SYMPOSIUM TP01

Caloric Materials for Highly Efficient Cooling Applications
November 26 - November 28, 2018

Symposium Organizers
Sakyo Hirose, Murata Manufacturing Co Ltd
Lluis Manosa, Universitat de Barcelona
Vitalij Pecharsky, Ames Laboratory
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* Invited Paper

SESSION TP01.01: Magnetocaloric Materials and Systems I
Session Chairs: Christian Bahl, Feng-Xia Hu, Vitalij Pecharsky and Anja Waske
Monday Morning, November 26, 2018
Sheraton, 3rd Floor, Berkeley AB

8:30 AM *TP01.01.01
Exploiting First and Second Order Phase Transitions in Magnetocaloric NiMn-Based Heusler Compounds Franca Albertini[1], Cecilia Bennati[1], Simone Fabbrici[1], Riccardo Cabassi[1], Francesco Cugini[2, 1], Nicola Sarzi Amadè[1], Massimo Solzi[2, 1], Antonio Pepiciello[3] and Ciro Visone[3]; [1]IMEM-CNR, Parma, Italy; [2]Università di Parma, Parma, Italy; [3]Università del Sannio, Benevento, Italy.

Room temperature magnetic refrigeration requires materials with large isothermal entropy and adiabatic temperature changes at around 293 K and negligible thermo-magnetic hysteresis, when cycled in magnetic fields below 2T.
Ferromagnetic shape memory Heusler compounds with metamagnetic martensitic transformations are among the most studied materials for magnetocaloric applications thanks to their high adiabatic temperature changes (ΔT_ad)related to their inverse magnetocaloric effect [1]. These materials are rare earth free, easy-to-prepare and offer large tailoring possibilities. Remarkably, thanks to the strong discontinuities of the physical properties at the martensitic transformation (e.g. magnetization, volume), caloric effects can be obtained not only by applying magnetic fields but also stress and pressure, enabling multicaloric applications [2,3]. Although very high values of adiabatic temperature change have been reported, metamagnetic Heuslers show poor reversibility due to hysteresis and spreading of the transition.
By taking advantage of suitable substitutions, in NiMn-based Heusler alloys it is possible to tune the order and the number of transitions that can be exploited for magnetocaloric applications. In the present talk we will report some particular cases in the phase diagram of NiMnGa and NiMnIn compounds and discuss the reversible and irreversible contributions to the magnetocaloric effects, based on in-field calorimetry and direct ΔT_ad measurements. Interesting effects occurs when the first order magnetostructural and second order Curie transition are almost coincident. In In-based compounds, for example, the coexistence of direct and inverse magneto caloric effects can be obtained [4]. The possible exploitation of direct and inverse MCEs in alternative refrigeration cycles will be discussed.
[1] J. Liu et al., Nature Mat. 11, 620 (2011)
[2] X. Moya et al., Nature Mat. 12, 52-58 (2013)
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[4] C. Bennati et al., submitted.

9:00 AM TP01.01.02
Tailoring the Magnetocaloric Potential of $AlFe_2B_2$ Using Conventional and Additive Manufacturing Processing Schemes Radhika Barua[1], Brian Lejeune[2], Brandt Jensen[3], Ryan Ott[3], Matthew J. Kramer[3] and Laura Lewis[2, 4]; [1]Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia, United States; [2]Department of Chemical Engineering, Northeastern University, Boston, Massachusetts, United States; [3]Division of Materials Science & Engineering, Ames Laboratory, Ames, Iowa, United States; [4]Department of Mechanical Engineering, Northeastern University, Boston, Massachusetts, United States.

Material processing schemes play a critical role in guiding the development of emerging magnetocaloric materials for energy-related applications such as magnetic refrigeration and thermomagetic energy conversion.[1] To this end, the intermetallic boride $AlFe_2B_2$ has attracted considerable attention due to its low cost, promising thermal properties that promote effective heat transfer (specific heat capacity C_p=120 $Jmole^{-1}K^{-1}$; thermal conductivity κ=5.6 $Wm^{-1}K^{-1}$), and moderate magnetocaloric response near room temperature (adiabatic temperature change ΔT_{ad} =1 K and magnetic entropy change ΔS=2.6 $Jkg^{-1}K^{-1}$ at μ_0H_{app} = 2 T).[2,3] In this work, a number of synthesis methods to form single-phase $AlFe_2B_2$ alloys were investigated. Further, the magnetocaloric potential of $AlFe_2B_2$ samples synthesized via conventional metallurgical routes (casting) and additive manufacturing technology (laser engineered net shaping (LENS)) was evaluated.

Suction-casting allows fabrication of samples of various composition, including $Al_{1.2}M_xFe_2B_2$ (M=Ga and/or Ge, x≤0.1). Experimental data obtained using structural and magnetic probes indicate that the unit cell volume, saturation magnetization (M_s), Curie temperature (T_c) and specific heat capacity (C_p) of the samples increase with increased Ga and Ge content (x). Relative to the unmodified parent $AlFe_2B_2$ sample, a larger than two-fold improvement in magnetocaloric effect (MCE) was observed in the $Al_{1.1}Ge_{0.05}Ga_{0.05}Fe_2B_2$ specimen (ΔS= 6.5 $Jkg^{-1}K^{-1}$, ΔT_{ad} = 2.2 K at μ_0H_{app}=2 T). Intriguingly, the solid solubility of Ga and Ge in $AlFe_2B_2$ was determined to be negligible and it is deduced from calorimetric data that additions of these substituent elements alter the solidification route for formation of the $AlFe_2B_2$ phase. The enhanced MCE of the $Al_{1.2-x}(Ga/Ge)_xFe_2B_2$ samples is ascribed to a combination of chemical bonding and electronic effects arising from a hypothesized enrichment of Fe atoms on the Al sites within the (ac) plane of the $AlFe_2B_2$ lattice.

These results provide fundamental insights regarding the phase stability of the Al-Fe-B ternary system, and guide development of $AlFe_2B_2$ samples of complex geometries using laser engineered net shaping (LENS). The MCE of cylindrical LENS samples (5 mm dia; 30 mm length) was found to be comparable to that of corresponding undoped suction-cast samples (ΔS_{LENS}=2.8 $Jkg^{-1}K^{-1}$, $\Delta T_{ad,LENS}$=1.1 K at $\mu_0 H_{app}$=2 T). Further, the feasibility of 3D-printing honeycomb shaped samples was explored. It is surmised that $AlFe_2B_2$ is amenable for construction of magnetocaloric heat exchangers where the working material may be shaped as channel structures to facilitate efficient heat transfer between the solid refrigerant and the heat exchange fluid. Overall, this study provides strategies for maximizing the magnetofunctional potential of $AlFe_2B_2$.

References:[1]J. Lyubina, J Phys. D: Appl. Phys. 50(5), 053002, 2017; [2]R. Barua *et. al.*, J. Alloys and Comp. 745, 505, 2018; [3]B.T. Lejeune *et. al.*, Materialia, 2018.

9:15 AM TP01.01.03

Disorder and Electron Correlation Effects in the Ground State of Ni-Co-Mn-Sn Alloys with Heusler Structures Bernardo G. Barbiellini[1, 4], Aki Pulkkinen[1], Johannes Nokelainen[1], Vladimir Sokolovskiy[2], Vasiliy Buchelnikov[2], Mikhail Zagrebin[2], Katariina Pussi[1], Erkki Lähderanta[1] and Alexander Granovsky[3]; [1]Physics, LUT, Lappeenranta, Finland; [2]Chelyabinsk State University, Chelyabinsk, Russian Federation; [3]Physics, Moscow State University, Moscow, Russian Federation; [4]Department of Physics, Northeastern University, Boston, Massachusetts, United States.

We consider ab-intio calculations of Co-doped Ni-Mn-Sn shape memory alloy. The Co doping leads to a decrease in both the martensitic transformation temperature and the Curie temperature of martensite and to an increase in the Curie temperature of austenite. Besides, large magnetisation changes occur in the vicinity of structural transformation. As a result, the tuning of Co and Mn contents can lead to favorable magnetocaloric properties [1]. In this work, we focus on the effect of atomic disorder and electron correlation on the structural, magnetic and electronic properties of Ni-Co-Mn-Sn systems by using the Density Functional Theory (DFT) implemented in the VASP and SPR-KKR packages [2, 3] within a 32-atom supercell and the coherent potential approximation, respectively. The optimized atomic positions for compositions studied are obtained by the USPEX package [4]. To study the effect of exchange-correlation, a series of ground state calculations were performed using both the GGA-PBE functional and Meta-GGA with SCAN functional of DFT [5].

[1] Huang et al, APL 104 (2014)132407
[2] Kresse, et al., Phys. Rev. B 54 (1996) 11169
[3] Ebert et al., Rep. Prog. Phys. 74 (2011) 096501
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9:30 AM TP01.01.04

Magnetic and Magnetocaloric Properties of Fe-(W)Ta Thin Films Surabhi Shaji[1], Nikhil R. Mucha[1], Prakash Giri[2], Christian Binek[2] and Dhananjay Kumar[1]; [1]North Carolina A&T State University, Greensboro, North Carolina, United States; [2]University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

A first hand magnetocaloric effect (MCE) in rare-earth free Fe-W (Ta) thin film systems, induced by simultaneous transformation in structural and ordered magnetic phases, is reported. The MCE has been realized by varying the levels and types of dopants in the Fe-host. These materials systems in thin film form have shown a crystallographic phase transition from a regular body center cubic (BCC) crystal structure to a distorted BCC. Applying the Maxwell relation to the magnetization (M) versus magnetic field (H) curves at various temperatures, we have calculated dM/dT vs H the integration of which provides a quantitative information about isothermal entropy change. We have observed positive a MCE with a maximum entropy value of 6.9 $J/K\text{-}m^3$ for the magnetic field changing from 0.05 – 0.5 T. The mass specific entropy changes are small in comparison with existing magnetocaloric material. A peak in dM/dT versus H has shown that maximum entropy change takes place around 0.15 T, which is more than an order of magnitude lower than the magnetic fields generally used to realize a large MCE effect.

9:45 AM TP01.01.05

Thickness Dependent Size Effects on Hysteresis in Electrochemically Deposited Thick Film NiMnSn Heusler Alloys Yijia Zhang, Julia Billman and Patrick Shamberger; Texas A&M University, College Station, Texas, United States.

