Book of abstracts

CHC Eurotherm Seminar 13th / 14th / 15th of July 2021

The first Eurotherm seminar on Caloric Heating and Cooling (CHC) will be an online event on 13th-15th July 2021. This seminar will gather scientists and engineers to present the state of the art and the modern trends in caloric heating and cooling technologies and to foster an environment conducive to exchanging ideas. Theoretical, numerical and experimental approaches will be presented for development of Caloric Materials & Devices. CHC seminar will include Plenary lectures given by keynote speakers followed by contributed presentations.

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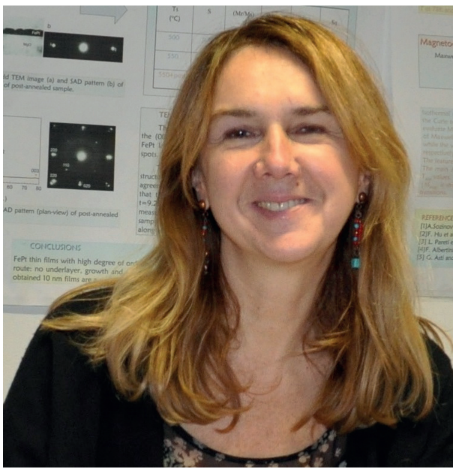

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New concept of electromagnetic field source for magnetic refrigeration

Simon Nosan[1], Urban Tomc[1], Katja Klinar[1], Andrej Kitanovski[1]

[1]University of Ljubljana, Faculty of Mechanical Engineering, Ljubljana, Slovenia

Abstract

This article reports on the latest research achievements on development of static magnetic refrigerators and heat pumps systems. In the article we present the results on the numerical investigation on the novel design of the static magnetic field source. The investigated magnetic field source represents a substantial improvement versus the solution, that concerned the use of electromagnetic field sources with the regeneration of magnetic energy and was presented by Klinar et al. [1]. The results of the study represent an important basis for the future development of static electromagnetic field sources in the domain of magnetic refrigeration and heat pumping.

Electromagnets heat up during operation due to the Joule losses in the winding. By significantly reducing the Joule heat, the electromagnet can achieve energy efficiency comparable to structures of permanent magnet assemblies with motor driven rotation, which are usually applied in magnetic refrigeration or heat pumping.

Fast magnetization/demagnetization process is crucial for the compactness of device, since it defines the frequency of the operation. An instant step-change of the magnetic flux density in the magnetocaloric material cannot be achieved with permanent magnets regardless the principle of the movement. By implementing the magnetic energy recovery into electromagnetic field source it is not only possible to achieve higher efficiency, but also faster field change due to accumulated electric energy in each cycle. With additional modification of previously presented electronic circuit, it is possible to ensure a constant magnetic field during magnetized state of magnetocaloric material.

We have designed 14 conceptual solutions for which we have tested the feasibility of operation and implementation. The most promising concept was evaluated using the Ansoft Maxwell software tool. Based on the obtained results, we chose a geometry for more detailed analysis, for which we made numerous iterations regarding the iron core and windings, and for each geometry several iterations to obtain the most appropriate value of the magnetic flux density in the air gap. One of the most promising geometries was experimentally evaluated to confirm the numerical model.

According to simulations, a form of magnetic structure can be achieved which allows the magnetic field alternately to be established efficiently in the air gap with high efficiency at the increase of operating frequency. This reflects as a lower input power, that needs to be provided to the electromagnet, which results in the lower electrical power consumption of a structure and lower heating of the windings.

Keywords: electromagnetic, numerical analysis, experimental validation

[1] Klinar K, Tomc U, Jelenc B, Nosan S, Kitanovski A. New frontiers in magnetic refrigeration with high oscillation energy-efficient electromagnets. Appl Energy 2019

Cool future: magnetocaloric devices based on static and rare earth free magnetic field sources

Urban Tomc[1], Stefano Dall'Olio[1], Katja Klinar[1], Simon Nosan[1], Urška Erjavec [1], Matej Šadl[2], Hana Uršič[2], Andrej Kitanovski[1]

1 University of Ljubljana, Faculty of Mechanical Engineering, Slovenia
2Electronic Ceramics Department, Jozef Stefan Institute, Ljubljana, Slovenia

Abstract

The magnetocaloric refrigeration and heat pumping is considered to be one of the most important alternatives to existing vapour-compression technologies. In the past two decades we have witnessed a substantial increase in basic and applied research efforts to bring this technology to the market. Despite the significant research progress that has been made, there are several critical issues that need to be solved in the near future. These concern efficient heat transfer, the reduction or removal of moving parts and rare-earth-free and stable energy-efficient magnets and magnetocaloric materials.

Today's state-of-the-art magnetocaloric technology is based on the so called Active Magnetic Regeneration (AMR) principle. The AMR is based on the reciprocating movement of the fluid through a porous magnetocaloric (MC) structure. Such a system usually comprises a large amount of caloric material and a fairly complex hydraulic system, which is more suitable to be implemented in large cooling, refrigeration or heat pump devices. On the other hand, miniaturized electronics also produce vast amounts of heat that need to be efficiently managed. In this manner, an alternative research approach is emerging in the fields of MC technology. It involves new concepts of devices, which would apply so called thermal switches. The application of thermal switches could lead to drastic improvements in the heat transport from/to the MC material and consequently to the miniaturization of MC devices.

An interesting domain, to look for thermal switch mechanisms, is microfluidics, which has enabled the development of integrated lab-on-chip devices. Although most microfluidic devices are based on a continuous flow of liquids in microchanells, there has been an increasing interest for the past couple of years in devices that rely on manipulation of discrete droplets using surface tension effects. One such technique is ElectroWetting On Dielectric (EWOD), which is based on wettability of liquids on a dielectric solid surface by varying the electrical potential.

In the first part of this contribution we will present a new magnetic refrigeration prototype that operates with a rare-earth-free magnetic field source. Its main novelty, in comparison to existing state-of-the-art magnetic prototypes, is the application of a static electromagnet assembly that can regenerate magnetic energy and enables a rapid alternation of the magnetic field (up to 25 Hz), which is one of the crucial operating parameters that could lead towards the future miniaturization of magnetocaloric devices. The device consists of two regenerators working in parallel, containing around 100 g of gadolinium (Gd) spheres in total. Design aspects as well as experimental results of the prototype will be presented.

In the second part of this contribution we will present a new concept of a magnetocaloric device which couples MC effect and EWOD droplet actuation as a thermal switch mechanism. We will show different potential designs of such devices and their operation. Furthermore, the materials and its properties which constitutes the whole device will be discussed.

Keywords: rare-earth free, electromagnet, prototype, thermal switch, electrowetting

Ferromagnetic shape memory Heuslers: a journey from bulk to nano

Franca Albertini

IMEM-CNR, Parco Area delle Scienze 37/a, 43125 Parma, Italy

Abstract

Ferromagnetic shape memory materials, introduced in 1996, have constantly shown new emerging properties exploitable in different technological sectors, among which solid state refrigeration. Their excellent responsiveness to external fields, i.e. magnetic field, pressure and stress and their combined application, makes them promising for multifunctional exploitation. This phenomenology is originated from the occurrence of a martensitic transformation and a strong coupling between magnetism and structure. Thus, the hysteretic character of the martensitic transformation and its broadness strongly affect the performances of materials, mainly in cyclic applications.
In my talk I will present some recent results on NiMn-based Heuslers, including nano/micro scale materials, obtained by different fabrication methods, i.e. epitaxial thin films, patterned nanostructures, mechanically-milled particles. Thin films and nanostructures are of particular interest not only for the realization of miniaturized new-concept devices, but also for providing insights into the magneto-structural coupling at the different length scales and suggesting possible strategies for the optimization of materials also for bulk applications. The talk will focus on microstructure tuning and microstructure-related effects on the martensitic transformation, in view of the possible exploitation of this class of materials in solid state refrigeration and energy-related applications.

Keywords: magnetic shape memory materials, thin films, nanostructures, microstructure, hysteresis

Elastocaloric materials for active cooling regenerators

Lucia Ianniciello[1], Jaka Tušek[2], Lluís Manosa[3], Eduard Vives[3], Kurt Engelbrecht[1]

[1]Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, 2800 Kgs. Lyngby, Denmark, luciann@dtu.dk,
[2]Faculty of Mechanical Engineering, University of Ljubljana, Aškerčeva cesta 6, SI-1000 Ljubljana, Slovenia,
[3]Departament de Física de la Matèria Condensada, Facultat de Física,
Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Catalonia.

Abstract

The use of elastocaloric technologies instead of classic cooling systems is an interesting alternative. In fact, they represent a cooling method that is potentially more efficient and more environmentally friendly. A large variety of shape memory alloys can be employed for this purpose, either Cu-based, Fe-based or Ni-based. The study of elastocaloric systems starts from the study of the material in order to choose the most suited one, followed by the study of the regenerator shape and design. First, calorimetry measurements need to be done in order to confirm the transformation temperatures of the material. Then, testing can be performed using a mechanical tester. Adiabatic temperature change measured using IR camera and acoustic emissions can be monitored while the material is being strained or released, for different strains, and different strain amplitudes. It is especially interesting to see how the materials will evolve with cycling (functional fatigue), the best conditions to cycle the material and how many cycles it can withstand (structional fatigue). Then, after choosing a material, an elastocaloric regenerator can be made and tested. Different types of regenerator have been developed, either made to be strained or compressed, with different shapes. Regenerators that operate in tension are typically stacks of dog-bone shaped plates and those that operate in compression are composed of tubes. In order to test elastocaloric regenerators, we built up a flow system coupled to a mechanical tester; it is composed of two loops, one to extract the heat and the second to cool the load. Water is used as the heat transfer fluid. To assess the performances of the system different strain amplitudes, different waiting times at the end of loading and unloading and different straining speed can be tested.

Keywords: elastocaloric materials; shape memory alloys; fatigue life; caloric devices; cooling; regenerator.

Energy harvesting using thermomagnetic generators with magnetocaloric materials

A. Waske[1,2], D. Dzekan[2,3], K. Sellschopp[4,2], D. Berger[2], A. Stork[2,3], K. Nielsch[2,3] and S. Faehler[2].

[1]Leibniz IFW Dresden, Dresden, Germany
[2] BAM, Berlin, Germany
[3] TU Dresden, Dresden, Germany

Abstract

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]

Thermomagnetic materials are a new type of magnetic energy materials, which enable the conversion of low temperature waste heat to electricity by three routes: Thermomagnetic motors, generators and microsystems. Taking our recent work on thermomagnetic generators [1] as a starting point, in this talk we analyse the material requirements for a more energy and economic efficient conversion. We will describe the influence of magnetisation change and heat capacity on thermodynamic efficiency, as well as the consequences of thermal conductivity on power density. Our analysis will allow selecting the best thermomagnetic materials in Ashby plots and illustrate the substantial different properties compared to magnetocaloric materials.

References:

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Keywords: thermomagnetic power generation, magnetocaloric materials, waste heat conversion

Large-scale Facilities: Grand Opportunities for Caloric Materials Research

Bing Li
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, China
bingli@imr.ac.cn

Caloric materials are systems that exhibit significant thermal effects at phase transitions induced by external fields like temperature, pressure, stress, magnetic fields and so forth. They can be used for the solid-state refrigeration through a designated cooling cycle. The core physical issue of caloric materials is the evolutions of atomic structures and interactions as a function of these driving forces in multiple spatial and temporal scales. State-of-the-art characterization techniques based on large-scale facilities such as the neutron scattering are highly desirable in this case due to the powerful experimental abilities and versatile sample environments.

Very recently, we have reported colossal barocaloric effects (CBCEs) (barocaloric effects are cooling effects of pressure-induced phase transitions) in a class of disordered solids called plastic crystals [1]. The discovery of CBCEs in plastic crystals was critically benefited from the utilization of large-scale facilities, which is expected to provide an emergent routine for caloric materials research in the future. In this presentation, I will describe in detail how we come to realize that plastic crystals might exhibit CBCEs and how pressure-dependent neutron scattering and synchrotron X-ray scattering results confirm this discovery from the basic physical principles. The established microscopic mechanism here would be helpful for designing more practically promising caloric materials.

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Thermo-hydraulic analysis of shell-and-tube-like geometries for elastocaloric regenerators

Žiga Ahčin[1], Jierong Liang[2], Kurt Engelbrecht[2], Jaka Tušek[1]

[1]Faculty of Mechanical Engineering, University of Ljubljana, Aškerčeva 6, 1000 Ljubljana, Slovenia
[2]Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, 2800 Kgs. Lyngby, Denmark

Abstract

With growing cooling demands and rising environmental concerns over the use of refrigerants with low environmental impact in vapor compression systems or the development of high efficiency alternative cooling technologies is necessary. Solid-state caloric refrigeration technology is based on environmentally harmless refrigerants and are one of the most promising alternatives to vapor compression. Among these, elastocaloric cooling, which utilizes the elastocaloric effect (eCE) associated with the latent heat of martensitic transformation in shape memory alloys (SMAs), shows one of the largest potentials for future applications.

