat engine, which require proper constitutive equations. To understand the complex behavior of the energy harvester, we compare the predictions of a model built upon the measured physical properties of the active material and the real-life performance of a working device prototype.

A commercial-grade La(Fe,Si)$_{13}$-based magnetocaloric alloy (CALORIVAC HS) with operating temperatures around 30 °C was received from VACUUMSCHMELZE (Germany). The phase composition of the material was examined by X-ray diffraction, whereas the magnetic and thermal properties were determined using the PPMS platform. The magnetization curves in applied field of up to 9 T and specific heat values were obtained in a temperature interval encompassing the phase transition.

Cubic La(Fe,Si)$_{13}$ phase undergoes an isostructural transition associated with changes in magnetization and volume. The thermodynamic description of this first-order phase transition is given in terms of a Landau-type model with magnetoelastic coupling which has been recently applied to the (Mn,Fe)(P,Si) magnetocaloric material [2]. The magnetization and temperature of the sample measured during a thermodynamic cycle in the energy harvester are compared to the results of simulations using the model and experimental data.

This research has received funding from the project HiPerTherMag (ANR-18-CE05-0019) managed by the French National Research Agency.

Key Words: La-Fe-Si, magnetocaloric materials, thermomagnetic energy conversion, first-order phase transitions.

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Magnetocaloric heat exchangers

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Hydrogenated La(Fe,Mn,Si)13 alloys are considered as promising and cost efficient materials for active magnetic regenerators operating near room temperature. However, due to their poor mechanical and chemical stability this alloys can not be directly implemented in a cooling machine. A natural solution is the production of a composite magnetocaloric materials by polymer-bonded techniques. Main disadvantage of those composite is the fatigue due to the mechanical stress caused by the large magnetostriction effect [1,2].
Here we present the methods and equipment used to produce metal-bonded magnetocaloric material. Further a comparative investigation of the magnetocaloric properties of polymer-bonded and metal-bonded magnetocaloric material is presented [3,4].
Two heat-exchangers geometries are theoretically compared: stacked flat plate/channel structure and packed bed of spherical particles. The optimal operation frequency and the maximal cooling power were calculated by using a similarity theory based model, combined with unsteady heat transfer approach [5].

Key Words: (magnetocaloric materials, heat exchangers).

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Magneto-Optical Spectra of an elastocaloric Antiferromagnet: Theory and Experiment

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The first observation of the Magneto-optical Kerr Effect (MOKE) in an antiferromagnetic (AF) metal was reported last year [1]. Here we present MOKE spectra in a non-collinear AF structure of metallic Mn_3NiN which is closely related to the AF structure of Mn_3Sn studied earlier [1].

Mn_3NiN belongs to a family of Mn-based antiperovsktie nitrides which show promise for a wide range of applications in spintronics [2,3] and solid-state cooling [4,5,6]. The functionality is mainly derived from the frustrated exchange interactions in the triangular AF structure and its response to strain [7,8]. We simulate the intrinsic contribution to MOKE spectra of the relaxed and strained Mn_3NiN using density functional theory and linear response approximation.

We measure the corresponding spectra above and below the Neel temperature in Mn_3NiN thin films deposited on different perovskite oxide substrates and compare this data to the theory. The observed qualitative agreement of the data confirms the presence of the triangular AF structure which is crucial for achieving the caloric effects in this material.

Key Words: Elastocaloric effect, Magneto-optical Kerr effect, Antiperovskite

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Magnetocaloric Effect in the $(Mn,Fe)_2(P,Si)$ System: From Bulk to Nano

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In the field of nanoscale magnetocaloric materials, some novel devices/ideas have been proposed, including microrefrigerators, thermal switches, microfluidic pumps, energy harvesting devices and biomedical applications. However, reports about nano-scale $(Mn,Fe)_2(P,Si)$-based materials which are one of the most promising bulk materials for solid-state magnetic refrigeration are rare. Thus, in this project we have synthesized nano-scale $(Mn,Fe)_2(P,Si)$-based nanoflakes, and investigated systematically the influence of the grain size and defects structure on the magnetocaloric effect. The results show that the decreased saturation magnetization (M_s) is mainly attributed to the introduced defects during synthesis process, and with decreased the particle size, both the hysteresis and T_c are reduced. In addition, when we annealed our nano-scale materials under protective atmosphere (N_2/Ar) in medium temperature (600 ^{o}C), the *M*-*B* curve at 5 K showed that M_s increased from 120 to 148 Am^{2}kg^{-1}, while the grain size obtained from X-ray diffraction only increased by about 13% (27.9 to 31.6 nm). To characterize the introduced defects and the microstructure of our materials, advanced electron microscopy techniques are applied.