Characteristic length scales of Heusler alloy films, including film thickness and grain size, affect the transformation hysteresis by altering internal energy barriers to interphase boundary motion. Previous studies have illustrated strong film thickness effects on transformation temperatures ofnanoscale TiNiCu thin filmwith film thickness < 100 nm, and that stress hysteresis and temperature hysteresis of CuAlNi microwires increased with decreasing wire diameter with diameter < 100 µm. However, length-scale dependent hysteresis has yet to be determined for other classes of caloric materials, including Heusler alloys. Understanding such transformation behavior at small length scales is critical for microelectronic and micromechanical applications, for promoting rapid heat transfer through caloric alloy thin films and thin wires, in strain-coupled magnetoelectric composites, and in microstructured multifunctional composites and foams.

By annealing electrochemically deposited multi-layer monatomic (Ni, Mn, Sn) films, $Ni_{0.5}Mn_{0.386}Sn_{0.114}$ Heusler alloy films with decreasing thicknesses, 14.5, 8.7, and 2.9 µm, were synthesized. Phase transformation temperatures and sizes of nearly four hundred grains on each film were collected optically while the samples were heated or cooled. These data showed that the average grain areas/volumes decrease with decreasing film thicknesses. For grains within a single film (constant thickness), there is no statistically significant correlation between grain area or volume and hysteresis width. At the same time, film hysteresis increases with decreasing film thicknesses (from 4.9 ^oC at 14.5 µm to 15.7 ^oC at 2.9 µm). Previously, Chen and Schuh (2011) attributed the size effect in the hysteresis of small CuAlNi alloy microwires to the enhanced internal frictional work during transformation, associated with an increase in surface area and volume ratio. Our thickness dependent size effects could be similarly explained by internal friction-induced energy dissipation, whereby the thinner the film is, the stronger the interactions between interphase boundaries and the film-substrate interface, and the more energy is dissipated by frictional work. A power law model is fit to hysteresis width-film thickness data, and is used to elucidate scaling relationships which govern size dependence of hysteresis in Heusler alloy thin films, which are compared against previously observed size-dependent hysteresis in other thermoelastic martensitic transformations.

10:00 AM BREAK

10:30 AM OPEN DISCUSSION

11:00 AM TP01.01.07
Orientation Relationships and Lattice Matching Effects on Hysteresis in $(Mn,Fe)_2(P,Si)$ Phase Transitions Timothy D. Brown and Patrick Shamberger; Texas A&M University, College Station, Texas, United States.

Hysteresis associated with the non-diffusive phase transformation in magnetocaloric $(Mn,Fe)_2(P,Si)$ alloys creates substantial energy dissipation undesirable for cooling applications. Although reduced hysteresis has been achieved in this system through tuning of Mn/Fe and P/Si site occupancies, a deeper understanding of the underlying mechanisms necessary for designing low-hysteresis materials across a wide range of critical temperatures has proved elusive. A successful and general mechanistic theory relating hysteresis to lattice matching has been developed for similar transformations in thermoelastic martensites, dependent on both the change in lattice parameters and the orientation relationships between the parent and daughter crystal lattices. Despite the theory's success and generality, the parent-daughter orientation relationships in $(Mn,Fe)_2(P,Si)$ have not yet been established, and the lattice matching theory has not yet been tested against hysteresis in this system. In this work, we establish the orientation relationships for basal and prismatic planes in hexagonal $(Mn,Fe)_2(P,Si)$ alloys through two independent experiments: (1) comparison of temperature-dependent x-ray diffraction pole figures below and above the phase transition and (2) electron backscatter diffraction orientation mapping of adjacent grains of coexisting magnetic parent and non-magnetic daughter phases. Afterwards, we combine these orientation relationships with experimental measurements of lattice parameter discontinuities in order to calculate the lattice mismatch parameter λ_2 for several representative alloys in the $(Mn,Fe)_2(P,Si)$ system. Finally, the calculated mismatch is correlated with the samples' hysteresis as measured from calorimetry experiments and compared with the predictions of the theory, thereby establishing whether lattice matching effects may also be used to control hysteresis in $(Mn,Fe)_2(P,Si)$ alloys' phase transitions.

11:15 AM TP01.01.08
Effect of Phase Segregation on Phase Transformation Behavior in $(Mn,Fe)_2(P,Si)$ Alloys Timothy D. Brown, Jonathan S. Van Buskirk, Daniel Galvan and Patrick Shamberger; Texas A&M University, College Station, Texas, United States.

Alloying in quaternary $(Mn,Fe)_2(P,Si)$ allows for highly tunable phase transformation temperatures and hystereses, potentially enabling high-efficiency magnetocaloric cooling over a wide range of temperatures. However, compositional control of the alloy is also subject to complex thermodynamic constraints, as evidenced by segregation of multiple transforming hexagonal phases, as well as precipitation of a non-transforming cubic P-poor $(Mn,Fe)_3Si$ phase. In either case, the composition, and therefore hysteresis and transformation temperature, of the transforming phases are modified significantly from the nominal bulk composition, thereby obscuring direct causal relationships between composition and transformation behavior. Thus, in order to recover these relationships, as well as to control the expression of transforming phases of interest for cooling applications, it is critical to map out the thermodynamic phase coexistence of the alloy system. In this work, we investigate thermodynamically driven phase segregation behavior in $(Mn,Fe)_2(P,Si)$ by measuring the compositions and mass fractions of coexistent transforming and non-transforming phases for a range of nominal alloy compositions ($1.20<Mn<1.25$; $0.35<P<0.50$) through quantitative wavelength dispersive spectroscopy and backscatter electron imaging. It is found that oxygen preferentially segregates to the cubic phase over the hexagonal phase (5 at. % vs. <1 at. %), suggesting oxygen plays some role in mediating the stabilization of the cubic phase. Measured compositions of the expressed transforming hexagonal phases are then combined with critical transformation temperatures and thermal hystereses from calorimetry experiments to map out the underlying dependence of the transformation behavior on the phase compositions. The analysis suggests Mn/Fe site occupancy plays a much larger role than P/Si in controlling hysteresis of the phase transition, providing insight into the nature of the energy barriers that fundamentally control hysteresis in this alloy system.

11:30 AM TP01.01.09
Spatially and Temporally Resolved Temperature Measurements of Magnetocaloric Materials Under Varying Applied Magnetic Field Florian J. Erbesdobler, Christian Bahl, Rasmus Bjørk, Anders Smith and Kaspar K. Nielsen; DTU Energy, Roskilde, Denmark.

We present an experiment where magnetocaloric samples are spatially and temporally resolved using infra-red (IR) thermography. The spatial resolution is approximately 10x10 microns, while the temporal resolution is 170 Hz. The magnetic field applied to the sample is varied in a controlled way and thus the dynamics of the first order phase transition are observed on the sample surface.
We also present complimentary differential scanning calorimetric (DSC) measurements and are therefore able to relate the specific heat peaks of a single sample with the temperature distribution as observed by IR. This work presents our preliminary results for the first order phase transition of La(Fe,Si,Mn)13Hz compounds and describes the challenges of bringing the device into operation. Moreover, an outlook for comparing the results with a time-dependent numerical model, which can predict the material behaviour by finding its internal magnetic field and including finite heat transfer calculations, is given.

11:45 AM OPEN DISCUSSION

SESSION TP01.02: Electrocaloric Materials and Systems I
Session Chairs: Emmanuel Defay and Sakyo Hirose
Monday Afternoon, November 26, 2018
Sheraton, 3rd Floor, Berkeley AB

1:30 PM *TP01.02.01
Optimizing the Electrocaloric Effect by Molecular Dynamics Simulations Anna Grünebohm; University of Duisburg Esssen, Duisburg, Germany.

In this talk I will discuss the benefits of *ab initio* based molecular dynamics simulations [1] for the optimization of the electrocaloric effect (ECE). The basic principles of the ECE are now well understood [2]. A further optimization asks for a detailed understanding of the impact of phase transitions as well as atomic, defect and domain structures on the ECE and its reversibility. Simulations allow to isolate these factors and predict design rules for ferroelectric materials and composites with superior cooling responses.
I will focus on the factors giving rise to a large inverse caloric response [3], in particular phase transitions [4] and internal bias fields [5].

[1] M. Marathe *et al.*, Phys. Rev. B **93**, 054110, '16,
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[3] A. Grünebohm *et al.*, Energy Technol. 10.1002/ente.201800166, '18,

[4] M. Marathe *et al.,* Phys. Rev. B **96**, 014012, '17,
M. Marathe *et al.*, Phys. Status Solidi (b) **225**, 1700308, '18,
[5] A. Grünebohm *et al.*, Phys. Rev. B **93**, 134101, '16,
Y.-B. Ma *et al.*, arXiv:1805.04380, '18.

2:00 PM TP01.02.02
Electrocaloric Studies on Epitaxial $BaTiO_3$–Based Thin Films Stefan Engelhardt[1, 2], Pengfei Song[1, 2], Christian Molin[3], Sylvia Gebhardt[3], Sebastian Faehler[1], Kornelius Nielsch[1, 2] and Ruben Huehne[1]; [1]IFW Dresden, Dresden, Germany; [2]TU Dresden, Dresden, Germany; [3]Fraunhofer IKTS, Dresden, Germany.

Electrocaloric (EC) materials show reversible thermal changes in response to the variation of an applied electric field. This EC effect got a renewed interest within the last decade due to the quest for energy-efficient cooling technologies and recent discoveries of large adiabatic temperature changes ΔT in various ferroelectric thin films during the application or removal of an electric field. Among them, lead-containing oxides exhibit strong caloric effects but contain hazardous elements. $BaTiO_3$ (BT) based materials might be a more environment-friendly alternative to these compounds. Therefore, we have chosen $BaZr_xTi_{1-x}O_3$ (BZT) and $BaHf_xTi_{1-x}O_3$ (BHT) as model systems for our studies in order to investigate the correlation between the composition dependent phase transitions, the dielectric and ferroelectric properties as well as the EC effect of such BT based thin films. Moreover, we use epitaxial films, which additionally enable a detailed microstructural analysis as well as a study of orientation dependent properties.
Accordingly, epitaxial BZT and BHT films were grown by pulsed laser deposition on single crystalline substrates utilizing a conducting oxide buffer layer and additional top electrodes to obtain capacitor like structures. The grown films were studied by X-ray diffraction as well as scanning electron and atomic force microscopy. Depending on the specific growth parameters, a twin-free epitaxial growth and a smooth surface morphology is observed. Temperature depended measurements of the relative permittivity suggest diffuse phase transitions, where the transition temperature clearly varies with the film composition. The EC properties of the thin films were determined by an indirect method from temperature dependent polarization measurements showing values of up to 0.3 K for a ΔE of 170 kV/cm. We assume that the clamping of the thin films to the rigid substrate reduces the magnitude of the EC effect significantly compared to the respective bulk materials. Finally, we will present our approaches for the direct measurement of the EC effect in our epitaxial thin films.