It has been shown that one of the most promising ways of utilizing the eCE is the active regenerative cycle. Active elastocaloric regenerators (AeCR) consist of a porous structure made of SMA, through which a heat transfer fluid (HTF) is pumped in a counter-flow direction. To date the developed AeCRs were based on tensile loading, where short fatigue life was shown to be a limiting factor. It is known that compressive loading can significantly prolong the fatigue life, but bulky elastocaloric elements with limited heat transfer characteristics are generally favourable under compression. However, thermo-hydraulic properties greatly influence the performance of active caloric regenerators. Geometries with good heat transfer such as thin sheets or wires can only be applied under tensile loading. In order to utilize the eCE under compressive loading, structures that can withstand compression without buckling are required. A promising geometry for compressive loading is a tube(rod)-based regenerator (similar to the shell-and-tube heat exchanger), where the tubes (rods) are stacked and supported by additional supporting elements that prevent them from buckling and guide the heat transfer fluid in a cross-flow around each tube (rod).

In order to assess the thermo-hydraulic properties of the proposed geometry, a set of shell-and-tube-like passive regenerators was build and tested using an oscillating flow regenerator characterization test stand. The influence of the tube wall thickness, tube (rod) diameter and tube spacing were analysed over a wide range of utilization factors (*UF*) and frequencies (*f*). It has been shown that in general, effectiveness is increasing with *f* for all evaluated geometries due to the relatively large longitudinal thermal conductivity of the regenerator that prevails over convective heat transfer at low *f*. On the other hand, the highest effectiveness is obtained at the smallest *UF* since at high *UF* the HTF penetrates too deep into the regenerator and reduces its temperature span. The results further showed that the best preforming regenerators are the ones with the smallest porosity when constant tube thickness is considered. In the case of the tubes with the same outer diameter (3.175 mm), increasing wall thickness results in poorer performance since the heat cannot be effectively transferred between solid and HTF. The opposite trend is observed in the case of tubes with outside diameter of 1.067 mm, where thick walls (rods) performed better. Finally, the Nusselt number and friction factor were calculated from regenerator effectiveness and pressure drop, and the results show that tube and rod-based regenerators present excellent compromise between heat transfer and pressure drop properties. This makes shell-and-tube-like geometry very promising for implementation in AeCR (and also other caloric regenerators).

Keywords: active elastocaloric regenerator, shell-and-tube-like geometry, passive testing, thermo-hydraulic properties, compression

Low temperature magnetocaloric RVO_4 (R=Gd and Dy) nanomaterials

Sung-Myung Ryu[1] and Chunghee Nam[1,2]

[1]Department of Photonics and Sensors, Hannam University, Daejeon 34430, South Korea
[2]Department of Electrical and Electronic Engineering, Hannam University, Daejeon 34430, South Korea

Conventional vapor-compression refrigeration technology has practical limitations because of its environmental destruction. Recently, new cooling technologies to replace it have been underway, including thermoelectric cooling, thermoacoustic refrigeration, and magnetic refrigeration, etc. Among them, magnetic refrigeration is based on the thermodynamic magnetocaloric effect (MCE). In this study, microwave hydrothermal synthesis was employed to fabricate RVO_4 (R=Gd and Dy) nanostructures as a MCE material for hydrogen liquefaction. During synthesis, EDTA was added as a chelating agent to obtain uniform RVO_4 nanowires and their magnetic properties were compared with those of irregular shaped RVO_4.nanoparticles. The structure and morphology were studied by using scanning electron microscope (SEM) and transmission electron microscope (TEM) measurements. Antiferromagnetic (AFM) properties of nanostructrured RVO_4 were observed with the Neel temperature (T_N) at less than 10 K, and suppression of their AFM properties was thought to be induced by the size effects. The Curie-Weiss fitting showed the weak antiferromagnetism for the both samples. However, the effective magnetic moments for the both samples had lower values than that of bulk RVO_4 because of the size effects, where uncompensated spins on the surface of the nanostructures induce suppression of antiferromagnetism.

The magnetic entropy change ($-\Delta S_M$) of nanostructrured RVO_4 was measured based on isothermal magnetization measurements with applied magnetic fields (1 ~5 T). $GdVO_4$ and $DyVO_4$ had relatively high MCE effects with 35.5 $Jkg^{-1}K^{-1}$ and 10.6 $Jkg^{-1}K^{-1}$, respectively. Although $DyVO_4$ had a lower MCE value than that of $GdVO_4$, an anomaly of $-\Delta S_M$ due to the Jahn-Teller effect for $DyVO_4$ induced high relative cooling power because of an increase of the full width of the maximum $-\Delta S_M$ of temperature by the quadrupole coupling.

Keywords: $DyVO_4$, $GdVO_4$, magnetocaloric effects, hydrogen liquefaction

Thermomagnetic Oscillator for Conversion of Waste heat into Electricity

Deepak Kamble[1,2], Raju V. Ramanujan[1]

[1]School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798
[2]*Present address*: Leibniz IFW Dresden, Institute for Metallic Materials, Helmholtzstraße 20, 01069 Dresden, Germany

Abstract

Low grade waste heat is an undesirable and unavoidable product of many industrial processes. Thermal management technology is necessary to convert waste heat into electricity. In this work, we demonstrate a novel hybrid thermomagnetic oscillator (HTMO) device for conversion of heat to electricity by coupling the magnetic response with electromagnetic induction to generate electrical output [1].

As a first step, the alloy of composition $(MnNiSi)_{1-x}(Fe_2Ge)_x$ with tunable T_C near room temperature exhibiting a first order phase transition was synthesized and characterized for thermomagnetic properties [2]. As a second step, the alloy with a suitable composition (x = 0.3) having a T_C of 144℃ was utilized as a thermomagnetic alloy (TMA). The cylindrical TMA was placed in a vertical quartz tube with a heat load (180℃) at the top and heat sink (water at ambient) at the bottom. A permanent magnet (P1) was placed at the top of the heat load, the magnetic force due to P1 pulls up the TMA towards the heat load. The TMA becomes paramagnetic at the heat load, loses attraction to P1 and falls back to the heat sink due to gravity. The heated TMA releases the heat at the heat sink and becomes ferromagnetic. This cycle repeats continuously and the TMA oscillates between the heat load and the heat sink. The Cu coil wound around the quartz tube experiences change in the magnetic flux due the oscillation of TMA and generates electrical output.

In an advanced setup, the oscillations of the TMA were coupled with another permanent magnet (P2) by connecting it with a spacer below the TMA. Higher voltage output of 11 V/cycle was achieved due to simultaneous oscillation of TMA and P2 through their respective Cu coils. The HTMO also has an additional feature of transporting heat from heat load to the heat sink which results in cooling of the heat load by upto 70℃ during each cycle. The optimization of the device parameters was performed using COMSOL Multiphysics by varying the magnetic field strength of P1, mass of TMA and length of the device.

Keywords: Thermomagnetic Oscillator, Energy Harvesting, Magnetic phase transition, Thermomagnetic generator

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Investigation on the size effect and defects effect on the microstructural and magnetic properties of nanoscale $(Mn,Fe)_2(P,Si)$ based MCE material

Fengqi Zhang, Xinmin You, Niels van Dijk, Ekkes Brück

Fundamental Aspects of Materials and Energy (FAME), Faculty of Applied Sciences, Delft University of Technology, Delft, The Netherlands

Abstract

In the nanoscale magnetocaloric materials field, some novel devices/ideas have been proposed, including microrefrigerators, thermal switches, microfluidic pumps, energy harvesting devices, or for the biomedical applications such as hyperthermia or drug delivery. However, there are rarely reports that have been addressed about nano-scale $(Mn,Fe)_2(P,Si)$-based materials. And there are also no published papers completely dedicated to the influence of size-reduction on the magnetocaloric properties of Fe_2P or more generally $(Mn,Fe)_2(P,Si)$. Due to the increasing relevance, this material has been receiving at the macroscale, and its size-reduction studies are certainly an open avenue yet to explore. These are our main research motivations about this project.

Thus, in this project, we have synthesized nanoscale $(Mn,Fe)_2(P,Si)$-based MCE materials, and investigated systematically what role the size of samples and defects structure play for magnetocaloric materials. From current results, we can indicate the defects distributed in our materials have more influence for the decreasing of saturation magnetization (M_s), and with the grain size decreased, hysteresis and Curie temperature all have negative shift. In addition, if we heat up our nanoscale materials in medium temperature and under protective atmosphere, the M-B curve at 5K exhibited that M_s increased from 120 to 148 Am^2kg^{-1}, but the grain size only increased about 12%, which indicated from XRD data. And this result is also consistent with Mössbauer spectroscopy data. And our future plan is further investigating defects effect and the microstructure of our nanoscale materials by using advanced electron microscopy techniques.

Keywords: nanoscale; MCE material; size effect; defects effect

EUROTHERM115-13

Implementation of caloric effects in COMSOL Multiphysics: methods and limitations.

António Lopes[1], Tiago Santos[1], Daniel Silva[2], Carla Roque[1], Vítor Costa[3], João Amaral[1]

[1]University of Aveiro, CICECO – Aveiro Institute of Materials, Department of Physics, Campus Santiago, 3810-193 Aveiro, Portugal.
[2]IFIMUP – Institute of Physics for Advanced Materials, Nanotechnology and Photonics, Faculty of Science of the Porto University.
[3]University of Aveiro, Center for Mechanical Technology and Automation, Department of Mechanical Engineering, Campus Santiago, 3810-193 Aveiro, Portugal.

Abstract

With modern society's increasing concerns about climate changes, sustainable heat pumping and refrigeration technologies are required to minimize human carbon footprint. Scientists and engineers have been designing and developing numerical computational tools, to simulate heat transfer processes involving non-conventional caloric effects. Caloric effects rely on temperature variations upon external stimuli, e.g. magnetic or electric fields, which induce variations on the thermal properties, and on the temperature, of the caloric material.

The need to have more efficient caloric devices has propelled the development of numerical tools to accurately simulate caloric materials' behavior and processes. The simplest way to simulate the caloric effect is by imposing an adiabatic temperature change or heat flow due to the isothermal entropy change. Earlier works simplified the thermal behavior of caloric materials by assuming a constant specific heat or neglecting its dependence on temperature and on the applied external field, while more recent approaches started considering less simplified behaviors (*Aprea et. al., 2018*).

In this work we focus on the magnetocaloric effect implementation, using COMSOL Multiphysics. By imposing an instantaneous adiabatic temperature change and implementing the magnetocaloric material's specific heat (*Cp*) temperature dependence, a two-dimensional model of a magnetocaloric process is considered to simulate the heating/cooling of a gadolinium (Gd) sphere immersed in a fluid container, initially at different temperatures (Figure 1).

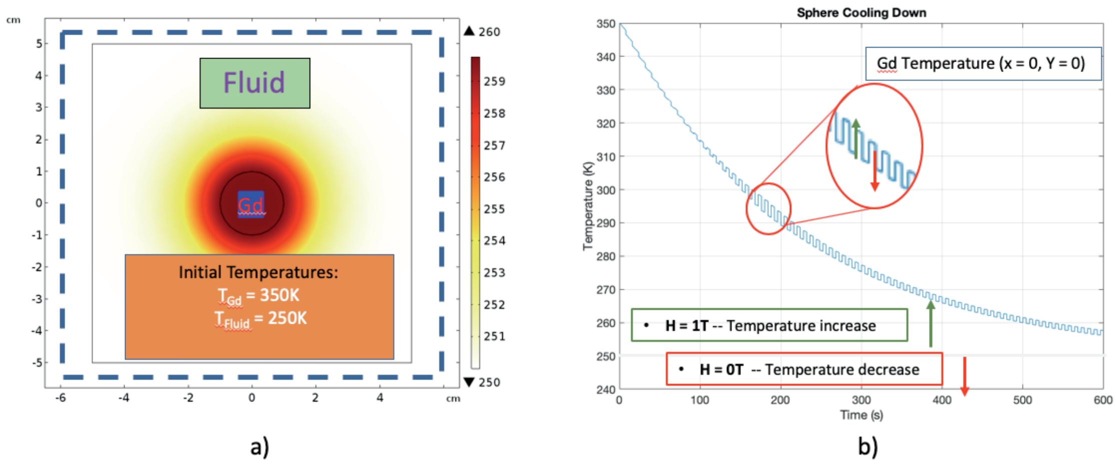

Figure 1: **a)** Representation of the 2D COMSOL Multiphysics model; **b)** Temperature over time evolution of the Gd sphere during cooling under applied magnetic field cycling, highlighting the temperature resulting magnetocaloric effect.

Combinatorial synthesis of Cu doped Ni-Mn-Ga films for micro energy harvesting

Lukas Fink[1,2], Anett Diestel[1], Kornelius Nielsch[1,2], and Sebastian Fähler[1]

[1]Leibniz IFW Dresden, Institute for Metallic Materials, D-01069 Dresden, Germany
[2]TU Dresden, Institute of Materials Science, D-01062 Dresden, Germany

In a world that heats up, it is decisive to make efficient use of primary energies. This includes the need to recover waste heat, where the maximum is available just above room temperature. However, except for thermoelectrics, there is hardly any technology available to harvest low temperature waste heat. Lately, first thermomagnetic microsystems[1,2] were developed as an alternative approach, using magnetocaloric material as active material. By using thin films the surface-to-volume ratio is increased, which enables for a faster heat transfer, resulting in high cycling frequencies and power densities compared to bulk devices[3]. Next to the device, the right choice in material properties[4] and processability has to be chosen. One of the possible choices are Ni-Mn-Ga Heusler alloys, since they exhibit a large change of magnetization in a small temperature range around the first or second order transition. Those properties can be tuned further by composition variation or doping a fourth element[5].