3D-Printed High-Entropy Alloy Micro- and Nanoparticles for Magnetocaloric Energy Conversion – *HI-ENTROPY*

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Summary: Materials for magnetocaloric energy conversion –magnetic cooling, heating and power generation, tend to exhibit a large magnetocaloric effect. However, they rely heavily on the use of critical elements (rare earth) and can furthermore suffer from cracking and fatigue, which severely limits their useful lifetime. Transition metal-based high entropy alloys (TM-HEAs) on the other hand offer supply chain and cost stability, and possess superior mechanical properties such as ductility, corrosion resistance, machinability, all of which ease manufacturing and bolster product longevity. They have only very recently been considered for magnetocaloric applications [1-3]. The use of HEAs as materials offers the possibility of structural strength and chemical stability needed in the active magnetic regenerator (AMR) which is the key component of any device used for magnetocaloric energy conversion. The idea of utilizing the unique possibilities of additive manufacturing in shaping the core part of the AMR from HEAs may lead to devices with significantly improved heat exchange. The combination of a widely unexplored materials class (HEAs) and additive manufacturing is a new approach and could potentially change the way how we design and construct future generations of magnetocaloric energy conversion devices. If successful, the project will contribute significantly to the development of both methodology and technology.

Key Words: additive manufacturing, high entropy alloys

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Analysys of the Field Dependence Of Magnetocaloric Effect Of La(Fe,TM,Si)$_{13}$ (TM=Cr,Ni) Alloys

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Recently proposed criterion based on the field dependence of the isothermal entropy change (which can be expressed as a power law of the form $\Delta s_T = a(T)\Delta H^n$) is used for identifying first order phase transition (FOPT) [1], whereby the field exponent n yields an overshoot >2. In addition, n at the transition temperature ($n(T_{trans})$) can further reveal the critical composition of the crossover of FOPT to second order phase transition (SOPT) as $n(T_{trans}) < 0.4$ indicates FOPT, $n(T_{trans}) > 0.4$ for SOPT and $n(T_{trans}) = 0.4$ for the crossover (critical SOPT-FOPT) [2].

In this work, we characterize the magnetocaloric response and the associated thermomagnetic phase transitions for two series of transition metal doped $LaFe_{11.6-x}TM_xSi_{1.4}$ alloys (TM=Ni and Cr) [3,4]. In the case of Ni-doped series, small dopant addition produce very slight modification of the transition temperature and magnetization, though with a significant reduction of the magnetocaloric response. Using the proposed analyses, these features were found to be ascribed to a FOPT transformation into SOPT with increasing doping concentration, determining the critical SOPT-FOPT composition for a Ni content x = 0.19. In the case of Cr-doped series, the alloys are found to exhibit a sustained magnetocaloric response up to x ≈ 0.3 despite the dopant diluting the overall magnetic moment, which it is ascribed to an enhancement of the FOPT-character. For higher Cr content, the series exhibit a crossover of FOPT to SOPT for x = 0.53. For both series, it was shown that the proposed magnetocaloric analyses surpass the accuracy of conventionally used Banerjee's criterion for determining the order of magnetic phase transitions.

Key Words: La(Fe,Si)$_{13}$ alloys, Thermomagnetic phase transitions, Magnetocaloric field dependence analysis

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Curie-temperature and Geometrical Variation of $La(FeSi)_{13}$ Heat Exchangers produced via Laser Beam Melting

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A key factor to optimize the efficiency of magnetocaloric systems and to reduce the amount of rare earth material necessary to achieve high cooling power is to increase the systems frequency. Since one main factor limiting the frequency is the heat transfer from the magnetocaloric material, thin-walled heat exchanger structures are required. Casting and machining of the magnetocaloric alloys, as for example $La(FeSi)_{13}$, is challenging and costly due to the materials brittleness and difficult phase formation.

Among other technologies, Laser Beam Melting is currently examined for the shaping of magnetocaloric heat exchanger structures. As an Additive Manufacturing process, it offers high freedom of design and at the same time low waste rates. Our investigations show that structures with minimum wall thickness of 300 µm can be achieved and that the high cooling rates during Laser Beam Melting facilitate the formation of the magnetocaloric 1:13 phase.
Microchannel structures (Fig. 1), as well as plate-like (Fig. 2) structures with Curie-temperatures in the range of 275 K to 345 K have been produced from $LaCe(Fe,Mn,Si)_{13}$ alloys, adjusting the alloy composition by varying the mixing ratio of two base powders.

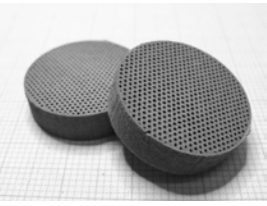

Fig.1: microchannel structures

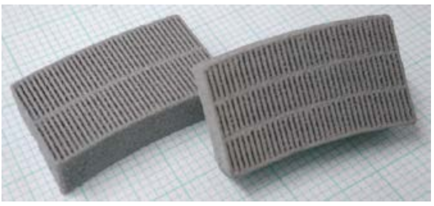

Fig. 2: plate-like structures

Key Words: AMR, $La(FeSi)_{13}$, Laser Beam Melting, Heat Exchanger