This work is supported by DFG priority program 1599 “Ferroic cooling”.

2:15 PM TP01.02.03
Epitaxial $Na_{0.5}Bi_{0.5}TiO_3$ Based Thin Films for Electrocaloric Studies Bruno M. Magalhaes[1], Stefan Engelhardt[1], Sebastian Faehler[1], Christian Molin[2], Sylvia Gebhardt[2], Kornelius Nielsch[1, 3] and Ruben Huehne[1]; [1]IFW Dresden, Dresden, Germany; [2]Fraunhofer Institute for Ceramic Technologies and Systems, Dresden, Germany; [3]Technische Universität Dresden, Dresden, Germany.

Substantial efforts are being employed to the search and development of efficient and environmentally friendly materials with potential for solid state cooling. Motivated by recent discoveries, electrocaloric cooling might be a promising solution as an innovative refrigeration technique, as it shows a significant variation in temperature by adiabatically switching an applied electric field. Among them, lead-free thin films have raised an increased interest in research as they avoid the harmful effects of lead-containing materials. The purpose of our study is to investigate the electrocaloric effect in such lead-free epitaxial thin films. In particular, we are focusing on microstructural changes close to the phase transition of $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) in order to understand the basic mechanisms of the caloric effects, which might enable a further optimization of the electrocaloric properties for specific applications. Accordingly, the growth of NBT thin films with $BaTiO_3$ and $SrTiO_3$ additions is targeted to study the influence of the deposition parameters on the microstructural and the electrocaloric properties in this material system.

Therefore, NBT-based epitaxial thin films were grown by pulsed laser deposition on a variety of single crystalline substrates using $La_xSr_{1-x}CoO_3$ as a bottom electrode for a subsequent ferroelectric characterization. The structural characterization displays an epitaxial growth of NBT on the different substrates. Temperature and frequency dependence of the dielectric properties were assessed to measure the temperature of maximum permittivity T_m. Simultaneously, the electrocaloric temperature change was determined indirectly by the dependence of polarization on temperature and electric field strength. Finally, we will discuss the impact of the deposition parameters on the structural and functional properties of the grown films.

This work is supported by the DFG priority program 1599 “Ferroic cooling”

2:30 PM TP01.02.04
Large Electrocaloric Effects in PST Multilayer Capacitors Over a Wide Range of Useful Temperatures Bhasi Nair[3], Tomoyasu Usui[1], Sam Crossley[3, 2], Xavier Moya[3], Sakyo Hirose[1] and Neil D. Mathur[3]; [1]Murata Manufacturing Co., Ltd., Nagaokakyo-shi, Japan; [2]Applied Physics, Stanford University, Palo Alto, California, United States; [3]Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

Using both thermocouples and infrared imaging, we report large electrocaloric effects in $PbSc_{0.5}Ta_{0.5}O_3$ multilayer capacitors near room temperature. For field changes of 29.0 V μm^{-1}, we find changes of temperature that peak at 5.5 K, and exceed 3 K for starting temperatures that span 176 K. This directly measured performance in a macroscopic body improves upon the magnetocaloric response of gadolinium when driven by expensive permanent magnets, suggesting the possibility of a straight swap in prototype cooling devices.

2:45 PM TP01.02.05
A New Class of Electrocaloric Materials—Exhibiting Large Electrocaloric Response at Low Electric Field Xin Chen, Wenhan Xu, Biao Lu, Tian Zhang, Qing Wang and Qiming Zhang; The Pennsylvania State University, University Park, Pennsylvania, United States.

Electrocaloric effect (ECE) is the temperature and entropy change in a dielectric material as the applied field changes. ECE occurs due to electrical field induced dipole-entropy change in dielectrics, which is an extremely efficient form of energy conversion exhibiting minimum losses, e.g., polarization-electric field coupling approaching 100% efficiency. The past decade has witnessed the discovery and advancement in electrocaloric polymers, which display large electric field induced temperature and entropy changes.

In contrast with a burgeoning literature on large ECE in various ferroelectric materials, there are no EC devices employing these materials, demonstrating a meaningful cooling power. The critical barrier for the transition from high performance EC materials to practical EC devices is the dielectric breakdown. Hence, EC devices have to work under electric fields far below their dielectric breakdown. On the other hand, EC devices to achieve sufficient cooling power require large size EC films, which can further reduce their dielectric breakdown. To address these issues, high performance EC materials should possess a large EC response at fields far below dielectric breakdown. However, the EC response of the state-of-art EC polymer P(VDF-TrFE-CFE) at these practical field range is not high even though it possesses a large ECE at high electric fields (> 100 MV/m).

In this work, inspired by the materials concept of high entropy alloys, in which the presence of a large number of elements increases the entropy of the alloys, we developed a new class of EC polymer, tetrapolymer, which possesses a large dipolar entropy. Moreover, the tetrapolymer exhibits a critical end point behavior at low electric fields, thus leading to a giant EC response at low electric fields, which have the promise for high performance and highly reliable EC coolers.

3:00 PM BREAK

SESSION TP01.03: Mechanocaloric Materials and Systems I
Session Chairs: Jun Cui and Jaka Tusek
Monday Afternoon, November 26, 2018
Sheraton, 3rd Floor, Berkeley AB

3:30 PM *TP01.03.01
Energy-Efficient Elastocaloric Cooling Based on Magnetic Shape Memory Alloys Jian Liu; Ningbo Institute of Materials Technology and Engineering, Ningbo, China.

Elastocaloric cooling is currently under extensive study owing to its great potential to replace the conventional vapor-compression technique. In the first part, I will present a $Ni_{50.0}Fe_{19.0}Ga_{27.1}Co_{3.9}$ ferromagnetic shape memory single crystal, which exhibits giant elastocaloric effect of 11 K and ultralow fatigue behavior during above 12,000 mechanical cycles. The numerical simulation shows that this unique alloy offers 18% energy saving potential and 70% cooling capacity enhancement potential than the conventional shape memory nitinol alloy in a single-stage elastocaloric cooling system, making it as a great candidate for the energy-efficient air conditioner application. Second, I will introduce a $Ni_{50}Mn_{31.5}In_{16}Cu_{2.5}$metamagnetic shape memory alloy exhibiting giant adiabatic temperature changes of 13 K upon loading. Simultaneously, a small thermal hysteresis of 3 K and an exceptional phase transformation stability over 10^5 magnetic field cycles have been achieved by ensuring the compatible kinematic conditions of specific lattice interface. Moreover, we proposed an approach to reduce hysteretic losses and improve the reversibility of magnetocaloric effect by manipulating transformation paths evoked by magnetic field and stress, and therefore such a multicaloric approach is attractively beneficial for reaching high energetic utilization efficiency.

4:00 PM TP01.03.02
Stability of Additive Manufactured NiTi for Compressive Elastocaloric Properties Beyond One Million Cycles Huilong Hou[1], Emrah Simsek[2], Tao Ma[2], Suxin Qian[3], Drew Stasak[1], Naila Al Hasan[1], Lin Zhou[2], Yunho Hwang[1], Reinhard Radermacher[1], Matthew J. Kramer[2, 4], Ryan Ott[2], Jun Cui[2, 4] and Ichiro Takeuchi[1]; [1]University of Maryland, College Park, College Park, Maryland, United States; [2]Ames Laboratory, Ames, Iowa, United States; [3]Xi'an Jiaotong University, Xi'an, China; [4]Iowa State University of Science and Technology, Ames, Iowa, United States.

We report on properties of additive manufactured Ni–Ti alloys in the geometries of solid rods and hollow tubes. We have characterized their room-temperature superelastic and elastocaloric properties after one million cycles. Alloy compositions are flexibly and quickly adjusted by controlling the flow rate of elemental powders during synthesis. Unique microstructure in the material results from rapid solidification and thermomechanical processing with the phase transformation occurring near room temperature. A quasi-linear superelasticity and elastocaloric cooling temperature changes up to 4.1 K are observed in the additive-manufactured alloys under uniaxial compressions at room temperature. We perform extended cycling tests of the alloys while in-situ monitoring their stress-strain properties. Elastocaloric properties are monitored after every 200,000 cycles. After 1,000,000 cycles, the alloys exhibit elastocaloric Delta T with minimal change compared to start of the cycling test. Microstructural investigation sheds lights on the observed quasi-linear superelasticity and the stability of alloys after a large number of cycles.

4:15 PM TP01.03.03
Fatigue Influencing Factors in NiTi Based Shape Memory Alloys for Elastocaloric Cooling Lars Bumke[1], Hanlin Gu[2], Florian Bruederlin[3], Christoph Chluba[1], Manfred Kohl[3], Richard James[2] and Eckhard Quandt[1]; [1]Institute for Materials Science, Kiel University, Kiel, Germany; [2]Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, Minnesota, United States; [3]Institute of Microstructure Technology, Karlsruhe Institute of Technology, Karlsruhe, Germany.

Caloric cooling is an emerging technology with the potential to replace traditional technologies like environmentally harmful vapor compression systems, which already operate close to their theoretical efficiency limit or rather inefficient thermoelectric devices. Within the field of calorics, elastocaloric materials show high latent heats larger than 20 J g^{-1}. The elastocaloric effect in shape memory alloys (SMAs) is based on the reversible stress induced martensitic phase transformation. Binary NiTi is a benchmark material for elastocaloric materials, since it shows a high effect size > 15 K and is widely accessible. On the other hand NiTi shows a poor fatigue life resulting in an early breakdown of the device. It is assumed that the material has to withstand at least 10^7 cycles. Recently it was demonstrated that magnetron sputtered TiNiCu based SMAs show negligible fatigue for 10 million cycles, an effect size > 10 K and tuneable transformation temperatures below RT [1,2]. These materials possess a unique microstructure with coherent precipitates, acting as nucleation centres for the phase transformation and a grain size in the sub µm range. In addition they show a nearly perfect compatibility of the austenite and martensite phase, which can be expressed by the cofactor conditions [3]. If fulfilled an unstressed transition layer between the corresponding phases is created, leading to a phase transformation without slip, reduced hysteresis and an increased fatigue life. First demonstrators using a solid to solid heat transfer show a maximum temperature span of 14 K [4]. Within this talk several NiTi based shape memory alloys will be discussed in terms of microstructure, compatibility and fatigue life to determine critical parameters for the design of SMAs with a sufficient fatigue life.