Here, we prepare Cu-doped Ni-Mn-based Heusler films via a magnetron sputter deposition. By using a combinatorial method, a library of Ni-Mn-Ga-Cu films can be established. The effects of composition and chemical order on properties like 1) transition temperatures, 2) hysteresis losses and 3) difference of magnetization at the martensitic transition are shown. According this library the decisive properties for thermomagnetic harvesting of low temperature waste heat can be evaluated.

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Keywords: Magnetic films, martensitic transformation, magnetocaloric effect, combinatorial experimentation

Barocaloric effects in a novel spin-crossover compound

Michela Romanini[1], Lluís Mañosa[1], Pol Lloveras[2], Josep Lluís Tamarit[2], Antoni Planes[1], Kubra Gurpinar[3], Baris Emre[4], Orthan Atakol[3], Michael Shatruk[5], YiXu Wang[5,6]

[1]Departament de Física de la Matèria Condensada,
Facultat de Física, Universitat de Barcelona, Barcelona, Catalonia, Spain
[2]Grup de Caracterització de Materials, Dep. Física, Universitat Politecnica de Catalunya, Barcelona, Catalonia, Spain
[3] Department of Chemistry, Faculty of Science, Ankara University, Ankara, Turkey.
[4] Department of Physics, Eng. Faculty of Engineering, Ankara University, Ankara, Turkey.
[5]Department of Chemistry and Biochemistry, Florida State University, Florida, United States
[6]School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, People's Republic of China

Abstract

Spin crossover (SCO) compounds, among the most studied molecular-switch complexes, have recently attracted considerable attention for their potential implementation in novel multifunctional devices. In SCO compounds, the spin state of a metal ion (typically, Fe^{2+}) can be interconverted between two distinct magnetic states (low-spin, LS, and high-spin, HS) by a redistribution of *d*-electrons among two non-equivalent sets of orbitals, leading to modification of the crystal field strength. The HS-LS phase transition is accompanied by a change in the crystal structure of the compound and can be induced by a variety of external stimuli such as temperature and pressure changes or light irradiation [1,2].

Among the peculiar properties associated with spin-state switching, one with potential technological impact is the giant barocaloric effect, which has been reported only very recently in a SCO compound [3]. This effect relies on the application or removal of hydrostatic pressure [4] to induce a phase change characterized by a very large associated latent heat of transition [5]. The search for materials with giant caloric effects (including magnetocaloric, electrocaloric, elastocaloric and barocaloric effects) has become a hot topic in materials science, owing to the potential of such systems as environment-friendly replacement of current refrigeration technologies, which raise serious environmental concerns and looming energy crisis [6-9]. Within this scenario, SCO compounds may play a crucial role for solid-state refrigeration via pressure-induced phase change.

For successful implementation in Brayton cycles for solid-state refrigeration, SCO compounds must be found that display a large barocaloric effect (large latent heat of the HS-LS transition) and at the same time a negligible thermal hysteresis of the HS-LS transition. We have chosen a SCO compound which has been recently shown to exhibit abrupt spin-state switching with negligible thermal hysteresis ($Fe_3(bntrz)_6(tcnset)_6$ (bntrz=benziltriazole and tcnset=tetracyanothioalkylpropenide) [10]), and have synthetized it again to study the associated barocaloric effect and the hysteresis response under pressure. Differential scanning calorimetry characterization (Fig. 1) and magnetization data confirm the occurrence of the HS-LS transitions with a very narrow hysteresis at 318 K. This transition is accompanied by a large entropy change of ~80 J kg^{-1} K^{-1}. Powder X-ray diffraction and calorimetry reveal that the material is highly susceptible to an applied hydrostatic pressure. In particular, the transition temperature can be made to increase continuously between its value of 318 K at ambient pressure to a value of 383 K under an applied pressure of 2.6 kbar [11]. Despite such large shift in the spin-transition temperature, the non-hysteretic character of the transition is maintained also under applied pressure. Such behavior leads to a remarkably large and reversible barocaloric effect in the Bryton cycle, characterized by the temperature change of 35 K and the entropy change of 120 J kg^{-1} K^{-1}, which are among the highest reversible values reported for any caloric material thus far.

EUROTHERM115-16

Curie-temperature Variation and long-term stability of $La(FeSi)_{13}$ Heat Exchangers produced via Laser Powder Bed Fusion

Christina Breitzke, Sandra Wieland
Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Wiener Straße 12, 28359 Bremen, Germany
christina.breitzke@ifam.fraunhofer.de; sandra.wieland@ifam.fraunhofer.de

Abstract

The technology of magnetocaloric cooling devices is facing challenges with low operating frequencies and insufficient long-term stability of the magnetocaloric material. In existing prototypes, the frequency is rather low, due to slow heat transfer and, in case of packed beds, high pressure drop. Therefore, thin-walled parts, such as plates and micro channels, are considered beneficial, but production techniques like casting or machining are challenging as the often favored material, $La(FeSi)_{13}$, is brittle and the phase formation is an energy-consuming, costly process.

At IFAM, thin-walled structures are produced by Laser Powder Bed Fusion (LPBF). With this production process, plate like-structures with a wall thickness of 300 µm are achieved (Fig. 1), as well as micro channel geometries with a diameter of 300 µm (Fig. 2). As an Additive Manufacturing process, LPBF offers high freedom of design and at the same time low waste rates. A variation of the Curie-temperature was achieved by mixing two $La_{1-x}Ce_x(Fe_{13-y-z}Mn_ySi_z)$ base powders with T_C ca. 5 °C and T_C ca. 80 °C and adjusting the mixing ratio prior to each LPBF process.

Parts with ten different, cascading T_c were produced.

Different heat treatments with varied peak temperature and holding times were performed, in order to achieve a homogenous magnetocaloric 1:13 phase, with a low amount of α-Fe and a high ΔS. Subsequently, the parts were fully hydrogenated.

The amount of 1:13 phase and the homogeneity of the microstructure have been evaluated via SEM, and the magnetic entropy change has been characterized by VSM for several samples of each T_C-level to assure the powder mixing route is not introducing compositional inhomogeneities.

Further testing included the proof of long-term stability in a changing magnetic field. For hydrogenated $La(FeSi)_{13}$ alloys this is especially important, as they are known to be brittle and likely to fail in the cycling process. The parts were tested at their specific Curie-temperature in a magnetic field of 0.95 T for ~10.000 cycles.

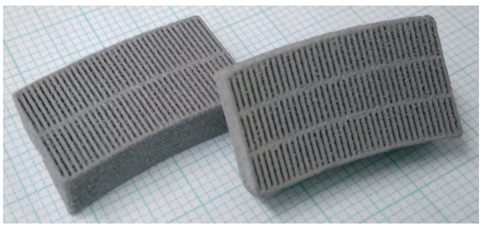

Fig. 1

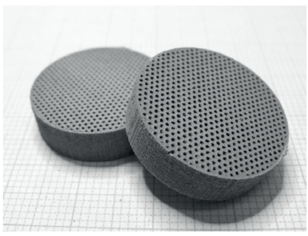

Fig. 2

Keywords: Magnetocaloric, LaFeSi, Shaping, LPBF, Powder metallurgy

Study of the elastocaloric effect in natural rubber for innovative refrigeration systems

Hiba Haissoune[1,2], Gildas Coativy[2], Jean-Marc Chenal[1], Gaël Sebald[3], Laurent Chazeau[1]

[1]Univ Lyon, INSA-Lyon, CNRS, MATEIS, UMR 5510, F-69621 Villeurbanne, France
[2.] Univ Lyon, INSA-Lyon, LGEF, EA682, F-69621, Villeurbanne, France
[3] ELyTMaX UMI 3757, CNRS, Université de Lyon, Tohoku University, International Joint Unit, Tohoku University, Sendai, Japan,

Abstract

Natural rubber (NR) is well known for its elastic properties, which makes it not only the most used polymer in tire industry, but also a very good elastocaloric material: its thermal response under mechanical solicitation can reach ΔT = 12°C. This temperature variation comes from two main phenomenon: elastic entropy and strain-induced crystallization (SIC). The contribution of the latter in the temperature variation is preponderant ($\Delta T_{crystallization}$ = 8°C). When elongated, macromolecules of natural rubber starts aligning leading to the formation of small crystalline domains and temperature increase, some decades of milliseconds after the deformation. Moreover, this phenomenon can last for about 100 s. During retraction, the crystallites melt instantaneously leading to the decrease of the material's temperature. The more the latter important is, the more the elastocaloric effect significant is. This explains the importance of the optimization of crystallization in the elastocaloric effect.

The strain-induced crystallization depends on both material's properties (crosslink density, elastic active chains lengths heterogeneities …) and mechanical program parameters (frequency of deformation, type of cycle and interval of elongation). In the present work, the study was mainly focused on the second part in both monotonic and dynamic conditions. In the first kind of tests, the sample was deformed adiabatically at 1600% s^{-1} between λ=1 and different finale elongations (between λ_f =4,5 and 6.5). Thermal measurements were recorded using an Infrared camera during 150 s. These experiments were done in order to follow the kinetic of crystallization from the end of the deformation until heat exchange finishes. Furthermore, the main objective of the dynamic tests is to study the influence of the cycle's parameters on the temperature variation and then on the crystallization. The results related to the mechanical hysteresis and the heat flow will be discussed.

Keywords: Natural rubber, kinetic of crystallization, infrared camera, elastocaloric effect.

Eurotherm Seminar #115
CALORIC HEATING AND COOLING

EUROTHERM115-18

Scalable Elastocaloric Refrigeration & Heat Pumping: Thermomechanical Modelling Modelling, Analysis & Evaluation

Keith Warren[1,2], Kevin O'Toole[2], Mark McGrath[3]

[1] School of Mechanical and Design Engineering, Technological University Dublin

[2] Exergyn Ltd, Dublin

[3] School of Mechanical and Design Engineering, Technological University Dublin

Recent research into the Elastocaloric [EC] effect has demonstrated its potential as a solid-state alternative to traditional Vapour Compression [VC] refrigeration or heat pumping approaches. The EC cycle takes advantage of the Superelastic behaviour of Shape Memory Alloys [SMA's], which facilitates, through cyclic uniaxial loading and unloading, the absorption of heat from a low temperature source and its rejection to a higher temperature sink. Prototype devices to date have provided temperature lifts of <20 K with associated thermal outputs of <1 kW, substantially lower than commercially available VC systems. This paper assesses the maximum theoretical performance of a potential Nitinol based EC system across operating conditions as defined by European Directive EN14511. An established phenomenological thermomechanical SMA model is selected through systematic assessment and implemented within the MATLAB/Simscape modelling environment. This facilitates the analysis of Ideal Thermodynamic cycles coupled with the thermomechanical behaviour of the SMA material. Various ideal and Hybrid Thermodynamic cycles are modelled and, in each case, the resulting available heat, mechanical work input and COP values are determined for full and partial phase transformations. This will ultimately provide the basis for a comprehensive evaluative framework for the assessment of EC system architecture for commercially viable application into the future.

Keywords: Heat Pump, Refrigeration, Nitinol, Phenomenological Model, Thermodynamic Cycles, Scalability

Elastocaloric effect in thermoplastic polyurethane

Gildas Coativy[1], Hiba Haissoune[1,2], Laurence Seveyrat[1], Laurent Lebrun[1], Gaël Sebald[3], Jean-Marc Chenal[2], Laurent Chazeau[2]

[1] a Univ Lyon, INSA-Lyon, LGEF, EA682, F-69621, Villeurbanne, France
[2] Univ Lyon, INSA-Lyon, CNRS, MATEIS, UMR 5510, F-69621 Villeurbanne, France
[3]ELyTMaX UMI 3757, CNRS, Université de Lyon, Tohoku University, International Joint Unit, Tohoku University, Sendai, Japan,

Abstract

Solid state cooling systems need the development of new materials exhibiting order/disorder transitions. The polymeric materials have the advantage of being low-costs and relatively easy to process. In the case of elastomers, two main contributions are responsible of their elastocaloric effect: the orientation/disorientation of the macromolecules towards the strain direction (entropic elasticity), and their ability to crystallize under strain. Although, the strain induced crystallization (SIC) is the dominant effect, it is not observed in all elastomers. So far, the elastocaloric effect of natural rubber was the most studied. In the present work, we compare the elastocaloric effect of natural rubber (NR) with the one of two thermoplastic polyurethanes (TPU) which present the advantage of being compatible with melt processing. The two polyurethanes contain soft segments with different lengths. The molecular weight of soft segment of TPU1 is about 1 000 $g.mol^{-1}$ while the one of TPU2 is about 2000 $g.mol^{-1}$. X ray diffraction study shows that the TPU2 (having the longest soft segments) and NR exhibit a reversible strain induced crystallization, while the TPU1 not. It evidences the impact of initial microstructure on SIC. Regarding the elastocaloric effect, TPU1 exhibits a temperature variation of about ΔT=-4°C while TPU2 shows a temperature variation of about ΔT= -8°C for an elongation of λ=5 which is comparable to the one of Natural Rubber ΔT= -8°C at λ=5. At higher elongation, the temperature variation does not increase for TPU because of plastic deformation, while the one of natural rubber can reach ΔT=-13°C for an elongation of λ=7. Although the elastocaloric properties of NR is higher than the one of TPU, this study evidenced that other elastomers having a specific initial microstructure can present a strong elastocaloric effect.

Keywords: Natural Rubber, Polyurethane, Elastocaloric effect

Eurotherm Seminar #115
CALORIC HEATING AND COOLING

EUROTHERM115-21

Magneto

Michael Maschek[1],

[1]Delft University of Technology

Magneto B.V. is a spin-off startup from Delft University of Technology. Its goal is to design, manufacture and commercialise magnetocaloric materials for sustainable power conversion applications such as heat pumps, refrigerators or power generators. Magneto will connect and advance the fundamental research and design performed by Delft University of Technology from lab scale towards first demonstration units.
The current focus is to explore shaping techniques of Mn-FeP-Si based compounds for power conversion applications such as thermomagnetic motors.

Keywords: Magnetocaloric materials, production, shaping

EUROTHERM115-22

Multicaloric effects in Fe-Rh alloys and FeRh-based magnetoelectric composites

Abdulkarim Amirov[(a),(b)], Alexander Kamantzev[(a),(c)], Vladislav Zaporozhets[(d)], Alisa Chirkova[(e)], Akmed Aliev[(b)], Konstantin Skokov[(e)]

[(a)] Immanuel Kant Baltic Federal University, Kaliningrad, 236013 Russian Federation
[(b)] Amirkhanov Institute of Physics of Daghestan Scientific Center Russian Academy of Sciences, Makhachkala, 367003 Russian Federation
[(c)] Kotel'nikov Institute of Radioengineering and Electronics, Moscow, 125009 Russian Federation
[(d)] Donetsk National University, 83001, 24 Universitetskaya, Donetsk, Ukraine
[(e)] Materials Science, TU Darmstadt, Darmstadt, 64289 Germany

amiroff_a@mail.ru

Abstract

Recent prospectives in the studies of functional materials with giant caloric effects for energy-efficient technologies are related to an idea based on the combination of external field (magnetic, electric, elastic) stimuli known as multicaloric effect. It is well known, that stress/strain could be applied as one of the driving forces for tunning of transition temperature and hysteresis in some materials with first-order magnetic phase transition (FOMPT). From this point of view, a model object is the equi-atomic ordered phase of FeRh that exhibits a FOMT from the low temperature antiferromagnetic (AFM) to the high-temperature ferromagnetic (FM) phase, accompanied by resistivity, entropy and lattice changes.

In present work, the two approaches for multicaloric studies were chosen:

1) By combination two external forces – magnetic with hydrostatic pressure and magnetic field with uniaxial strain

2) Through the fabrication of magnetoelectric composites, where voltage induced strain/stress on piezoelectric component mechanically is acted to FeRh.

The Fe-Rh alloys with compositions $Fe_{48}Rh_{52}$, $Fe_{49}Rh_{51}$ were fabricated and magnetocaloric (MCE), barocaloric (BCE) and elastocaloric (ElCE) in them were studied. It was observed maximum adiabatic temperature changes and isothermal entropy changes around AFM-FM transition temperature ~310 K, induced by the magnetic field, pressure and, uniaxial strain. The combination of elastic strain and magnetic field shift transition temperature to lower temperatures, while magnetic field and pressure play opposite effect and depends on values of combined external fields.

In bilayer bonded FeRh/PZT composites the small shift ~ 1 K of AFM-FM transition temperature was observed from MCE measurements, when the electric voltage on PZT layer was applied. The deformation induced by combined magnetic and electric field deformation is inhomogeneously distributed in the sample volume and in results composite is bending.

The work was supported from the Russian Scientific Foundation (№ 18-79-10176)

Keywords: Multicaloric effect, magnetocaloric effect, elastocaloric effect, barocaloric effect, Fe-Rh, multicalorics, multicaloric composites

Progress in Caloric Technologies

Dr. Nikolaus Vida
Swiss Blue Energy AG

Abstract for a poster

Endurance testing of a Thermo Magnetic Motor (TMM) in an industrial environment. The primary goal of the long-term test was to show the reliability of the TMM under industrial conditions for permanent 24/7 power generation for at least 5000 hours. The operating conditions were hot industrial wastewater at 54°C, cold water from the river Rhine at 12°C and resulting mechanical power was 1 kW at a rotational speed of 80 rpm. The TMM is equipped with a rotor containing magneto caloric material (Gd) and 5 permanent two gap magnets (stator). The main objective was the overall endurance regarding the high number of heating/cooling cycles in particular. Finally, the TMM made 15`000 hours and is still running. The next generation TMM now under design will strongly focus on performance improvements and economic efficiency. Enhancing the heat transfer between fluid and magneto caloric material as well as reducing the back-work-ratio (BWR) are major steps towards significant advancements of the TMM.

Barocaloric effects in Adamantane derivatives

Araceli Aznar[1], Pol Lloveras[1], Maria Barrio[1] and Josep Lluís Tamarit[1]

[1]Grup de Caracteritzacio de Materials, Departament de Fisica and Barcelona Research Center in Multiscale Science and Engineering, Universitat Politecnica de Catalunya, EEBE, Campus Diagonal-Besos, Av. Eduard Maristany 10-14, 08019 Barcelona, Catalonia, Spain.

Abstract

The study of potential materials exhibiting giant caloric effects associated with solid-solid first-order phase transitions is on the rise triggered by the environmental urgency of replacing hydrofluorocarbon (HFC) gases with large greenhouse effect used in refrigeration devices [1]. Unfortunately, the exchanged latent heat associated with solid-solid transitions corresponds to a very small amount compared to those that come from evaporation. Nonetheless, it has been recently demonstrated that comparable amounts of exchanged heat to those obtained with HFC can also be achieved by means of pressure driven first-order phase transitions in plastic crystals [2,3]. Plastic crystals consist of molecular solids with positional ordering and high orientational disorder, which allows them to present a large number of molecular configurations while their center positions are kept in the crystal locations in the high-temperature plastic phase. By cooling down they undergo a first-order phase transition where molecules evolve to well defined orientations while the lattice experiments a decrease in symmetry. The ratio of molecular configurations of the plastic phase (N_1) with respect to the configurations of the ordered phase (N_2) yields a contribution to the transition entropy change ($\Delta S = RM^{-1}\ln(N_1/N_2)$) which can become colossal in some cases. For instance, for neopentylglycol (a neopentane derivative) the configurational contribution reaches outstanding values of 330 J K^{-1} kg^{-1} [3]. For this reason, we deemed appropriate to extend our previous studies to other plastic crystals, in particular adamantane derivatives ($C_{10}H_{16}$). More precisely, we focus on 1- and 2-adamantanol, and 1-Cl- and 1-Br-adamantane which are commercially available since they are easy to synthesize by replacing adamantane hydrogen atoms for Cl, Br and OH^- groups, placed at different positions [4]. In order to characterize pressure induced caloric effects (i.e. barocaloric effects), we used the quasi-direct method, for which we performed measurements of standard and modulated Differential Scanning Calorimetry, pressure dependent Differential Thermal Analysis and X-Ray Diffraction. We observed that cyclic pressure application and removal up to 2.6 kbar yields giant reversible isothermal entropy changes from 140 J K^{-1} kg^{-1} to 250 J K^{-1} kg^{-1} and adiabatic temperature changes between 15 K and 50 K, depending on the specific compound. It is also interesting to highlight that the small hysteresis of 2-ada and 1-cl-ada yields minimum required pressures to perform these reversible cycles of 0.3 kbar and 0.5 kbar respectively. Importantly, these small pressures give rise to approximately minimum barocaloric effects of 80 J K^{-1} kg^{-1} and 30 J K^{-1} kg^{-1} accordingly. On the other hand, hysteresis around 10 K for 1-adamantanol and 1-Br-adamantane results in higher required pressures to achieve reversibility. We also notice that giant barocaloric effects above 120 J K^{-1} kg^{-1} and 12 K can be obtained, depending on the studied compound, in a temperature span from 10 K to 50 K by means of 2.3 kbar pressure change. Apart from technical aspects, it is also worth considering that these materials enjoy an affordable production, which would lead to more economically accessible devices. We conclude that all the studied compounds show remarkable features that define them as suitable materials to take into account when designing future refrigeration prototypes.

Keywords: Barocaloric, Plastic crystals, Adamantane, Refrigeration.

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Barocaloric effects in [TMA][$Mn(N_3)_3$] and $[TMA]_2[NaFe(N_3)_6]$ hybrid organic-inorganic perovskites

Araceli Aznar[1], Wen-Juan Wei[2], Pol Lloveras[1], Maria Barrio[1], Josep Lluís Tamarit[1], Xavier Moya[3] and Wei Li[2]

[1]Grup de Caracteritzacio de Materials, Departament de Fisica and Barcelona Research Center in Multiscale Science and Engineering, Universitat Politecnica de Catalunya, EEBE, Campus Diagonal-Besos, Av. Eduard Maristany 10-14, 08019 Barcelona, Catalonia, Spain
[2]School of Materials Science and Engineering, Nankai University, Tianjin 300350, China
[3]Department of Materials Science, University of Cambridge, Cambridge, CB3 0FS, UK
araceli.aznar@upc.edu

Abstract

The growing family of hybrid organic-inorganic perovskites (HOIP) is used in a wide range of applications such as photovoltaic cells, sensors and catalyst electrodes [1-3]. Research of new potential applications of these well-known materials is a subject of much interest. For instance, recent pressure-induced caloric measurements (i.e, barocaloric effects) have delivered promising results, showing their potential application in the development of environmentally-friendly refrigeration devices [4]. In this work we perform barocaloric analysis of two HOIPs with perovskite (ABX_3) and double perovskite ($AB'_{0.5}B''_{0.5}X_3$) structures. More precisely, samples under study correspond to [TMA][$Mn(N_3)_3$] and $[TMA]_2[NaFe(N_3)_6]$. Close to room temperature they undergo a solid-solid first-order phase transition from a disordered high-temperature phase to an ordered low-temperature phase. In the high-temperature phase, disorder is present in both azido linkers (N_3) and [TMA] cations allowing a large number of configurations. By cooling down they experience a shift of [TMA] and N_3 ligands as well as tilting of the inorganic octahedrons, which gives rise to a lowering of the configurational modes in the low-temperature phase and a structural change towards a low-symmetry lattice. This change in configurational modes yields high values of transition entropy changes which defines them as potential materials to present high barocaloric responses [4-6]. In order to characterize barocaloric effects we have performed measurements of standard and modulated Differential Scanning Calorimetry, pressure dependent Differential Thermal Analysis and X-Ray Diffraction. Solid-solid phase transition of both materials present low hysteresis, corresponding to 3.8 K and 2.4 K for perovskite and double perovskite respectively. This feature is directly related to the minimum required pressure to obtain reversible isothermal entropy changes, which is around 0.2 kbar for the perovskite and 0.1 kbar for the double perovskite. Regarding adiabatic temperature changes, reversibility is observed upon 0.6 kbar and 0.3 kbar, respectively. These are remarkable performances to take into consideration since low pressures are technologically feasible to achieve. By means of cyclic applying and removing pressure we obtain giant values of 95 J K^{-1} kg^{-1} and 10 K at 1.5 kbar for the perovskite compound, and 110 J K^{-1} kg^{-1} and 9 K at 1.0 kbar for the double perovskite. We also highlight that with pressure changes of 1.5 kbar barocaloric effects of 87 J K^{-1} kg^{-1} and 7 K can be obtained in a temperature span of 6 K for the perovskite. As for the double perovskite, it shows barocaloric effects of 100 J K^{-1} kg^{-1} and 7 K with a temperature span of 5 K and with pressure changes of 1.0 kbar. For these reasons we are allowed to assert the viability of these materials as potential candidates to replace the present refrigeration gases in future devices. It is also important to emphasize that these giant barocaloric results are the highest ever achieved in the HOIPs family so far [7]. Therefore, we encourage further barocaloric research among HOIPs family.

Keywords: Barocaloric, HOIP, perovskites, Refrigeration.

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Fabrication of magnetocaloric composite wires by powder-in-tube process

L. Beyer[1], A. Funk[1,2], B. Weise[1], D. Seifert[1], A.Waske[1,2], J. Freudenberger[1,3], T. Gottschall[4], M. Krautz[1]

[1]Leibniz IFW Dresden, Germany, [2]BAM Berlin, Germany, [3]TU Bergakademie Freiberg, Germany, [4]Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany

Significant energy savings can be achieved by magnetocaloric refrigeration at room temperature [1]. Consequently, magnetocaloric materials and prototypes have been investigated deeply for the last two decades. One remaining problem towards application is the shaping of these brittle functional materials [2].

To overcome shaping difficulties composites from a magnetocaloric materials with a 2nd binder phase, e.g. ductile metals or epoxy, can be formed [3]. An alternative to this method is presented in [4]. Suitable regenerator geometries are generated with the help of the powder-in-tube process. The obtained wires are versatile semi-finished products.

To study the properties of the afore mentioned LaFeCoSi-composites pulsed magnetic field measurements were performed. By monitoring the temperature change on both composite components simultaneously, the thermal transfer between core and shell were investigated. We show that the achievable temperature change of the LaFeCoSi in the wire is reduced to 2 K (in 2 T), compared to the reference sample with 2.4 K (in 2 T), thus the steel shell acts as heat sink. At the steel shell itself only 0.7 K (in 2 T) were measured. With this, the achievable thermal span in a cooling device was evaluated. Also, the data serves as basis for simulations to identify critical factors for the heat exchange. The corresponding simulations are presented while conclusions, such as the need to reduce the wall thickness are drawn.