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

References
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4:30 PM *TP01.03.04

An Elastocaloric Cooling System Based on Latent Heat Transfer Kilian Bartholome, Andreas Fitger, Andreas Mahlke, Markus Winkler and Olaf Schaefer-Welsen; Fraunhofer Institute for Physical Measurement Techniques IPM, Freiburg, Germany.

Elastocaloric materials have a great potential for application in energy-efficient cooling systems without harmful refrigerants. Over a very broad temperature range they show excellent elastocaloric properties like very large adiabatic temperature change and isothermal entropy change. Based on these materials, several demonstrators of cooling systems have been developed and characterized by various groups.
In general, for an energy- and cost-efficient system, the heat transfer between elastocaloric material and heat sink and source is essential. While most published system use either thermal conduction or forced convection, here an elastocaloric system using latent heat transfer in combination with thermal diodes is presented. Similar to gravity-assisted heatpipes, thermal energy is efficiently transported by condensation and evaporation processes leading to heat transfer rates which are several orders of magnitude larger than in conventional systems. Furthermore, no additional pumps are required for transporting the heat exchange fluids, enabling systems with large temperature spans and competitive COPs at the same time.
In this work, an experimental setup based on this system approach is shown, using an extender wheel for providing compressive force on Nitinol tubes and showing the proof of concept of heat transfer in combination with elastocaloric materials.

SESSION TP01.04: Poster Session: Caloric Materials for Highly Efficient Cooling Applications
Session Chairs: Sakyo Hirose, Lluis Manosa, Vitalij Pecharsky and Anja Waske
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

TP01.04.01

Mechanochemical Synthesis and Magnetocaloric Properties of Nanostructured Equi-Atomic FeRh with the Ordered *B2* Structure Shalabh Gupta[1], Yaroslav Mudryk[1], Biswas Anis[1], Jacob Rabe[1] and Vitalij Pecharsky[1, 2]; [1]Ames Laboratory, Ames, Iowa, United States; [2]Material Science and Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States.

The equiaxed, sub-micron sized particles of $Fe_{50}Rh_{50}$ were synthesized by solvent-free mechanochemical co-reduction (MCR) of iron chloride ($FeCl_2$) and rhodium chloride ($RhCl_3$) followed by annealing between 600–1000 °C under argon. Typically, nearly equiatomic,ordered FeRh alloys exhibiting first-order transition are synthesized from the elements by arc-melting and annealing. The resulting large grains are difficult to scale-down because of the high ductility of the alloy. The bottom-up syntheses, such as MCR, inherently produce materials with grain-size in sub-micron to nano regime, allowing greater flexibility in tailoring the properties. In a typical MCR synthesis, the chloride (or fluoride) metal precursors are mixed in a 1:1 molar ratio in an agate mortar followed by high-energy milling along with a stoichiometric amount of Li-metal under argon. After about 2 h of milling, the reaction product contains no trace of halide salts. Prior to annealing, the LiCl (LiF) by-product is washed out with water-ethanol mixture. The cleaned sample is then heated under Ar at 600°C for 24 h and quenched in ice-cold water at which point the ordered *B2* structure is obtained in high-purity. The temperature dependence of magnetization, M(T), was measured in field cooled protocol between 5 K and 400 K at different magnetic fields, and the magnetic entropy change, DS_M, was calculated from the M(T) curves using Maxwell's equation. In contrast to regular magnetocaloric effect (MCE), in case of inverse MCE (I-MCE), magnetic field induced enhancement in magnetic configuration entropy is observed. The as-synthesized particles of $Fe_{50}Rh_{50}$ alloy exhibit maximum I-MCE around ~340 K, which is attributed to a first-order antiferromagnetic to ferromagnetic transition. The maximum value of DS_M near the transition is ~9 J $Kg^{-1}K^{-1}$ at 2 T, which is about 25 % smaller than that of bulk $Fe_{50}Rh_{50}$ but is larger than that of Gd, the benchmark material for the room-temperature magnetocaloric applications. In a fine particle system, grain boundaries play a vital role in determining magnetic and magnetocaloric properties. Grain boundaries are sources of crystalline disorder, which can affect the magnetic correlations. In some cases, disorder effects can suppress the first order transition. It is noteworthy that fine particles of $Fe_{50}Rh_{50}$ (average size <1 μm) retain a first order transition with large DS_M despite the large concentration of disordered grain boundaries.

This work is performed under auspices of the caloric materials consortium, CaloriCool®, which is a member of the Energy Materials Network and is supported by the Advanced Manufacturing Office of the Office of Energy Efficiency & Renewable Energy and managed jointly through the Advanced Manufacturing and Building Technologies Offices of the U.S. Department of Energy. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University of Science and Technology under Contract No. DE-AC02-07CH11358.

TP01.04.02

X-Ray Magnetic Circular Dichroism Study on Ni Based Thermoseeds for Self-Controlled Hyperthermia Applications Sudip Pandey[1], Alpha T. N'Diaye[2], Igor Dubenko[1], Anil Aryal[1], Sujoy Roy[2], Dipanjan Mazumdar[1], Shane Stadler[3] and Naushad Ali[1]; [1]Department of Physics, Southern Illinois University Carbondale, Carbondale, Illinois, United States; [2]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; [3]Department of Physics & Astronomy, Louisiana State University, Baton Rouge, Louisiana, United States.

Ni-Cu alloys are potential magnetocaloric thermoseed materials for application in self-controlled magnetic hyperthermia methods. The magnetic ordering temperatures and magnetic properties of Ni-Cu alloys can be tailored to fit within a range suitable for hyperthermia applications. To understand the details of the electronic and magnetic structures of these alloys, X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements were done at the $L_{2,3}$ absorption edges of Ni in ferromagnetic Ni-Cu. In this case, the XMCD technique has provided valuable information on how doping affects the relative magnetic moment on the Ni site. XMCD measurements employing the total electron yield method (i.e., surface sensitive to the depth of few nm) show that the collective of surface Ni atoms has a lower Curie temperature than that of the bulk. The influences of small compositional changes through the substitution of Cu for Ni on the electronic and crystal structures and thermomagnetic properties was studied to determine the optimized composition suitable for functional magnetic hyperthermia applications.

SESSION TP01.05: Magnetocaloric Materials and Systems II
Session Chairs: Franca Albertini and Julia Lyubina
Tuesday Morning, November 27, 2018
Sheraton, 3rd Floor, Berkeley AB

8:30 AM *TP01.05.01

Topology of Thermomagnetic Generators for the Conversion of Low Temperature Waste Heat to Electricity Anja Waske[1, 2], Daniel Dzekan[1], Kai Sellschopp[1], Alexander Stork[1], Kornelius Nielsch[1] and Sebastian Faehler[1]; [1]IFW Dresden, Dresden, Germany; [2]Bundesanstalt für Materialforschung und –prüfung (BAM), Berlin, Germany.

To date, there are only very few technologies available for the conversion of low temperature waste heat to electricity. More than a century ago, thermomagnetic generators were proposed, which are based on a change of magnetization with temperature, switching a magnetic flux, which according to Faraday's law induces a voltage. Here, we demonstrate that a pretzel-like topology of the magnetic circuit 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, based on magnetocaloric La-Fe-Co-Si plates, illustrates that this solid state energy conversion technology is on its way to become competitive with thermoelectrics for energy harvesting near room temperature.

In this talk we describe the impact of topology on thermomagnetic generators. We demonstrate that the key operational parameters strongly dependent on the genus, i.e. the number of holes within the magnetic circuit. All parameters, i.e. induced voltage, electrical output power, optimum frequency, and the ratio between experiment and maximum boundaries predicted by theory, improve by orders of magnitude when using a topology with genus = 3Though this pretzel-like topology represents a breakthrough for TMGs, further improvements are required to become competitive with thermoelectric generators. A further increase of genus might be one way, but the analysis of our TMG identifies two straightforward approaches for a further increase of output power. First, the remaining stray fields must be avoided and second, the cycle frequency must be increased by using thinner thermomagnetic plates. As both approaches benefit from a miniaturization, we predict that micro-TMGs will be most promising. As our TMG reaches most of the output power already at a very low temperature above ambient, micro-TMGs will be of particular interest for harvesting the temperature difference between human body and ambient for powering the increasing number of portable electronics devices, like smart watches, fitness bands, and health sensors.

9:00 AM TP01.05.02

Effect of Al and Fe Solubility on Magentostructural Properties of $AlFe_2B_2$ Brian Lejeune[1], Deborah Schlagel[2], Brandt Jensen[2], Thomas Lograsso[2], Matthew J. Kramer[2] and Laura Lewis[1]; [1]Northeastern University, Boston, Massachusetts, United States; [2]Materials Science and Engineering, The Ames Laboratory, Ames, Iowa, United States.

One of the main design criteria for caloric materials is the ferroic phase transition temperature. Here we present data connecting phase transition temperature, magnetism, and antisite lattice occupancy in the magnetostructural $AlFe_2B_2$ system. This orthorhombic system is comprised of abundant elements, possesses a near-room-temperature magnetostructural phase transition temperature T_t and exhibits good magnetic cooling potential ($\Delta S \sim 4.4$ J/kg-K @ $\mu_0 H_{app} = 2$ T) [1,2]. Preliminary results suggest that the magnetic phase transition temperature is highly sensitive to Fe and Al solubility within the $AlFe_2B_2$ phase, allowing for tuning of the transition temperature through control of processing conditions.

A drop-cast ingot of composition $Al_2Fe_2B_2$ was used as the initial charge for Bridgman single crystal growth of the $AlFe_2B_2$ phase, allowing for Al-Fe composition regulation down the pathway of solidification. The influence of Al and Fe antisite defects within the $AlFe_2B_2$ crystal structure was assessed with X-ray diffraction, temperature-dependent magnetometry and compositional assessment from energy dispersive spectroscopy. Clear trends in T_t, lattice constants *a, b, c,* and unit cell volume V were confirmed as a function of the Fe:Al at% ratios (1.94-2.06). In particular an Fe-rich $AlFe_2B_2$ phase due to Fe residing on the Al site results in an enhanced T_t relative to the stoichiometric composition. These findings quantify the sensitivity of the magnetic transition temperature in $AlFe_2B_2$ to antisite defects, where a 2 at% difference in Fe and Al content leads to a large change in T_t spanning 280-315 K. The interplay between Al and Fe site occupancy and the resultant structural and magnetic responses provides flexibility to tailor the magnetic phase transition temperature of the $AlFe_2B_2$ system.

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9:15 AM TP01.05.03

Magnetocaloric Properties of the Magnetically Frustrated Mineral, Gaudefroyite Colin Greaves[1], Rukang Li[2] and Guangjing Li[1]; [1]University of Birmingham, Birmingham, United Kingdom; [2]Beijing Center for Crystal Research & Development, Beijing, China.

New materials for refrigeration devices are needed for efficient, clean operation at a variety of temperatures. In adiabatic magnetic refrigeration using the magnetocaloric (MC) effect, cooling is related to the entropy change that occurs when a magnetic field is removed from a magnetic material. Efficient MC refrigeration requires stable materials that give a large change in magnetic entropy and has traditionally been achieved using expensive rare earth cations with large moments. In this presentation we will describe how mineral structures can point the way to new types of magnetic materials with excellent MC properties in the absence of rare earth cations.

The mineral schafarzikite, $FeSb_2O_4$, has a tetragonal structure comprising chains of edge-linked FeO_6 octahedra running along [001]. Following our studies of how the magnetic order of this structural family can be controlled, we then sought new materials with similar chains of linked octahedra, but frustrated interchain interactions, since enhanced MC behaviour has been predicted for frustrated magnetic materials.[1] The mineral gaudefroyite, $Ca_4Mn_3O_3(BO_3)_3CO_3$, was particularly attractive because its chains of edge-linked $Mn^{3+}O_6$ octahedra are located on a Kagome lattice perpendicular to the chains, and introduce inherent magnetic frustration between the chains.

The low temperature magnetic properties of gaudefroyite were therefore investigated: extremely high MC effects were observed at temperatures suitable for liquefying hydrogen,[2] *ca.* 20 K. The properties, which will be summarized, are better than those of existing optimized oxide materials at this temperature, but *no rare earth element is present*; the temperature changes are also exceptionally rapid because of the magnetic frustration. We now have low temperature neutron powder diffraction data collected in fields of 0-3 T within the temperature rang 0.1-15 K, and the presentation will focus on these results. We will report an ordered antiferromagnetic structure (q=0, 120° alignment) below 11 K, which transforms to a ferromagnetic ground state in fields greater than 1.5 T; ferromagnetism was also found at these fields for temperatures above 15 K. The results will be discussed in relation to the observed MC properties. The concept demonstrated could be of value for sustainable materials for liquefying hydrogen for transport/storage in a future hydrogen energy economy and could possibly be extended to materials operating at other temperatures.

M. E. Zhitomirsky, *Phys. Rev. B: Condens. Matter Mater. Phys*, **67**, 104421 (2003).
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9:30 AM TP01.05.04

XAS and XMCD Studies of Ni-Mn-In-B Thin Films Sudip Pandey[1], Alpha T. N'Diaye[2], Anil Aryal[1], Igor Dubenko[1], Sujoy Roy[2], Shane Stadler[3] and Naushad Ali[1]; [1]Department of Physics, Southern Illinois University Carbondale, Carbondale, Illinois, United States; [2]Advanced Light Source, Lawrence

Berkeley National Laboratory, Berkeley, California, United States; [3]Department of Physics & Astronomy, Louisiana State University, Baton Rouge, Louisiana, United States.

Ni-Mn-In-B thin films were synthesized on Si substrate using ultra high vacuum magnetron sputtering. Metamagnetic transition with thermal hysteresis has been observed on 30 nm $Ni_{50}Mn_{35}In_{14.25}B_{0.75}$ thin film from the magnetization measurements. The temperature dependences of magnetization curves are found to be similar with those of bulk counterpart with the shift in transition temperatures. Electronic and magnetic properties of $Ni_{50}Mn_{35}In_{14.25}B_{0.75}$ thin film were studied using X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements at Ni L_{23}, and Mn L_{23} edges. From the XMCD spectra, we have observed that Ni play dominant role in the overall magnetism. XMCD hysteresis loops of Ni have been compared at different temperature and observed that the hysteresis becomes minimum at martensitic transition temperature. Possible mechanisms responsible for the changes in electronic and magnetic properties on thin films by the effect of redistribution of d electrons are discussed.

9:45 AM BREAK

10:15 AM TP01.05.05
Experimental Evaluation and Optimization of a Novel Thermomagnetic Generator Daniel Dzekan[1, 2], Anja Waske[1, 2, 3], Kai Sellschopp[1, 2], Dietmar Berger[1], Kornelius Nielsch[1, 2] and Sebastian Faehler[1]; [1]IfW Dresden, Dresden, Germany; [2]Institut of Materials Science, TU Dresden, Dresden, Germany; [3]Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany.

The thermomagnetic generator (TMG) is a promising device to convert low temperature heat to electricity by using the change in magnetization with temperature of a ferromagnetic material placed in a magnetic circuit. Thus the magnetic flux, provided by permanent magnets, also changes and induces a voltage in a pick-up coil according to Faraday's law of induction. This principle of energy harvesting is known for more than a century but no prototypes and only few proof of concepts have been realized. However theoretical consideration predicted the efficiency of such a device approach the thermodynamic limit. Here we present a TMG with a new topology of the magnetic circuit. This topology allows the magnetic flux to change its direction, resulting in a doubled magnetic flux amplitude. Thus the electrical power of the generator is increased by a factor of four. The topology of the magnetic circuit within the generator is optimized with FEM simulations. An additional advance of the realized topology is avoiding hysteresis as well as magnetic stray fields, which results in further improvement in electrical power output. A La-Fe-Co-Si alloy, developed for magnetocaloric refrigeration, is used as thermomagnetic material, since it exhibits a large and sharp change of magnetization in a small temperature range. Thereby low temperature heat can be used to realize a large change in the magnetization of the material. The first step of the experimental characterization of the generator consists in the measurement of the induced voltage with time. From these the magnetic flux within the magnetic circuit is calculated by numeric integration. Furthermore the electrical power output of the generator under load conditions is determined. The volume flow and temperature of the heat exchange fluid, which thermally switches the thermomagnetic material, are experimental parameters as well. With these measurements and with the electrical power output, the efficiency of the energy conversion is determined. In the experiments the parameters are adjusted for an optimum in electrical power output and efficiency. These values of this TMG are significant higher in comparison to previously published proof of concepts. The experimental evaluation of this prototype allows to suggest further improvements of TMGs and paves the way for these devises to become competitive with thermoelectric generators for low temperature waste heat recovery.

10:30 AM OPEN DISCUSSION

SESSION TP01.06: Electrocaloric Materials and Systems II
Session Chairs: Anna Grünebohm and David Schwartz
Tuesday Morning, November 27, 2018
Sheraton, 3rd Floor, Berkeley AB

10:45 AM *TP01.06.01
Phase Transitions in Elastic Media and the Enhancement of Caloric Effects Peter B Littlewood[1], Gian Guzman-Verri[2] and Xavier Moya[3]; [1]James Franck Institute, University of Chicago, Chicago, Illinois, United States; [2]Materials Research Science and Engineering Center (CICIMA), University of Costa Rica, San José, Costa Rica; [3]University of Cambridge, Cambridge, United Kingdom.

The metal-insulator transition driven by strong electronic correlations – generically called the "Mott" transition – is usually described entirely by electronic Hamiltonians, with models designed to exhibit related emergent phenomena such as magnetism and superconductivity. In real solids, the electronic localization also couples to the crystal lattice, and it turns out that these elastic degrees of freedom insert important new entropic phenomena more familiar in soft matter physics.
The coupling to the lattice induces elastic strain fields, which have intrinsic long-range interactions that cannot be screened. When strain fields are produced as a secondary order parameter in phase transitions - as for example in ferroelectrics - this produces unexpected consequences for the dynamics of order parameter fluctuations, including the generation of a gap in what would otherwise have been expected to be Goldstone modes.
A very important class of transition metal oxides – the perovskites – can be thought of as an array of tethered octahedra where the Mott transition produces a shape-change in the unit cell. Coupling of the fundamental order parameter to octahedral rotations gives rise to large entropic effects that can shift the transition temperature by hundreds of degrees K[1], essentially by exploiting the physics of jammed solids. The insight might offer ways to make better refrigerators by enhancing electro-caloric and magneto-electric effects.[2]

[1] Elastic interactions and control of the Mott transition, G. G. Guzmán-Verri, R. T. Brierley, P. B. Littlewood arXiv:1701.02318

[2] Why is the electrocaloric effect so small in ferroelectrics? G. G. Guzmán-Verri, P. B. Littlewood, APL Mater. 4, 064106 (2016)

11:15 AM TP01.06.02
A Regenerative Electrocaloric Cooling Device—Numerical Modelling and Experimental Validation Uros Plaznik[1], Marko Vrabelj[2], Zdravko Kutnjak[2], Barbara Malic[2], Brigita Rozic[2], Jaka Tusek[1], Alojz Poredos[1] and Andrej Kitanovski[1]; [1]Faculty of Mechanical Engineering, University of Ljubljana, Ljubljana, Slovenia; [2]Jozef Stefan Institute, Ljubljana, Slovenia.

A research and development on a cooling device based on an active electrocaloric regenerator (AER) made of bulk ceramic material (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3–x$PbTiO_3$ (PMN-100xPT) will be presented. For that purpose, a new, 2D transient numerical model of the AER based on the energy equation for the solid electrocaloric material and the heat transfer fluid was developed and implemented in Matlab software. The model allows to investigate the cooling characteristics (temperature span, cooling power and efficiency) of an AER at different operating conditions (mass-flow rate, operating frequency, applied electric field change, etc). In addition, the model includes the impacts of the electrocaloric material's hysteresis and the electric-energy recovery released during the depolarization (discharging) of the electrocaloric material on the AER performance. The results of the numerical analyses show that the degree of electric energy recovery has a crucial impact on the efficiency of the electrocaloric device. By considering an idealised electric-energy recovery system, the energy efficiency (expressed by the coefficient of performance - COP) of the device could be increased by up to ten times compared to the case of without the energy recovery. A validation of the numerical model was performed through the design, construction and experiments on a new AER cooling device (without electric-energy recovery system). The experimental results revealed a maximum specific cooling power of 16 W kg^{-1} and a maximum temperature span of 3.1 K. A comparison between the numerical and experimental results shows that model can correctly predicts the trends of cooling characteristics with respect to various operating parameters. On the other hand, there is some deviation between the absolute values of the cooling characteristics calculated with the numerical model and the experimental results. These deviations are mainly due to some effects not included in the numerical model, for example flow maldistribution.

11:30 AM *TP01.06.03
Materials Considerations for Electrocaloric-Based Regenerative Cooling S. Eastman, W. Xie, A. Sur, A. Annapragada, P. Verma and Joseph V. Mantese; United Technologies Research Ctr, East Hartford, Connecticut, United States.