The progress in reducing the wall thickness and, therefore, also increasing the filling factor of the magnetocaloric powder in the wires is featured. We show the steps towards thinner wires with 0.5 mm diameter at below 100 µm wall thickness, that favor the filling factor in regenerators and heat exchange phenomena, as well.

[1] A. Kitanovski et al., Magnetocaloric Energy Conversion, Springer, (2015) p. 456

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[3] I. A. Radulov et al., Acta Mater., 127, (2017) pp. 389–399

[4] F. Funk et al. Mater Today Energy 9, (2018) 223

Keywords: composite, powder-in-tube, shaping process, magnetocaloric, simulations, heat exchange

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[4] F. Funk et al. Mater Today Energy 9, (2018) 223

Keywords: composite, powder-in-tube, shaping process, magnetocaloric, simulations, heat exchange

Computational screening of magnetocaloric materials.

Ivan Batashev[1], Gilles de Wijs[2], Ekkes Brück[1], Niels van Dijk[1], Michael Maschek[1], Biswanath Dutta[1]

[1]TU Delft, The Netherlands
[2]Radboud University, The Netherlands

Abstract

The interest in the magnetic cooling devices has led to an intensive search for suitable well-performing magnetocaloric materials. High-throughput studies based on density functional theory calculations can significantly simplify and increase the range of this search. Computational screening makes possible sieving through thousands of known compounds without the need to perform time-consuming measurements and therefore can play an important role to detect new magnetocaloric materials.

We demonstrate results of an effective approach to the screening of magnetocaloric materials with the largest crystallography database provided by AFLOWLIB as the initial source of material properties. To identify systems of interest several screening parameters were developed using properties of various well-known MCE materials as a reference. Along with magnetic properties, other factors important for practical applications are taken into consideration including price, availability and toxicity of candidate materials. Combining these criteria an algorithm for the screening process is suggested. It utilizes both information readily available in the database and additional *ab-initio* calculations. A step-by-step application of initial screening parameters to sort out unsuitable materials before performing more computationally heavy assessments allows fast processing of a large number of candidates. This results in a shortlist of promising compounds to serve as a guide for experimental research.

Keywords: *ab-initio* calculations, magnetocaloric materials, screening, database

Comparison of materials efficiency in electrocaloric and magnetocaloric materials

Youri Nouchokgwe[1, 2], Pierre Lhéritier[1], Alvar Torello [1, 2], Chang-Hyo Hong[3], Wook Jo[3], Christian Bahl[4], Emmanuel Defay[1]

[1]*Luxembourg Institute of Science and Technology, 41 rue du Brill, L-4422 Belvaux, Luxembourg*

[2]*University of Luxembourg, 2 Avenue de l'Université, 4365 Esch-sur-Alzette, Luxembourg*

[3]*School of Materials Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan 44919, South Korea*

[4]*DTU Energy, Technical University of Denmark, Kgs.Lyngby, Denmark*

Caloric cooling has been proposed as an efficient and environmentally friendly alternative to the vapor compression cooling system that is noisy and source of greenhouse gases [1]. Among the materials used as refrigerants in caloric cooling, Gadolinium (Gd) and Lead Scandium Tantalate (PST) remain the most active in respectively magnetocaloric [2-4] and electrocaloric devices [5-6]. However, the energy efficiency of these materials called *materials efficiency* has barely been studied. Recent research [7-10] in the topic defines the materials efficiency **η** as the ratio between the isothermal heat **Q** and the work **W** needed to drive this heat. The former represents the energy exchanged between the material and its environment, and the latter is the corresponding energy done by driving the field mechanically or electrically. Here, by direct measurements using IR camera and DSC for heat, and a dedicated setup for work, we report quantitative results on **η** of B-cations highly ordered PST bulk ceramics and commercial-grade Gd spheres. We measured an adiabatic temperature change of 3K at 22kV/cm in PST around room temperature. We reveal a maximum **η** of 150 in PST at 11kV/cm. Moreover, for the same heat exchanged, we reveal that PST driven electrically (11kV/cm) is an order of magnitude more efficient than Gd driven by permanent magnets (0.75T). Our study gives a deeper insight into materials efficiency as a figure of merit to select caloric materials for efficient cooling devices.

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Martensitic Ni-Co-Mn-Al Heusler alloys in magnetic field and hydrostatic pressure for caloric applications

Bruno Weise[1], Anja Waske[1,2], Kornelius Nielsch[1,3], Sebastian Fähler[1], Maria Krautz[1]

[1]Leibniz IFW Dresden, Dresden, Germany
[2] BAM, Berlin, Germany
[3] TU Dresden, Dresden, Germany

Abstract

Martensitic Heusler alloys are a promising material for environmentally friendly solid-state cooling applications. Ni-Mn-X (X = In, Sn, Al) Heusler alloys are known for their first order structural transition between martensite and austenite, accompanied by a large change in entropy. The cubic austenite phase transforms to tetragonally twinned martensite by various external stimuli, such as temperature, mechanical stress or magnetic field. A recently introduced concept showing the potential of a multicaloric cooling cycle makes use of multiple stimuli to enhance the performance of such materials [1].

We studied the effect of elemental substitution in $Ni_{52-x}Co_xMn_{48-y}Al_y$ ($7 < x < 13$, $16 < y < 19$), prepared by arc melting followed by a dedicated heat treatment for 3 d at 1373 K. Temperature and field-dependent phase transitions where studied by SQUID, VSM, DSC and heat capacity measurements. It can be stated, that the transition temperature between martensite and austenite strongly depends on the Co content substituting Ni (shift of transition by Co substitution: 40 K/at.-%). On the other hand, the substitution of Mn by Al shows a weaker effect on the phase transition temperature. After annealing the Ni-Co-Mn-Al alloys show a thermal hysteresis between martensite and austenite of 10-15 K and a magnetic entropy change of 6.5 J/kgK in a field change of $\Delta B = 2$ T is realized in $Ni_{41}Co_{11}Mn_{31}Al_{17}$ which is high compared to other studies on Ni-Co-Mn-Al [2]. Induced by magnetic field, the transition shifts by up to $dT/dB = 3$ K/T, additionally, a strong pressure dependence of $dT/dp = 10$ K/kbar is observed in $Ni_{39}Co_{13}Al_{31}Mn_{17}$ by pressure dependent magnetization measurements up to $p = 11$ kbar. Furthermore, the microstructure is investigated with optical and electron microscopy.

There are various concepts to either overcome or make use of the thermal hysteresis, which is commonly seen as main obstacle preventing utilization of Heusler alloys in caloric applications. Some of these concepts are e.g. operating in minor loops [3] or multicaloric cooling cycles [1]. Due to the multi-stimuli behavior of the studied alloy the latter is investigated in this study. Here, a comprehensive examination of the functional properties of Ni-Co-Mn-Al as well as the microstructure modified by magnetic field and hydrostatic pressure is presented in order to promote utilization of Ni-Co-Mn-Al Heusler alloys.

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Keywords: Ni-Co-Mn-Al, Martensitic Heusler alloy, magnetocaloric effect, barocaloric effect, multicaloric cooling

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

B. Huang[1,2], N.H. van Dijk[1], E. Brück[1]

[1]*Fundamental Aspects of Materials and Energy, Faculty of Applied Sciences, TU Delft, Mekelweg 15, 2629 JB Delft, the Netherlands*
[2]*School of Materials Science and Engineering, South China University of Technology, Guangzhou, 510640, China*

Abstract

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.

Keywords: magnetocaloric, heat pump, prototype, performance, multi-layer.

Material design for the exploiting hysteresis multi-stimuli cooling cycle

Benedikt Beckmann[1], Andreas Taubel[1], Franziska Scheibel[1], Lukas Pfeuffer[1], Alisa Chirkova[1], Tino Gottschall[2], Konstantin P. Skokov[1] and Oliver Gutfleisch[1],

[1]Technical University of Darmstadt, Institute of Material Science, Alarich-Weiss-Str. 16, 64287 Darmstadt, Germany
[2]Dresden High Magnetic Field Laboratory (HLD-EMFL), Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany

Energy-efficient solid-state cooling relies on efficient caloric materials used as a working body in a magnetic refrigerator. The largest caloric effects can be obtained in materials with first-order phase transitions. However, a major challenge is the mastering of thermal hysteresis [1,2], which is inherent to all first-order phase transitions and is detrimental to the efficiency of a magnetocaloric refrigerator under cyclic operation.

While there are many attempts to reduce the thermal hysteresis in first-order materials, in order to increase their cyclic performance, an alternative is to actually exploit the thermal hysteresis by using an additional stimulus, such as mechanical stress, to affect the transformed state of the material [3]. In this novel multi-stimuli cooling cycle, the application of magnetic field is used to transform the material to the high-magnetization state, which remains stable after the field removal due to the large thermal hysteresis. At the next step, an external uniaxial stress is applied to transform the material back to the low-magnetization state. In the multi-stimuli cooling concept, the heat transfer and the (de)magnetization process of the magnetocaloric material can be decoupled, which allows to eliminate the need of a large amount of permanent magnets that are otherwise required for a magnetocaloric refrigerator. However, the requirement for the material to be used is a large sensitivity towards both stimuli as well as an excellent mechanical stability.

Most promising materials for this novel cooling cycle are inverse magnetocaloric Heusler alloys that cool down upon magnetization and show a tunable thermal hysteresis, for example, Ni-(Co)-Mn-In. Furthermore, the all-*d*-metal Heusler alloys exhibit both, a large magnetocaloric effect and a large volume change during the martensitic transformation. Ni-Co-Mn-Ti alloys show an enhanced mechanical strength compared to the above-mentioned alloys [4,5].

We present a systematic study of magnetocaloric and mechanical properties under uniaxial load for the most promising Heusler alloys. We comprehensively demonstrate how the magnetic field sensitivity of the phase transition, the thermal hysteresis and the mechanical

Near-net-shape production of LaFeSi micro-channel regenerators

Konrad Löwe[1], Hugo A. Vieyra[1], Alexander Barcza[1], Matthias Katter[1]

[1]Vacuumschmelze GmbH & Co. KG
Hanau, 63450, Germany, konrad.loewe@vacuumschmelze.com

Abstract

The good magnetocaloric properties of the LaFeSi-based alloy family CALORIVAC® make it very attractive for magnetic cooling applications on a large scale. Furthermore, the currently used powder metallurgical fabrication route for LaFeSi-alloys is suitable for production upscaling. Nevertheless, typical shaping techniques based on compaction and sintering of fine powder with subsequent secondary machining are not cost effective. In addition, the available machining technologies are unable to yield the intricate regenerator geometries required for cooling machines having high coefficient of performance.

In this work alternative near net-shape production methods for LaFeSi-based regenerators are presented. The use of compatible organic additives during shaping opens up new possibilities for the production of more complex geometries. Furthermore, such methods have the benefit of high production yield and minimal requirements for secondary machining. Methods like extrusion and tape casting combined with a suitable debinding process prove successful for the production of fully dense organic-free parts with hydraulic diameters less than 0.3 mm and good magnetocaloric properties.

The most recent efforts towards industrialization of LaFeSi alloys for room and low temperature applications are also presented.

Keywords: magnetocaloric materials; LaFeSi, shaping

Unraveling the role of the multi-double-exchange mechanism in enhancing the magnetocaloric behavior $LaAgCaMnO_3$ compound

Mourad Smari[1]

[1]LIBPhys-UC, Department of Physics, University of Coimbra,
P-3004-516 Coimbra, Portugal

Abstract

The effect of magnetic phase coexistence on the electrical and magnetic properties of the $LaAgCaMnO_3$ system compound was investigated. Substitution of lanthanum by silver produces large modifications of magnetic, electrical, and thermal properties of manganite. The LaAgCaMnO3 sample synthesized by the conventional sol-gel method showed an increase of 80% in the absolute value of the magnetic entropy change (ΔS) at low temperature for an applied field of 2T with respect to previous studies, followed by an increase in the temperature coefficient of resistivity value.20 We give a direct discussion of the presence of phase separation and multi-double exchange interaction (Multi DE) within the sample and the effect of Ag doping on the magnetoelectric properties of the sample. Colossal magnetoresistance (CMR) has also been reported for various applied magnetic fields. Therefore, the observed CMR values pave the way to $LaAgCaMnO_3$ for potential application in magnetic field sensing. The goal behind using silver in LCMO samples is to find a cheaper alternative for various applications that rely on magnetic materials.

Keywords: Phase Separation, Charge-ordering, Colossal magnetoresistance (CMR), temperature Coefficient of Resistivity (TCR), multi-double exchange phenomenon.

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Direct Measurements of the Electrocaloric Effect in Solid Ferroelectric Materials Via Thermoreflectance.

Layla FARHAT[1,2], Mathieu BARDOUX[1], Stéphane LONGUEMART[1], Ziad HERRO[2], Abdelhak HADJ SAHRAOUI[1]

1. Unité de Dynamique et Structure des Matériaux Moléculaires, Université du Littoral Côte d'Opale, 59140 Dunkerque, France

2. Laboratoire de Physique Appliquée, Faculté des Sciences, Université Libanaise, Fanar, Liban

Keywords: Electrocaloric effect, Thermoreflectance, Ferroelectricity, cooling system.