It has been more than two decades since electrocaloric-based temperature lifts on the order of 20°C were first reported in the ceramic materials and more than a decade since equivalent lifts were observed in polymeric thin films. Yet, since that time, the demonstration of even a single high performance electrocaloric-based cooling module has not been realized. Indeed, only modest performance (<5°C total lift) has been achieved when such modules have been challenged against a temperature incline. Coefficients of performance (COP) have been either unreported or inconsequential. Conversely, theoretical models predict the potential for regenerative cooling with lifts in excess of 10°C at COPs of ~6. In this talk we examine the cause of the shortfall in module performance from a material perspective. We discuss: (1) The impact of performance parasitics. (2) Active area loss due to dielectric breakdown and local arcing. (3) Degraded performance due to stress concentration, clamping from the electrode metallization and cyclic fatigue. Solutions to film and electrode failures can potentially be found by using material engineering to improve electrical, mechanical, and thermal-caloric properties.

SESSION TP01.07: Mechanocaloric Materials and Systems II
Session Chairs: Kilian Bartholome and Jian Liu
Tuesday Afternoon, November 27, 2018
Sheraton, 3rd Floor, Berkeley AB

1:30 PM *TP01.07.01
Active Elastocaloric Regenerators—Tension vs Compression Loading Jaka Tusek; Faculty of Mechanical Engineering, University of Ljubljana, Ljubljana, Slovenia.

The elastocaloric effect (eCE) associated with a stress-induced martensitic transformation in shape memory alloys (SMA) has recently shown a promising route for high-efficiency, solid-stated cooling and heat-pumping applications. It was already demonstrated that the most effective way of utilizing the caloric effects (magnetocaloric, electrocaloric, elastocaloric) in a practical cooling device is so-called active caloric regenerator, which is a porous structure made of caloric material. It has a double function in a caloric cooling device; it works as a refrigerant as it contains active caloric material as well as a regenerator and enables an enhancement of the temperature span between heat sink and heat source.
In this talk different possibilities of active elastocaloric regenerator geometries to be loaded in tension and compression will be review and discussed. Both tension and compression loading has some important pros and cons for elastocaloric cooling. The main advantage of tension loading is the ability to apply thin elements and small channels for the fluid-flow that allows for fast and efficient heat transfer, while its main disadvantage is reduced fatigue life when compared to compression loading. However, thin elements which would enhance heat transfer characteristics are difficult to compress without buckling. It is therefore a big challenge to design an active elastocaloric regenerator that is geometrically stable during compression loading, while maintaining high eCE and highly efficient heat transfer.
The fatigue strain limits and the associated eCE for durable operation (>10^5 cycles) of Ni-Ti plates to be applied in efficient active elastocaloric regenerator loaded in tension will be presented. In addition, different potential geometries of an active elastocaloric regenerator to be loaded in compression, such as block with holes, set of tubes in a holder, shell-and-tube-like regenerator, etc., will be discussed together with the main challenges associated with those geometries.

2:00 PM TP01.07.02
Comparison of Electrocaloric Materials on Basis of Material Related Cooling Power Florian Weyland[1] and Nikola Novak[2]; [1]TU Darmstadt, Darmstadt, Germany; [2]Institute Jozef Stefan, Ljubljana, Slovenia.

The centerpiece of solid state coolers using caloric effects, i.e. electrocaloric, magnetocaloric or mechanocaloric, is the caloric material. In the search of a refrigerant for electrocaloric cooling devices a large number of ferroelectric materials, with their respective adiabatic temperature change, have been identified. To find the most suitable material not solely the electrocaloric but also the thermophysical properties need to be accounted for. To compare materials with each other a useful figure of merit is the material related cooling power, as it considers the material properties, i.e. electrocaloric effect and thermophysical behavior, without including device specifications. The performance characteristics of ferroelectric materials are determined to a large degree by the nature of the paraelectric to ferroelectric phase change. Here, the electrocaloric and thermophysical properties of $BaTiO_3$ (BT) and 0.72$PbMg_{1/3}Nb_{2/3}O_3$-0.28$PbTiO_3$ (PMN-28PT) single crystals and polycrystalline Ba(Zr_xTi_{1-x})O_3 (BZ_xT) ceramics are compared. BT and PMN-28PT are typical representatives of first order and relaxor-like ferroelectrics, respectively. Furthermore, they both show a dielectric permittivity peak around ~400 K. The BZ_xT ceramics are BT derived compositions with Zr-ions substituted on the Ti-ion site. By the amount of Zr-ion substitution the phase change characteristic and transition temperature is modified. The dependence of the material related cooling power of those materials on the dimensionless temperature, characteristic distance and holding time for heat transfer is determined on the basis of directly measured electrocaloric temperature changes, thermophysical properties and a simple model based on Newtonian cooling of a thin plate. It is demonstrated that a maximum cooling power can be obtained for a dimensionless temperature of 0.28, and that an optimum thickness of the electrocaloric plate exists, related to the dimensionless temperature.

It is shown, that a decrease in the holding time for heat transfer increases the cooling power. It is found that the higher thermal conductivity of BT contributes significantly to its large cooling power. At temperatures near the Curie point the electrocaloric temperature change of BT is large and hence, the cooling power is large. In contrast, the relaxor-like PMN-28PT exhibits a much broader range of peak cooling power, which can be useful for widening the temperature range of operation. The $BZ_{20}T$ displays a broad peak of maximum cooling power near room-temperature. Although device-level factors, such as thermal resistances at electrode interfaces are ignored, the results suggest a simple basis of comparison for ferroelectric materials. In addition, the derived equation for the material related cooling power is used to compare the different caloric effects with each other.

2:15 PM *TP01.07.04

Copper Based Elastocaloric Materials Jun Cui[2, 1], Gaoyuan Ouyang[1], Emry Farmer[1], Xubo Liu[2], Ichiro Takeuchi[3] and Vitalij Pecharsky[2, 1]; [1]Materials Science and Engineering, Iowa State University, Ames, Iowa, United States; [2]Materials Science and Engineering, Ames Laboratory, Ames, Iowa, United States; [3]Materials Science and Engineering, University of Maryland, College Park, Maryland, United States.

Elastocaloric cooling has high Coefficient of Performance and minimum environmental impact. In 2014, U.S. Department of Energy ranked it as the most promising new HVAC technology to replace vapor compression. While many alloys exhibit elastocaloric effect, few can simultaneously meet the criteria on delta T, biasing stress, and cost. To date, NiTi remains as the best material for elastocaloric cooling application. While NiTi alloy has high latent heat and long fatigue life under compression, it requires large stress (>600 MPa) and it is prohibitively expensive, which makes it difficult for wide spread industrial and consumer applications. This talk reviews the concept of elastocaloric cooling, the challenges and the progress of developing copper based elastocaloric materials using combinatorial materials development approach.

2:45 PM BREAK

SESSION TP01.08: Magnetocaloric Materials and Systems III
Session Chairs: Sebastian Fahler and Julie Slaughter
Tuesday Afternoon, November 27, 2018
Sheraton, 3rd Floor, Berkeley AB

3:30 PM TP01.08.01

Synchrotron and Neutron Diffraction Studies of Boron Doped Ni-Mn-In Heusler Alloys Sudip Pandey[1], Tej Lamichhane[2], Amal Al-Wahish[3], Alpha T. N'Diaye[4], Anil Aryal[1], Pinaki Das[2], Igor Dubenko[1], Sujoy Roy[4], Dipanjan Mazumdar[1], Helmut Kaiser[3], Shane Stadler[5] and Naushad Ali[1]; [1]Department of Physics, Southern Illinois University, Carbondale, Illinois, United States; [2]Department of Physics & Astronomy, Iowa State University, Ames, Iowa, United States; [3]University of Missouri Research Reactor, University of Missouri-Columbia, Columbia, Missouri, United States; [4]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; [5]Department of Physics & Astronomy, Louisiana State University, Baton Rouge, Louisiana, United States.

Powder neutron diffraction experiments on $Ni_{50}Mn_{35}In_{14.25}B_{0.75}$ were carried out at a temperature between 7 and 375 K in 25 K increments to observe the evolution of the magnetic and crystal structures. The full proof analysis of neutron diffraction data reveals a clear structural transition from high temperature cubic to a monoclinic phase with significant temperature hysteresis. Traces of the low temperature phase were detected up to 380 K. Changes in the electronic structure of the elements of $Ni_{50}Mn_{35}In_{14.25}B_{0.75}$ alloys at the phase transition were determined from X-ray absorption spectroscopy (XAS) measurements from 80 to 380 K and compared with the parent compound. The change in the intensities with temperature in the XAS spectra show that the magnetostructural transition as well as boron doping results in the redistribution of d electrons. The data indicate boron doping in $Ni_{50}Mn_{35}In_{15}$ results in an enhancement of the Ni covalency and stronger Ni-In chemical bonds.

3:45 PM TP01.08.02

Low Temperature Magnetocaloric Materials for Cryogenic Gas Liquefaction by Magnetic Cooling Technique Sergey V. Taskaev[1, 2], Konstantin Skokov[3] and Vladimir Khovaylo[4]; [1]Chelyabinsk State University, Chelyabinsk, Russian Federation; [2]Functional Materials Lab., NRU SUSU, Chelyabinsk, Russian Federation; [3]FG Funktionale Materialien, TU Darmstadt, Darmstadt, Germany; [4]NITU MISIS, Moscow, Russian Federation.

Natural gases are one of the main sources of energy nowadays and will be of increasing importance in the near future. Currently, there is an upward trend of the production and consumption of this type of energy including methane, hydrogen, oxygen etc. For its storage, liquefaction is needed, which requires complex energy-intensive compressor devices operating at cryogenic temperatures. The efficiency of traditional liquefaction methods is quite low at temperatures below 150 K. We propose here a fundamentally different approach to liquefy gases - the emerging magnetic cooling technology. With the recent progress in superconducting magnets with static magnetic fields of up to 15 – 22 T, cooling at cryogenic temperatures can enable a revolution in the technology of gas liquefaction. A review on recent scientific publications reveals the large variety of different magnetic materials showing a significant magnetocaloric effect in the relevant temperature region of 15 to 150 K [1]. Thus, the efficient liquefaction of almost any natural gas in the same type of magnetic cooling machine would be possible [2-5].
In this work we report on the results of investigation of low temperature magnetocaloric materials based on $ReTm_2$ compounds (Re- rare earth's, Tm – transition metals) for magnetic refrigeration in cryogenic application. Special accent made for investigation an influence of severe plastic deformation on magnetocaloric properties of such alloys.