Electrocaloric (EC) effect refers to the isothermal entropy or adiabatic temperature changes of a dielectric material induced by an external electric field. This phenomenon has been largely ignored for application because only modest EC effects (2.6 K) have been detected in bulk ceramics materials such as Pb0.99Nb0.02(Zr0.75Sn0.20Ti0.05)0.98O3 [1]. The discovery of a giant electrocaloric effect by Mischenko et al. [2] in thin films (up to 12 °C with E=480 kV.cm^{-1}) renewed interest in electrocaloric materials and related cooling technologies. It is indeed the development of thin structures that has made it possible to obtain high dielectric rigidity and significant electrocaloric effects.

Several methods have been developed to characterize EC effect. "Direct methods" measure the EC temperature change or released heat in the material on application or withdrawal of the electric field. ''Indirect method'' employs Maxwell equations to calculate the EC effect from the change of polarization with temperature.

In fact, ferroelectric thin films exhibit significant dielectric losses ($tan\delta$>0.1). Furthermore, EC thin layer being deposited on a solid substrate, the thermal capacity of the assembly is very high compared to that of the thin layer alone. Thus, even if the change in specific entropy following the application of an electric field is very large, the change in total entropy is almost undetectable because of the very low volume of the thin films. The temperature variation will also be hardly detectable because of the rapid dissipation of the heat in the substrate that is behaving as a heat sink. Due to these limitations, till now it has been difficult to present experimental values of electrocaloric properties in thin films from direct measurements, and the use of indirect methods is privileged [3]. It is therefore imperative to study these materials using instruments offering high resolution and dynamic.

To overcome these difficulties, we propose a novel characterization method based on thermoreflectance for measuring directly the electrocaloric effect. This method allows the study of systems such as thin films, multilayers, and nanoparticle. It is a non-contact and non-destructive measurement method with a very large temporal dynamic, which allows the study of extremely rapid phenomena [4]. It exploits the temperature-dependent reflectivity of a surface which is probed using the intensity variation of a reflected laser beam. We report laser-based direct measurements of ECE in various solid ferroelectric materials in the form of multilayered capacitor and thin films as a function of the applied electric field. Using appropriate model, the signal can be used to retrieve electrocaloric properties of embedded or stacked electrocaloric layers.

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The Antiferro to Ferromagnetic Phase Transition in $Mn_2Sb_{1-x}Bi_x$ Compounds

Qi Shen, Ivan Batashev, Fengqi Zhang, Hamutu Ojiyed, Niels van Dijk, Ekkes Brück

Fundamental Aspects of Materials and Energy, Faculty of Applied Sciences, TU Delft, Mekelweg 15, 2629 JB Delft, The Netherlands

Keyword: Antiferro to ferrimagnetic phase transition; Inverse magnetocaloric effect

Mn_2Sb is a ferrimagnet with T_C around 550 K crystallizing in the tetragonal Cu_2Sb-type structure[1]. By doping other elements into the system, a Antiferromagnetic-Ferrimagnetic (AFM-FIM) transition can be induced in Mn_2Sb [2,3]. Tunable transition temperature and small thermal hysteresis makes these compounds extremely attractive for heat recovery applications[3]. The influence of partial substitution of Bi for Sb on the structure, magnetic properties and magnetocaloric effect of $Mn_2Sb_{1-x}Bi_x$ (x = 0, 0.02, 0.04, 0.05, 0.07, 0.09, 0.15, 0.20) compounds has been investigated.

As shown in Fig. 1, The transition temperature of the AFM-FIM transition initially increases with increasing Bi and decreases above 9%. Density functional theory calculations indicate that the Bi atoms prefer to occupy only the Sb site, which accounts for the large magnetization jump in $Mn_2Sb_{0.93}Bi_{0.07}$. As large lattice parameters are found for Bi substituted Mn_2Sb, the origin of the AFM-FIM transition in $Mn_2Sb_{(1-x)}Bi_x$ compounds is ascribed to an enhanced coefficient of thermal expansion along the c axis, resulting from the Bi substitution. The moderate entropy change of 1.17 J/kgK under 2 T originating from the inverse magnetocaloric effect and the strong magnetic field dependence of the transition temperature of $dT_t/d\mu_0H$ = -5.4 K/T in $Mn_2Sb_{0.95}Bi_{0.05}$ indicate that this alloy is a promising candidate material for magnetocaloric applications.

Development and Performance of a Magnetocaloric Heat Pump

Christian R.H. Bahl[1], Marvin Masche[1], Jierong Liang[1], Stefano Dall'Olio[2] and Kurt Engelbrecht[1]

[1]Department of Energy Conversion and Storage, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
[2]Faculty of Mechanical Engineering, University of Ljubljana, 1000 Ljubljana, Slovenia

Abstract

A magnetocaloric heat pump has been developed and tested. It is a part of the RES4Build project focused on research into ways of decarbonizing the building energy consumption in the EU.

The heat pump has a rotating two-pole permanent magnet, which generates an average field of 1.46 T. The magnetocaloric material used is LaFeSiMnH, known as Calorivac-HS and supplied by Vacuumschmelze in Germany. The material is in the form of spheres, packed in 13 tapered AMR beds, without epoxy bonding. Ten compositions are layered in each bed designed for a temperature span of up to 20 K. A high degree of automation is ensured by computer control of the fluid circuit flow characteristics by solenoid valves. These valves allow control of the cycle timing, and it will be shown how this can be used to change between different operational modes with a trade-off between efficiency and heating power.

The performance is characterized by the temperature span between the hot and cold reservoirs, the heating power at the hot end and the heating coefficient of performance (COP_H). Here the COP_H is defined as the heating power divided by the sum of the magnetic work and the pumping work.

The heat pump has reached a maximum of 950 W of heating over a temperature span of 6.8 K. This was achieved with a COP_H of 7.0. In another test with a 11.4 K temperature span, a heating power of 333 W was achieved with a COP_H of 7.1. This is equivalent to a second law (Carnot) efficiency of 27.6%.

Keywords: Magnetocaloric, Heat pump, Efficiency

Development of Heusler-type magnetocaloric materials inks for additive manufacturing

B. Rodríguez-Crespo[a], D. Salazar-Jaramillo[a], V. Chernenko[a-c]
[a]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, Leioa 48940, Spain
[b]University of the Basque Country (UPV/EHU), Bilbao 48080, Spain
[c]Ikerbasque, Basque Foundation for Science, Bilbao 48009, Spain

Abstract

Magnetocaloric (MC) effect is the ability of the so-called magnetocaloric materials to change their temperature upon an external magnetic field in adiabatic conditions. These materials are suitable for magnetic cooling in the area of solid-state refrigeration which is seen as a great alternative to the less efficient conventional gas-compression-expansion refrigeration. The aim of the present work was to investigate MC materials based on the Heusler-type NiCoMnSn metamagnetic shape memory alloys (MetaMSMAs) and explore their potential application for the solid state cooling on macro- and microscales. The alloy composition, facilitating the martensitic transformation near room temperature with low thermal hysteresis, was elaborated. The actual alloy was fabricated by the induction method and casting. After solution heat treatment a part of the ingot was used to prepare melt-spun ribbons which, in turn, served for easy manufacturing a powder by a careful grinding. The material on each stage of technological processing was heat treated and characterized magnetically and structurally. MC effect was controlled by direct measurements of the magnetic field induced adiabatic temperature change, ΔT_{ad}. The powder of MetaMSMA was used for room temperature additive manufacturing. As a result, a printable ink MetaMSMA/polymer exhibiting inverse MC effect (ΔT_{ad} of about 2K in the field of 2T) was created for the first time. The technology can be used for 2D printing of cooling microdevices, e.g., for benefits of flexible electronics.

Keywords: Magnetocaloric, Heusler, Metamagnetic, Additive Manufacturing, Refrigeration

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CALORIC HEATING AND COOLING

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Numerical tool for evaluation of static thermal switches in caloric refrigeration and heat pumping

Katja Klinar[1], Katja Vozel[1], Andrej Kitanovski[1]

[1]University of Ljubljana, Faculty of Mechanical Engineering, Askerceva 6, 1000 Ljubljana, Slovenia

Abstract

Caloric refrigeration is considered one of the promising alternatives to vapor-compression refrigeration technology, but it needs a scientific breakthrough to become competitive. The main problem is poor thermal performance of caloric devices that is believed to be a consequence of low heat transfer rates. Thermal switches represent a potential solution to improve the energy efficiency and power density in caloric devices. They allow for higher operating frequencies than the principle of fluidic active caloric regeneration while keeping viscous and other parasitic losses low. Thermal switches are active elements whose thermal resistance changes in response to an applied external electric field, magnetic field, force, or pressure. We distinguish between static and dynamic thermal switches that are stationary in their position, or move between the different positions, respectively. The numerical model described in this work was developed to analyse operation and performance of static thermal switches in caloric refrigeration and heat pumping. The evaluated caloric assembly consisted of the magnetocaloric material sandwiched between two thermal switches connecting heat source and heat sink at each end. The heat sink was subjected to the ambient via convection and the boundary condition at the heat source was defined via input heat flux simulating the cooling power. The analyses comprised the evaluation of the impact of switching ratio of a thermal switch and the degradation of the overall thermal performance of the caloric assembly owing to the internal heat generation within the thermal switch and thermal contact resistance between components.

Keywords: heat transfer, thermal switch, magnetocaloric, refrigeration

Enhanced reversibility of the magnetoelastic transition in $(Mn,Fe)_2(P,Si)$ alloys via minimizing the transition-induced elastic strain energy

Xuefei Miao[1,*], Yong Gong[1], Fengqi Zhang[2], Yurong You[1], Luana Caron[3], Chin-Wei Wang[4], Feng Xu[1], Niels van Dijk[2], Ekkes Brück[2]

[1]MIIT Key Laboratory of Advanced Metallic and Intermetallic Materials Technology, School of Materials Science and Engineering, Nanjing University of Science and Technology, 210094 Nanjing, China
[2]Fundamental Aspects of Materials and Energy, Department of Radiation Science and Technology, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands
[3]Department of Physics, Bielefeld University, 33501 Bielefeld, Germany
[4]National Synchrotron Radiation Research Center, 30076 Hsinchu, Taiwan
*Email: xuefeimiao@njust.edu.cn

Abstract

Magnetocaloric materials undergoing reversible phase transitions are highly desirable for magnetic refrigeration applications. $(Mn,Fe)_2(P,Si)$ alloys exhibit a giant magnetocaloric effect accompanied by a magnetoelastic transition, while the noticeable irreversibility causes degradation of the magnetocaloric properties during consecutive cooling cycles. In the present work, we performed a comprehensive study on the magnetoelastic transition of the $(Mn,Fe)_2(P,Si)$ alloys by high-resolution transmission electron microscopy, *in situ* field- and temperature-dependent neutron powder diffraction as well as density functional theory calculations (DFT). We found a generalized relationship between the thermal hysteresis and the transition-induced elastic strain energy for the $(Mn,Fe)_2(P,Si)$ family. The thermal hysteresis was greatly reduced from 11 to 1 K by a mere 4 at.% substitution of Fe by Mo in the $Mn_{1.15}Fe_{0.80}P_{0.45}Si_{0.55}$ alloy. This reduction is found to be due to a strong reduction in the transition-induced elastic strain energy. The significantly enhanced reversibility of the magnetoelastic transition leads to a remarkable improvement of the reversible adiabatic temperature, compared to the parent alloy. Based on the DFT calculations and the neutron diffraction experiments, we also elucidated the underlying mechanism of the tunable transition temperature for the $(Mn,Fe)_2(P,Si)$ family, which can essentially be attributed to the strong competition between covalent bonding and ferromagnetic exchange coupling. The present work provides not only a new strategy to improve the reversibility of a first-order magnetic transition but also essential insight into the electron-spin-lattice multi-coupling in giant magnetocaloric materials

Keywords: Magnetocaloric effect; $(Mn,Fe)_2(P,Si)$; Hysteresis; Neutron diffraction; DFT; TEM

MnCoGe-based magnetocaloric alloys with low thermal hysteresis and wide working temperature range

Wenhui Guo, Xuefei Miao*, Feng Xu

MIIT Key Laboratory of Advanced Metallic and Intermetallic Materials Technology, School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China
*Email: xuefeimiao@njust.edu.cn

Abstract

Although the magnetocaloric effect (MCE) is intrinsic to all magnetic materials, it is most pronounced (the so-called giant MCE) in those exhibiting a first-order magnetic transition (FOMT) due to the presence of latent heat. In strong contrast to a conventional second-order magnetic transition, the FOMT is characteristic of the coincidence of a magnetic and a structural transition. Therefore, the search for promising magnetocaloric materials can be carried out either by screening the magnetic materials with a naturally coupled magnetic and structural transition, or by tailoring the naturally separated magnetic and structural transitions to coincide.

Stoichiometric MnCoGe alloy undergoes a martensitic transition at 430 K, while its ferromagnetic transition occurs at a much lower temperature of 345 K. Apparently, the magnetic and structural transitions are separated in the stoichiometric MnCoGe alloy. In the present work, we report the realization of a magnetostructural transition and a giant MCE in the off-stoichiometric $Mn_{1-x}Co_{1+x}Ge$ alloys. Based on neutron powder diffraction experiments and density functional theory calculations, the mechanism of the tunable magneto-structural coupling in the MnCoGe-based alloys was discussed. Interestingly, the $Mn_{1-x}Co_{1+x}Ge$ alloys exhibit a low thermal hysteresis of about 4 K, which is the lowest value reported in the MnCoGe-based alloys so far. Geometrically nonlinear theory has been widely used to explore the relationship between thermal hysteresis and structural compatibility across the martensitic transition in NiTi-based shape memory alloys and NiMn-based Heusler alloys. Based on the neutron diffraction data, we calculated the principal middle eigenvalue λ_2 of the transformation stretch tensor for the $Mn_{1-x}Co_{1+x}Ge$ alloys. The λ_2 was found to be very close to 1, which suggests good structural compatibility between the orthorhombic and hexagonal phase. The structural compatibility at the two phase interface was experimentally verified by high-resolution transmission electron microscope. Furthermore, the giant MCE with thermal hysteresis can tuned in a wide temperature range (from 263 K to 395 K) by doping with appropriate Si. Consequently, the combination of low hysteresis, giant MCE and wide working temperature makes the $Mn_{1-x}Co_{1+x}(Ge,Si)$ alloy promising for room-temperature magnetic refrigeration application.

Keywords: MnCoGe-based alloy, magnetocaloric effect, magnetostructural transition, thermal hysteresis, neutron diffraction, TEM

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Statistical model for the magnetic and structural transformations in Heusler alloys

Olga N. Miroshkina[1,2], Vladimir V. Sokolovskiy[2], Markus E. Gruner[1], Vasiliy D. Buchelnikov[2]

[1]University of Duisburg-Essen, 47048 Duisburg, Germany
[2]Chelyabinsk State University, 454001 Chelyabinsk, Russia

Abstract

To date, multifunctional materials exhibiting the magnetocaloric effect (MCE) at first-order phase transitions are subject to intense fundamental and applied research throughout the world since they are considered as a more efficient and ecologically safe alternative to conventional compressor devices. Therefore, theory guide search for optimized MCE materials with large entropy and temperature change together with low temperature hysteresis.

In this work, we consider a one-dimensional statistical model based on a phenomenological approach for the description of the magnetic and magnetocaloric properties in Heusler alloys. This approach is based on the theory of diffuse phase transitions[1], the Bean–Rodbell model of first-order phase transitions[2], and molecular mean-field approach[3]. The proposed model is applied to two series of Heusler alloys with respect to the first-order magnetostructural and the second-order magnetic phase transitions, revealing the temperature dependence of strain, magnetization, and magnetic entropy change under externally applied magnetic field and pressure.

Our calculations reproduce the magnetic field shifts the martensitic-transition temperature and the magnetization inflection point to higher temperatures for Ni-Mn-Ga. The calculations of the magnetocaloric properties of $Ni_{2+x}Mn_{1-x}Ga$ (x = 0.16, 0.18, and 0.3)[4] predict that the compositions with x = 0.16 and 0.18 exhibit the largest changes in the magnetic part of the entropy. However, the highest refrigeration capacity is observed for the compound with x = 0.3, which, although characterized by a small change in the entropy at the magnetic transition, exhibits the MCE in a wider temperature range due to the second-order phase transition. In the case of $Ni_{1.83}Mn_{1.46}In_{0.54}Co_{0.17}$, both inverse and conventional MCE are present[5]. The conventional MCE is significantly smaller in comparison to the inverse MCE, where both magnetic and structural subsystems play a role. Here, applying external pressure leads to an increase in structural transition temperatures in contrast to the magnetic field. With increasing pressure, the magnitude of inverse MCE is found to increase substantially, whereas conventional MCE changes only insignificantly. We compared the results regarding external pressure and magnetic field with the available experimental data, which are in good agreement[6,7].

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Keywords: magnetocaloric effect, Heusler alloys, refrigeration capacity, magnetic cooling

Thermo-Magnetic Motor (TMM)

Nikolaus Vida[1]

[1]Swiss Blue Energy AG

Abstract

Efficiency and performance enhancements in combination with a cost-effective and robust design are the key challenges in developing an economic Thermo-Magnetic Motor (TMM). Swiss Blue Energy (SBE) is currently building its second generation TMM K2 which will generate a net electrical output of 1 kW. Increasing the heat transfer between fluid and thermomagnetic material as well as reducing the back-work ratio (BWR) by minimizing pressure losses are major development steps towards significant improvements of this technology. The TMM K2 is still based on the thermomagnetic material Gadolinium which restricts the overall efficiency to less than ~1 %. Ideally, new materials will allow overcoming this limitation in the mid-term future so that Gadolinium will be replaced finally and thereby reducing the costs considerably.

Besides that, the first generation TMM K1 has been running over 20’000 hours in an industrial environment from which a lot of valuable insights regarding the long-term performance have been gained. Particularly, the impact of high cycle counts of heating/cooling as well as the alternating forces by the magnetic field are of primary interest (fatigue strength). The main objective of this long-term test was to show the reliability of the TMM under industrial conditions for permanent 24/7 power generation.

Keywords: Thermo-Magnetic Motor (TMM), Waste Heat Utilization, Heat to Power

Performance Testing and Modeling of a Magnetocaloric Heat Pump

Marvin Masche[1], Jierong Liang[1], Christian R.H. Bahl[1] and Kurt Engelbrecht[1]

[1]Department of Energy Conversion and Storage, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

Abstract

There is great interest to employ energy-saving systems to reduce emissions from the space heating and cooling sector, while also providing robust operation and environmentally benign refrigerants. One of the most promising technologies that fit these requirements are magnetocaloric heat pumps that have great potential to reduce global energy consumption and eliminate the use of harmful refrigerants compared to conventional vapor compression systems. The active magnetic regenerator (AMR) heat pump, developed by the caloric group at the Technical University of Denmark, is part of the RES4Build project that aims to decarbonize the energy consumption in buildings (i.e., the RES4Build project). The heat pump employs a rotating two-pole permanent magnet (B=1.46 T), fixed 13 tapered regenerator beds filled with a total of 3.8 kg spheres of a second-order phase transition magnetocaloric material, and a parallel flow circuit using solenoid valves that allow the timing of the AMR cycle. The heat transfer fluid, water mixed with 10% antifreeze, oscillates through the system in synchrony with the periodically changing external magnetic field. The cooling/heating capacity can be measured at different operating conditions, e.g., different hot reservoir temperatures, flow rates, cycle frequencies, and valve openings (i.e., the blow timing fractions). It will be shown that the pressure drop through the regenerator beds is lower compared to the same AMR heat pump previously operated with a first-order phase transition material, providing potential for a higher coefficient of performance (COP). The efficiency of the heat pump is evaluated in terms of the COP in the heating mode, the temperature span between the cold and hot side of the AMR, the heating power at the hot side, and the second law efficiency. The COP is defined as the heating capacity supplied to the hot side and the net input power, consisting of the magnetic power peformed on the magnetocaloric material inside the regenerator and the pump power required to move the fluid around the AMR system. Performance data will be compared to the other state-of-the-art magnetocaloric prototypes and to a 1D AMR model. The device reached a high second law efficiencies > 20% and temperature spans above >15 K.

Keywords: Active magnetic regenerator, Magnetocaloric material, Heat pump, Second-order transition

Toward the construction of an in-depth picture for magnetic-state change via adiabatic route in $La(Fe,Si)_{13}$ - based magnetocaloric compounds

Asaya Fujita[1]

[1] Magnetic powder metallurgy research center (MAGMET), AIST, Japan

Abstract

An adiabatic temperature change, ΔT_{ad}, is one of the measures to evaluate the magnetocaloric effect, and also, ΔT_{ad} is one of the elemental thermodynamic processes which construct the active magnetic regenerative (AMR)-type heat-pump cycle. Compared to an isothermal or an iso-field process, a change in magnetic state through the adiabatic process is difficult to observe. Especially, in the first-order phase transition, the magnetic state changes from one state to another distinct state beyond the energy barrier, and therefore, simultaneous changes in temperature and magnetic field on the adiabatic process make it hard to detect a magnetic state. Accordingly, most observations are focused only on the temperature change via the adiabatic process. In this study, an AC magnetic susceptibility was detected together with temperature under the adiabatic field changes for $La(Fe,Si)_{13}$-based compound, and an initial and final magnetic state at an adiabatic process was determined. It has been discussed that the adiabatic temperature change corresponds to a width between cooling branch of the zero-field entropy (S)-temperature (T) line and heating one of the iso-field S-T line. By recording the whole initial and final magnetic states in the cyclic adiabatic process upon cooling and heating, thermal variation of magnetic susceptibility (χ) in the adiabatic path under the cyclic process is determined. In addition, we assume the χ −T variation on the transition progress reflects a volume balance of the ferromagnetic and paramagnetic phases, and then, the S −T variation is anticipated from variation of the χ −T line. The resultant adiabatic S-T lines run close to the iso-field S - T lines, but they do not overlap in the whole part. Another important issue is the mismatch between the first and subsequent cyclic responses in magnitude of ΔT_{ad}. On these arguments, one must care whether the initial state of the first adiabatic process is brought by the iso-field cooling (or heating). Even when the initial state was established by the iso-field process, the measured susceptibility of the final state in the first adiabatic process locates on the adiabatic χ −T line, and therefore, a subsequent adiabatic process cannot go back to the original iso-field state. This variation is actually explained from "influence of thermal hysteresis". However, if this hysteresis issue is discussed in analogy of the minor-loop problem, it may be insufficient. As stated in the 2nd law of thermodynamics (Caratheodory principle), "in every arbitrarily close neighborhood of a given initial state there exist states that cannot be approached arbitrarily closely by adiabatic processes". The irreversibility in the jump from the iso-field to adiabatic state would also influences by the thermodynamical principle. This issue is also important in the AMR cycle, since the adiabatic final state is connected to iso-field process (hot/cold blows). However, it must be made aware that, in the AMR cycle, the adiabatic final state already locates outside of the accessible by the iso-field process.

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Keywords: magnetocaloric, La(Fe,Si)13, adiabatic process, iso-field process

Modelling of regenerative cooling using elastocaloric elastomers

Gael Sebald[1], Alban Duval[1,2], Giulia Lombardi[1], Jacques Jay[3], Atsuki Komiya[1,2]

[1]ELyTMaX UMI 3757, CNRS – Université de Lyon – Tohoku University, International Joint Unit, Tohoku University, 980-8577, Sendai, Japan
[2] Institute of Fluid Science, Tohoku University, 980-8577, Sendai, Japan.
[3]Univ. Lyon, CNRS, INSA-Lyon, CETHIL, UMR5008, F-69621, Villeurbanne, France

Abstract

Regenerative cooling was proved in the last decades to be an efficient way to utilize caloric properties for effective refrigeration. In the objective of designing a proof of concept, the screening of possible geometries and operating conditions is hardly feasible in a reasonable time. The use of modelling permits to quickly achieve such a screening, provided that the modelling is in fact faster than the experiment. 3D models including Computational Fluid Dynamics constitute a powerful technique that was proved to be accurate at a price of large computational cost (i.e. a few hours to have one simulation of 1000 seconds).

Alternatively, it is proposed in this work an analytical model, able to provide with ultra-fast computing (<0.1s) for one operating condition. As several assumptions are necessary, the model is compared to (i) a 1D model of the coupled mass and heat transport and (ii) several preliminary experiments using natural rubber as elastocaloric material. Through this comparison, several physical insights of the regenerative cooling were confirmed. For example, the comparison between 1D model and analytical model highlighted quantitatively the impact of the active thermal conductivity, induced by the oscillating fluid and responsible for a decrease of the cooling device temperature span at high frequencies. In addition, the behavior at high frequency and small displacement of fluid revealed an optimum phase shift different from the usual 90° phase shift, which was confirmed experimentally.

The experiment, comprised one tube of rubber acting as the active material of an elementary regenerative cooling device, was tested under several operating conditions, such as displacement of the fluid and frequency of actuation, and compared to both analytical modelling and 1D modelling.

Keywords: regenerative cooling, elastocaloric, heat transfer, cooling device, 1D model, analytical model

Experimental results for three advanced microchannel active magnetic regenerator geometries

Jierong Liang[1], Cathrine D. Christiansen [1], Kristina Navickaitė [2], Kurt Engelbrecht[1], Konrad Loewe[3], Hugo Vieyra[3], Alexander Barcza[3], Rasmus Bjørk [1], and Christian R.H. Bahl[1]

[1]Department of Energy Conversion and Storage, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
[2]Beckmann-Institut für Technologieentwicklung e.V., Annaberger Str. 73, 09111 Chemnitz, Germany
[3] Vacuumschmelze GmbH & Co. KG, 63450 Hanau, Germany

Abstract

Toward the goal of commercialization of magnetic refrigeration, the scientific community has been searching for new geometries for active magnetic regenerators (AMRs) and continuously optimizing the existing geometries. In this work, we present the experimental results for three advanced microchannel AMRs, which consist of: (I) four freeze-cast AMRs with lamellar microchannels ($La_{0.66}Ca_{0.33-x}Sr_xMn_{1.05}O_3$), (II) three 3D-printed AMRs with double corrugated microchannels ($LaCe(Fe,Mn,Si)_{13}H_y$), (III) a stacked tape-cast AMR with triangular microchannels ($La(Fe,Mn,Si)_{13}H_y$).