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4:00 PM *TP01.08.03

Getting the Most Out of Your Magnetocaloric Heat Pump Christian Bahl, Stefano Dall'Olio, Dan Eriksen, Corrado Cibin and Kurt Engelbrecht; DTU

Energy, Technical University of Denmark, Roskilde, Denmark.

A magnetocaloric heat pump, dimensioned to the requirements of a domestic house in Northern Europe, has been designed, constructed and tested. The design has been optimised towards a heating power of 1500 W and a temperature span of about 20 K.
The regenerator beds are packed with 10 layers of spherical $La(Fe,Mn,Si)_{13}H_z$ particles. The use of such magnetocaloric materials with a first order magnetic phase transition imposes constraints on how the temperature span of a magnetocaloric device may be controlled, which again imposes constraints on the type of heating system the heat pump can be connected to. Different ways of dealing with this issue will be presented and discussed.
Part load conditions where less than the maximum heating power is required can be achieved by varying the flow rate or the frequency. However, by combining the control of the two parameters it is demonstrated how it is possible to increase the coefficient of performance (COP) for part load conditions. Finally, the experimental and modelling performance of the heat pump will be considered in the context of connection to a ground source and an underfloor heating system, for the heating of a model house.

4:30 PM TP01.08.04
Stability of Magnetocaloric $La(Fe_xCo_ySi_{1-x-y})_{13}$ in Water and Air Khushar Javed[1], Ravi L. Hadimani[1], Brent Williams[1], Shane Harstad[1], Vitalij Pecharsky[2, 3] and Shalabh Gupta[2, 3]; [1]Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia, United States; [2]Division of Materials Science and Engineering, Ames Laboratory, US Dept. of Energy, Ames, Iowa, United States; [3]Department of Materials Science and Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States.

Lanthanum Iron Silicide with Cobalt substitution, $La(Fe_xCo_ySi_{1-x-y})_{13}$ is a room temp magnetocaloric material and these particles exhibit different magnetic properties when stored in air and compared to the same stored in water. The sample with a nominal composition of $La(Fe_{0.842}Co_{0.073}Si_{0.084})_{13}$ was prepared by arc-melting and these Ingot pieces were annealed at 1050°C for 7 days followed by quenching in ice-cold water. The annealed pieces were crushed to particle size of 100μ and then ball-milled using a SPEX8000 mill for 10 min. PANalytical X'Pert Pro diffractometer shows that powder stored in water for 14 days appear to be missing some of the Bragg peaks and develop low-Bragg angle halos typical of non-crystalline components. It concludes that both types of powders; milled and course crushed samples react with water.
The course crushed powder stored in air and water show sharp transition at the Curie temp Tc = 300K without large magnetization above the Tc. The milled fine-particulate sample stored in air shows significantly broadened transition at Tc, and that stored in deionized water for 14 days shows no obvious magnetic transition; both show large magnetizations above 300K. This is indicative of relatively fast hydrolysis and removal of some or all La, likely as hydroxide, from fine powders, leaving behind La-poor or, potentially, La-free Fe-Co-Si containing ferromagnetic residue with much higher Curie temp. The milled sample stored in water also shows the highest saturation magnetization followed by both sample stored in air.
The course crushed sample stored in water shows the maximum MCE of $\Delta S = 11\ J\ Kg^{-1}K^{-1}$ near 300K with the change of 3T magnetic field and highest relative permeability while the milled sample stored in water has the lowest entropy change. The milling process has induced broadening of the transition. Course crushed sample stored in water and in air have similar magnetocaloric effect.
It can be concluded that the course crushed samples contain larger particles and smaller surface area as compared to milled samples which have less than micron size particles. Water added to the milled sample leads to hydrolysis and removal of some of the La as hydroxide from fine powders, leaving behind La-poor Fe-Co-Si containing ferromagnetic residue of possibly Fe_3O_4 or $CoFe_2O_4$ with much higher Curie temp as follows from the absence of the obvious magnetic transition(s) and large magnetization beyond 300K. The course crushed samples show much greater stability and sharper magnetic transition when stored both in air and water. The course crushed sample stored in water has sharper magnetic transition and higher magnetization hence it shows the highest entropy change among all 4 types of samples.

Acknowledgement
Synthesis of material was supported by the Division of Materials Sciences at Ames Laboratory that is operated for the U.S. Department of Energy(DOE) by Iowa State University of Science and Technology under contract No. DE-AC02-07CH11358.

4:45 PM TP01.08.05
Electron-Phonon vs. Moment-Volume Coupling in Hydrogenated and Mn-Doped $LaFe_{13-x}Si_x$ Compounds Markus E. Gruner[1], Alexandra Terwey[1], Joachim Landers[1], Soma Salamon[1], Werner Keune[1], Katharina Ollefs[1], Iliya Radulov[2], Valentin Brabänder[2], Jiyong Zhao[3], Michael Y. Hu[3], Thomas S. Toellner[3], Esen E. Alp[3], Oliver Gutfleisch[2] and Heiko Wende[1]; [1]Faculty of Physics and Center for Nanointegration, CENIDE, University of Duisburg-Essen, Duisburg, Germany; [2]Materials Science, Technical University Darmstadt, Darmstadt, Germany; [3]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois, United States.

Fully hydrogenated $LaFe_{13-x}Si_x$ is one of the most interesting candidates for room temperature magnetic refrigeration. The first order nature of the magnetic transition is connected to its itinerant electron metamagnetism, which gives rise to a peculiar coupling between all microscopic degrees of freedom. By combining first principles calculations in the framework of density functional theory (DFT) and nuclear resonant inelastic X-ray scattering (NRIXS) we investigate the interplay of electronic structure, magnetism and vibrational degrees of freedom in fully hydrogenated $LaFe_{13-x}Si_x$. In the past, we could show that for the non-hydrogenated ternary compound, the itinerant nature of the Fe moments, which is responsible for the large volume change, gives also rise to the adiabatic electron-phonon coupling [1,2]. This leads to a cooperative contribution of magnetic, electronic and vibrational degrees of freedom to the entropy change, which results in the excellent caloric properties [1,3]. By hydrogenation it is possible to shift the operating range to ambient conditions, which is required for mass market application. A common strategy is to fully load the material with hydrogen and fine-tune the transition temperature by adding other components, such as Mn.
In this contribution, we demonstrate that the same mechanism acting in $LaFe_{13-x}Si_x$ is also responsible for the superior magnetocaloric properties of the hydrogenated compound $LaFe_{13-x}Si_xH_y$. Again, the cooperative nature of the vibrational contribution to the entropy change is essentially determined by an anomalous softening of vibrational modes arising from the itinerant nature of the Fe moments, which is not destroyed by the hydrogenation. We find that hydrogen dominates the vibrational density of states at low energies, which one rather expects for heavy elements. Despite this, its contribution to the change in vibrational entropy remains rather small.Since full loading with hydrogen involves the occupation of only a part of the available (24d) lattice sites, we also discuss the site-occupation of hydrogen based on total energy calculations and by comparing vibrational density of states from DFT involving different distributions of hydrogen with the NRIXS measurements. Finally, we will give an outlook on the impact of a partial substitution of Fe with Mn on the vibrational properties and the coupling mechanism.

Financial support by the Deutsche Forschungsgemeinschaft via SPP1599 is gratefully acknowledged.

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SESSION TP01.09: Electrocaloric Materials and Systems III
Session Chairs: Joseph Mantese and Xavier Moya
Wednesday Morning, November 28, 2018
Sheraton, 3rd Floor, Berkeley AB

8:30 AM *TP01.09.01
CaloriSMART Test Capabilities for Magnetocaloric and Elastocaloric Materials and Regenerators Julie Slaughter; Ames Laboratory, Ames, Iowa, United States.

A new test system, CaloriSMART (Small-scale Modular Advanced Research Test station), is being developed to support new caloric materials development efforts. This system is intended for rapid evaluation of performance of caloric materials in small quantities, 5-50 grams, over a wide range of operating conditions (frequencies from 0.1 to 5 Hz, utilization from 0.2 to 1, and environment temperatures from -10 to 50 C) using magnetic, stress, and electric fields, and combinations thereof as the driving fields. CaloriSMART is capable of measuring temperature spans at known cooling loads, zero span cooling power, and passive heat transfer characteristics of regenerator beds.

The magnetocaloric system module can apply magnetic fields of 1.1 T or 1.4 T and exhibits very precise control over the flow profile and rotational speed. Thorough characterization of the system using Gd as a baseline material demonstrated operation over the full range of operating conditions. It was found that the no-load temperature span could be increased by as much as 10% using precise control and timing of the flow profile with respect to the field application. Testing also revealed the importance of equal dwell time inside and outside the magnetic field in obtaining maximum performance. Test results from several magnetocaloric materials will be presented.

The elastocaloric module design goals were to minimize forces needed to actuate materials while having the capability of testing samples in both tension and compression. Unique regenerator designs based on composite structures of passive materials and active sections have been developed for both tension and compression. While the compression arrangement limits access for heat transfer, it also allows for compression of a large sample without buckling. The presentation includes initial test results based on these regenerator configurations using readily-available NiTi materials.

Future plans for module designs and regenerator testing will be discussed with particular focus on electrocaloric and multi-caloric capabilities. Initial ideas for incorporating materials of different forms into useful and robust regenerator geometries are also presented.

This work has been carried out under the auspices of CaloriCool® – the caloric materials consortium – which is a part of the Energy Materials Network. The consortium is funded by the Advanced Manufacturing Office and is managed jointly by the Advanced Manufacturing Office and Building Technologies Office of the Office of Energy Efficiency and Renewable Energy of the United States Department of Energy. The research was performed at the Ames Laboratory. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under contract No. DE-AC02-07CH11358.

9:00 AM *TP01.09.02
Heat Conductivity and Energy Efficiency of Electrocaloric Materials Emmanuel Defay; Luxembourg Institute of Science and Technology, Belvaux, Luxembourg.

The specificity of electrocaloric (EC) materials among the other caloric materials is that electric field is the stimulus required to trigger the EC effect. The advantage is that it is rather straight forward to apply an electric field on an EC capacitor. The main drawback is that electrodes and electric threads have to be systematically associated to EC materials. These specificities induce two dedicated answers to two recurrent questions posed by all caloric principles, namely energy efficiency and effective thermal conductivity.
Regarding energy efficiency, one can address the challenge through intrinsic means, meaning finding the best materials able to provide the largest variation of entropy for the lowest input electric energy. Thanks to the electric nature of the stimulus, one can also think of extrinsic means to enhance substantially the overall effective efficiency of given EC heat exchangers, typically by recycling the electric energy used to trigger the EC effect.
Besides, the necessity of using electrodes to trigger the EC effect infers extra complications when it comes to exchange heat. Indeed, using electrically insulating calorific fluids limits their nature to poorly thermally conductive ones. On the other hand, figuring out EC prototypes without fluid infers complex engineering and raises specific issues about solid-solid heat exchange. Besides, EC materials are generally weak thermal conductors. This nowadays stands probably for the main hurdle to make convincing heat exchanger prototypes.
In this talk, we will address efficiency and thermal exchange of EC materials by drawing first the state of the art and then by giving potential solutions to envision future EC heat exchangers.

9:30 AM TP01.09.03
Predictive Modeling of Electrocaloric Heat Exchangers Alvar Torello Massana[1], Romain Faye[1], Tomoyasu Usui[2], Sakyo Hirose[2] and Emmanuel Defay[1]; [1]Luxembourg Institute of Science and Technology, Luxembourg, Luxembourg; [2]Murata Manufacturing Co., Ltd., Nagaokakyo, Japan.

In recent years, several Electrocaloric (EC) heat exchangers have been proposed, covering different kinds of mechanisms and working principles. Despite this fact, little has been told about the numerical modeling of these devices.
In this work, finite elements simulations carried out with COMSOL Multiphysics software are presented. These simulations consist of 2D-representations of the lead scandium tantalate multilayers capacitors (PST MLC) 22mm x 10.4mm x 1mm parallel-plates based active regenerator that is currently being developed in LIST, where a maximum temperature difference of 1K in the device has recently been measured. In the model, the EC effect is triggered by applying equivalent heat power square pulses synchronically with the induced bidirectional laminar flow of a dielectric fluid. The model is proved to match the experiment for the first two minutes of performance before experimental intrinsic losses make the data moderately diverge.
Within this transient regime, the model is able to predict the performance of our heat exchanger for new sets of parameters. The results obtained showed that by enlarging the length of the parallel plates by a factor of three or by decreasing their thickness by a factor of two, the temperature difference in the device could increase already up to 7 degrees. The performance of other working fluids, which at the moment are not experimentally feasible to implement, was also attempted. In the case of water, with better thermal properties, the frequency of the cycle was increased up to three times, displaying very encouraging results. In conclusion, the modeling investigated indicates plenty of scope for ongoing improvement, reporting more than 10 K when the simulation parameters were optimized.

9:45 AM BREAK

10:15 AM *TP01.09.04
Solid-State Electrocaloric Heat Pump David E. Schwartz, Yunda Wang, Michael Benedict, Jamie Kalb, Joseph Lee and Ziyang Zhang; PARC, Palo Alto, California, United States.

Electrocaloric materials have the potential to enable compact, high-efficiency cooling devices. One advantage of electrocaloric heat pumps is the capability for fully solid-state designs that do not rely on pumped fluid to transfer heat to and from the cooling elements. The core of an electrocaloric heat pump is a set of capacitors based on a dielectric material with a large electrocaloric effect (ECE). ECE can be characterized by adiabatic temperature change with applied electric field. Both polymer and ceramic materials with large ECE have been developed. However, realizing multilayer capacitors with large heat capacity has remained elusive. To date, the majority of electrocaloric heat pump demonstrations have utilized commercially available capacitors based on barium titanate (BTO), which have a small ECE <1K at maximum field, or capacitors with only one or two layers of polymer materials. This talk will describe PARC's approach to solid-state electrocaloric heat pump design capable of high temperature span with limited parasitic thermal mass. Recent results of a demonstration system utilizing high performance bulk ceramic multilayer capacitors will be presented.

SESSION TP01.10: Multicaloric Materials
Session Chair: Lluis Manosa
Wednesday Morning, November 28, 2018
Sheraton, 3rd Floor, Berkeley AB

10:45 AM *TP01.10.01
Multi-Field Modulated Hysteresis Loss and Multicaloric Effect Feng-Xia Hu[1, 2], Qing-zhen Huang[3], Ji-rong Sun[1, 2] and Bao-gen Shen[1, 2]; [1]Beijing National Laboratory for Condensed Matter Physics and State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing, China; [2]School of Physical Sciences, University of Chinese Academy of Sciences, Beijing, China; [3]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Solid state refrigeration based on magnetocaloric, electrocaloric, mechanocaloric effect (multicaloric effect) has attracted world-wide attention for its environmental-friendly and energy-saving superiority over the conventional vapor compression technique.

Here, we report our recent progress on multi-field modulated hysteresis loss and multicaloric effect for the well-known $La(Fe,Co,Si)_{13}$ [1], FeRh [2], and Ni_2In-type MM'X [3] materials. For a room temperature $La(Fe,Co,Si)_{13}$ magnetocaloric material, enhanced magnetocaloric effect (MCE) by hydrostatic pressure has been demonstrated by magnetic measurements under pressure. To understand the origin, we performed neutron powder diffraction studies on the crystal and magnetic structures as a function of temperature under different pressures [4]. The change of atomic local environments and 5 kinds of Fe-Fe bonds (B1-B5) with pressure were illustrated. Detailed analysis indicated that the sensitivity of intra-icosahedron Fe-Fe bonds (B1, B2, B3) to hydrostatic pressure is mainly responsible for the change of magnetic properties. Moreover, we found that the change of lattice volume $\Delta V/V$ across Curie temperature T_C becomes significantly larger with increasing pressure. Accordingly, lattice entropy change was estimated by Debye approximate. The results indicate that the contribution of entropy change from lattice increases by ~40% as the pressure increases to 11.3 kbar. This result indicates that hydrostatic pressure is an effective way to dig the lattice contribution. Multicaloric effect and the contribution from interplay between spin and lattice are also discussed. On the other hand, hysteresis loss is a longstanding problem harming refrigeration efficiency, which exists in most of giant magnetocaloric materials. Here we report a new way to reduce hysteresis loss in the model FeRh materials. Utilizing strain memory effect to engineer the magnetization process of FeRh film, a large reduction of hysteresis loss was achieved, consequently effective refrigeration capacity and COP (coefficient-of-performance) remarkably increases in a designed refrigeration cycle [5]. We also studied the impact of film strain on the magnetostructural coupling of Ni_2In-type Mn-Co-Ge-In films grown on different substrates. Strain modulated phase transition and MCE has been demonstrated [6].

This work was supported by the National Key Research and Development Program of China (2017YFB0702702, 2014CB643700), and the National Natural Sciences Foundation of China (51531008, 51771223, 51590880).

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11:15 AM TP01.10.02
Ultra-Low-Field Magneto-Elastocaloric Cooling in a Multiferroic Composite Device Huilong Hou[1], Peter Finkel[2], Margo L. Staruch[2], Jun Cui[3, 4] and Ichiro Takeuchi[1]; [1]University of Maryland, College Park, College Park, Maryland, United States; [2]U.S. Naval Research Laboratory, Washington, District of Columbia, United States; [3]Ames Laboratory, Ames, Iowa, United States; [4]Iowa State University of Science and Technology, Ames, Iowa, United States.

Given that caloric materials are ferroic materials which undergo first (or second) order transitions near room temperature, they open up intriguing possibilities for novel multiferroic devices with hitherto unexplored functionalities coupling their thermal properties with different fields (magnetic, electric, and stress) through composite configurations. Here, we demonstrate a composite magneto-elastocaloric effect with ultra-low magnetic field (0.16 T) in a compact geometry to generate a cooling temperature change as large as 4 K using a magnetostriction/superelastic alloy composite. Such composite systems can be used to circumvent shortcomings of existing technologies such as the need for high-stress actuation mechanism for elastocaloric materials and the high magnetic-field requirement of magnetocaloric materials, while enabling new applications such as compact remote cooling devices.

11:30 AM *TP01.10.03
Multicaloric Effects—Materials and Modeling Antoni Planes[1], Teresa Castán[1], Lluis Manosa[1] and Avadh Saxena[2]; [1]Física de la Matèria Condensada, Universitat de Barcelona, Barcelona, Spain; [2]Los Alamos National Lab, Los Alamos, New Mexico, United States.

Multicaloric materials thermally respond to changes in their properties induced by the application or removal of multiple external fields. Particularly interesting are a class of multiferroic materials which are characterized by a strong interplay between different ferroic properties in the region where these properties emerge via a phase transition. In this talk, we will discuss a general thermodynamic framework to describe multicaloric effects in this class of materials. We will show that multicaloric effects comprise the contributions from caloric effects associated with each ferroic property and the cross-contribution arising from their interplay. In these materials, the use of more than one driving field can induce larger thermal changes, with smaller field magnitudes, over wider ranges of operating temperature. In addition, this permits to reduce hysteresis in one driving field in a controlled manner by transferring it to another field. These results will be illustrated with available experimental data.

SESSION TP01.11: Mechanocaloric Materials and Systems III
Session Chairs: Markus Gruner and Antoni Planes
Wednesday Afternoon, November 28, 2018
Sheraton, 3rd Floor, Berkeley AB

1:30 PM *TP01.11.01
Giant Barocaloric Effects at Low Pressure in Organic Salts Xavier Moya; Department of Materials Science, University of Cambridge, Cambridge, United Kingdom.

Barocaloric materials driven by hydrostatic pressure are currently being considered for cooling applications, following the observation of giant barocaloric effects in a small number of magnetic materials and ferroelectric materials. Here I will present pressure-dependent calorimetry data to demonstrate giant barocaloric effects in two organic salts that are made of cheap abundant elements, and that operate under low pressure.

2:00 PM TP01.11.02
Design and Operation of a 100 W Elastocaloric Compression-Based Active Regenerator David Catalini[1], Nehemiah Emaikwu[1], Jan Muehlbauer[1], Suxin Qian[2], Yunho Hwang[1], Reinhard Radermacher[1] and Ichiro Takeuchi[1]; [1]University of Maryland, College Park, Maryland, United States; [2]Xi'an Jiaotong University, Xi'an, China.

We have constructed and operated a 100W single-stage elastocaloric active regenerator based on compression of a bundle of NiTi tubes. Commercially available NiTi tubes placed inside a metallic sleeve undergo stress-induced martensitic transformation via compression. We use water as the heat transfer fluid which flows through the tubes. A numerical model of the system was developed in the Matlab/Simulink environment to solve the dynamic heat transfer and accounting for the thermodynamics-based phase transformation kinetics model of NiTi. The numerical tool was used to evaluate the influence of the operating parameters in the system's performance and to find the optimal conditions for maximum temperature lift across the active regenerator. For compressive stress of 4%, where materials DT is 8K, an initial run has given the temperature lift of 13.5K under no cooling load conditions. The design can be scalable by adding parallel beds to increase cooling capacity and to add a work recovery mechanism to increase efficiency.