The hydraulic diameters of these AMRs range from 66.5μm to 300μm, while the porosities range from 15.5% to 72%. The potential of the AMR candidates is studied by means of geometrical characterization, thermal-hydraulic evaluation and cooling capacities. The machining accuracy of microchannels with brittle magnetocaloric materials (MCMs) is therefore qualified. The chemical and mechanical stabilities are validated by comparisons of heat transfer effectiveness, pressure drop and magnetocaloric properties of the AMRs before and after long-term testing. The challenges of each microchannel geometry are also discussed.

All these AMRs obtained excellent stability and satisfactory performance results during the experiments. The freeze-cast AMRs showed a large specific heat transfer area up to 2.66×10^4 m^{-1}. The 3D-printed AMRs exhibited a good mechanical strength without any functional degradation after the testing of at least seven days. The tape-cast AMR exhibited a low hydraulic resistance with an estimated 42% improvement of COP in a specific magnetic refrigerator, compared to an equivalent packed bed regenerator.

Keywords: Active magnetic regenerator, Microchannel, Thermo-hydraulic, Stability

Eurotherm Seminar # 115

CALORIC HEATING AND COOLING

EUROTHERM-115-52

Exploring the entropy change in barocaloric Ammonium Sulfate using Neutron Scattering

Helen Walker[1], **Bernet Meijer**[2], **Guanqun Cai**[2], **Shurong Yuan**[2], **Richard Dixey**[2], and **Anthony Phillips**[2]

[1] *ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Harwell Oxford, OX11 0QX, United Kingdom*
[2] *School of Physics and Astronomy, Queen Mary University of London, E1 4NS London, United Kingdom*

Abstract

Ammonium Sulfate has been studied for decades as a ferroelectric, but has more recently been identified as a barocaloric [1]. The structural origins of the electric polarisation are well established [2], but those of the large entropy change at the first order phase transition driving the barocaloric properties are still a matter of dispute.

The entropy change was initially explained in terms of configurational entropy in an order-disorder model, where the three tetrahedral units (two ammonium and one sulfate) are independent statistical units showing a two-fold disorder about the mirror plane above T_C but ordered below it. This gives rise to $\Delta S = 3R\ln 2$, in reasonable agreement with calorimetry results [3], and yet this model is inconsistent with the large body of accumulated crystallography data, which show no evidence of hydrogen disorder [2,4]. Furthermore the order-disorder model would only be valid if the three tetrahedral units are independently disordered, which is highly unlikely given the presence of strong hydrogen bonding in $(NH_4)_2SO_4$ suggesting a cooperative behaviour.

We will present a combined neutron scattering (Total Scattering, Quasi-elastic Neutron Scattering and Inelastic Neutron Scattering) and *ab-initio* simulation study of the phase transition as a function of temperature and pressure looking at the local structure and the dynamics, allowing the identification of the contributions from configurational and vibrational entropy.

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keywords- Total Scattering, QENS, INS, DFT, Configurational & Vibrational Entropy

Exploration in new room temperature magnetocaloric materials: structure and magnetocaloric properties in $Mn_5(Si,P)B_2$ compounds

Hamutu Ojiyed[1], Niels Van Dijk[1], Ekkes Brück [1]

[1]Fundamental Aspects of Materials and Energy, Faculty of Applied Sciences,
Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands.

Abstract

The M_5XB_2 materials system has been widely studied as permanent magnetic materials[1] [2]. As permanent magnetic materials, their coercivity and magnetic energy product are lower than those of the mainstream permanent magnetic materials. Xie *et al.*[3] and Cedervall *et al.*[4] proposed that the Mn_5PB_2 and $(Fe_{1-x}Co_x)_5PB_2$ compounds have the prospect of being applied as magnetocaloric materials due to their near room temperature Curie temperature. In this work, the structure and magnetocaloric properties of the $Mn_5(SiP)B_2$ compounds of the M_5XB_2 material system were studied. According to a refinement of the XRD data the $Mn_5(Si_{1-x}P_x)B_2$ compounds all crystallize in the Cr_5B_3–type body-centered tetragonal structure, with a small amount of Mn_2P as a secondary phase (less than 7%). The lattice parameters and the unit-cell volume of the compounds change linearly with the increase in P content. These experimental results are consistent with calculated DFT results. The Curie temperature of the compounds can continuously be adjusted between 305 and 411 K by changing the Si/P ratio. The introduction of P also caused a decrease in saturation magnetization. The magnetic phase transition of these compounds was determined using Arrot plots and the field exponent *n* for the magnetic entropy change based on Landau's theory. The studied compounds all show a second-order magnetic phase transition. Since the compounds show a second-order phase transition, the magnetic entropy change caused by the phase transition was not large: 1.9 and 1.4 J/kgK for Mn_5SiB_2 and Mn_5PB_2, respectively. However, the advantage of this series of compounds is that the Curie temperature can be adjusted continuously around room temperature.

Keywords: magnetocaloric effect, magnetic phase transition, Curie temperature, $Mn_5(Si,P)B_2$

Magnetic Pumping and System Level Analysis of Magneto-Caloric Refrigerator with No Moving Parts

Keerthivasan Rajamani[1], Theo van der Meer[1], and Mina Shahi[1]

[1]Faculty of Engineering Technology, Department of Thermal and Fluid engineering (TFE), University of Twente, 7500 AE Enschede, The Netherlands

Abstract (Times New Roman Bold 11 pt)

Magneto-Caloric Refrigeration (MCR) at room temperature is a potentially energy efficient and an environmentally friendly alternative to a vapor compression refrigeration system [1]. Existing prototypes of MCR systems built so far encompasses a porous Magneto-Caloric Material (MCM) through which a Heat Transfer Fluid (HTF) passes [2].

To increase the residence time and thereby increase the heat transfer performance, a new MCR system (Fig. 1 and Fig. 2) is designed that utilizes Magneto-Caloric Slurry (MCS), in which the MCM particles are suspended in a HTF. Experimental characterization of Gadolinium, MnFe(P,Si) based, and La(Fe,Mn,Si)H based compounds with Galinstan (a non-toxic, eutectic mixture of Ga:In:Sn (68:22:10 wt\%)) and water as HTF are performed to assess their suitability for usage as MCS. The influence of the different resulting combinations of MCS on MCR system performance is numerically analyzed by varying the mass flow rate of the MCS, and MCM volume fraction (0.4 to 0.6).

In order to realize a feasible MCR system, the magnetic field is limited to 1 tesla. Laminar, steady state, one dimensional (radial) conduction analysis of heat transfer at cold and hot heat exchangers is performed. The MCR system is designed such that the Péclet number is less than 10, thus assuring negligible convective heat transfer in the axial direction. Models to determine effective viscosity and thermal conductivity to account for various suspension fractions in MCS are incorporated. In the analysis of the MCR system performance, a mechanical pump was initially utilized for the circulation of the MCS within the system. To increase the system reliability, ferro-hydrodynamic pumping is optimized and designed, which enables the operation of a magneto-caloric refrigerator with no moving parts. The viscous dissipation and Eddy current losses caused by ferro-hydrodynamic pumping on galinstan are eliminated by utilizing low frequency magnetic fields (<1 Hz). A cooling load of up to 20 W at room temperature is obtained over a temperature difference of 0.5 K.

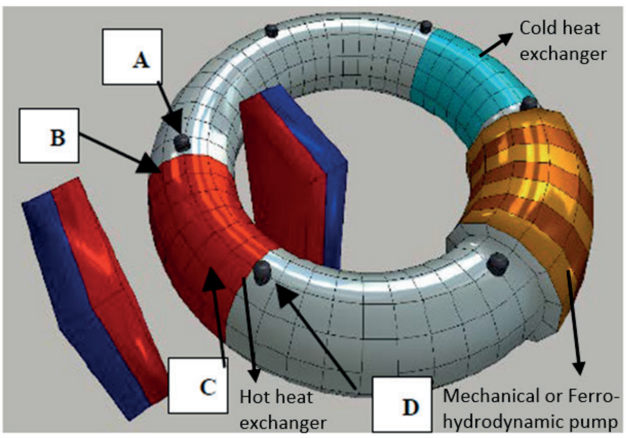


Figure 1: Schematic of the proposed MCR

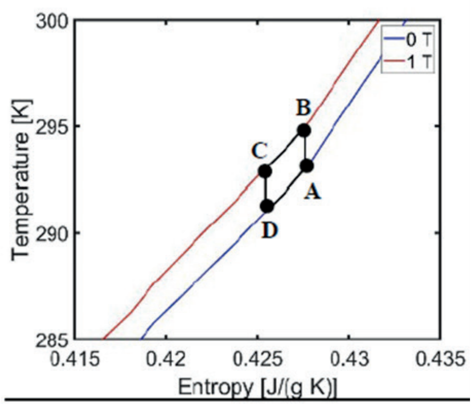


Figure 2: Magnetic Brayton refrigeration cycle marked in a temperature entropy curve.

Eurotherm Seminar # 115

CALORIC HEATING AND COOLING

EUROTHERM-115-55

Modelling the Thermo - Hydraulic Characteristics of a Magneto - Caloric Slurry

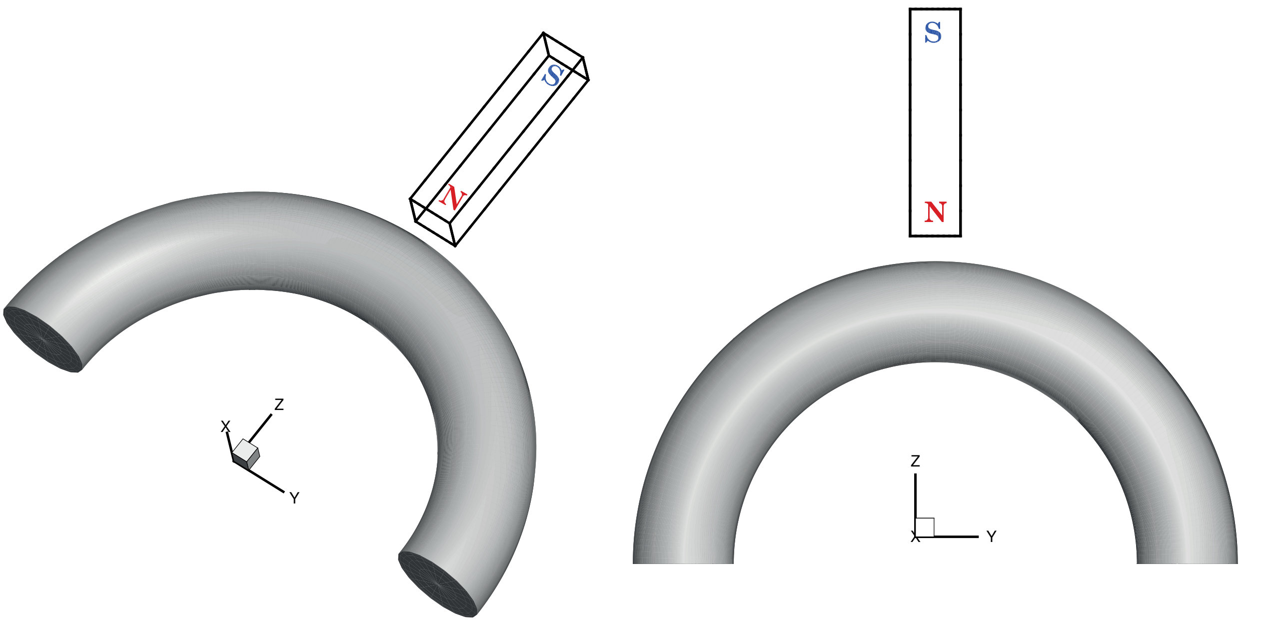
Shubham Dalvi[1], **Theo H. van der Meer**[1], and **Mina Shahi**[1]

[1] *University of Twente, Faculty of Engineering Technology, Enschede, The Netherlands*

Abstract

Over the past few years, increasing research has been carried out to study the distinct properties of Magneto - Caloric Materials (MCM) and their development [1, 2]. This has enabled the researchers to explore the MCM for their potential applications in the context of Magneto - Caloric Effect (MCE). On the similar lines, the present work is related to the development of a numerical model that examines a MCE based room - temperature cooling system. The geometrical representation of the considered system is shown in Figure 1, where a semi - toroidal loop is used as a working domain to ensure the minimal frictional losses associated with the fluid flow. Within this region, the colloidal mixture of suspended Calorivac particles in a liquid Galinstan is considered as a working fluid. To produce the desired temperature differences, a permanent magnet of high magnetic field strength is placed in the vicinity of the toroidal loop.

Investigating the thermal and flow response of Magneto - Caloric slurry in the presence of strong non - uniform magnetic field requires thorough understanding of the underlying mechanisms. Such phenomenons are best represented by the set of governing equations that includes the interaction of magnetic, hydrodynamic, and thermal variables as shown in Equations 1 - 5. To solve the coupled set of aforementioned governing equations, Finite Volume based discretization method is employed in the present work using a C++ based open-source CFD framework OpenFOAM [3]. Additionally, to resolve the complex solid - liquid interaction of the considered Magneto - Caloric slurry, Drift flux model [4] is used which allows the relative motion between the dispersed phase and the continuous phase.



(a) (b)

Figure 1: Schematic representation of the present system (a) Three dimensional view (b) Top view.