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Thermag IX Extended Abstracts

[Table of Contents \(hyperlinked\)](#)

<i>Comparing Caloric Cooling Systems Sensibly</i>	<i>8</i>
<i>Adoption of adsorption material and phase change cold storage material for air processing in extremely hot and humid spaces.....</i>	<i>9</i>
<i>Cryogenic Magnetic Cooling for Natural Gas Liquefaction: Materials, Challenges and Prospective.....</i>	<i>10</i>
<i>Empirical laws for the performance for magnetic refrigeration</i>	<i>11</i>
<i>Analysis of the critical components for a magnetic cooling device</i>	<i>12</i>
<i>Giant electrocaloric materials energy efficiency in highly ordered lead scandium tantalate ..</i>	<i>13</i>
<i>Optimization of regenerator design with respect to geometric and operational parameters for solid-state caloric cooling using 1-D transient system model</i>	<i>14</i>
<i>Improving performance of solid-state cooling cycles using two-phase zeotropic heat transfer fluids.....</i>	<i>15</i>
<i>Caloric effects in liquid crystals</i>	<i>16</i>
<i>Revisiting thermal penetration depth for caloric cooling system.....</i>	<i>17</i>
<i>SUSSTAIN-EL: the design of the first Italian elastocaloric device</i>	<i>18</i>
<i>Giant Barocaloric Effects in Fast-ion Conductors: A Promising Route Towards Ambient Solid-State Cooling.....</i>	<i>19</i>
<i>Achieving Directional Heat Flow by Complete Silent Operation for Electrocaloric Heat Pumping.....</i>	<i>20</i>
<i>Monte-Carlo Simulation of first-order Magnetocaloric Materials</i>	<i>21</i>
<i>Experimental investigations for annular effect in a regenerator-exchanger of magnetocaloric heat pump.....</i>	<i>22</i>
<i>Multicaloric effects in Ni-Mn-In-(Co) Heusler compounds</i>	<i>23</i>
<i>Study of the Performance of Layered Active Magnetic Regenerators Using a Semi-Analytical Model</i>	<i>24</i>
<i>Multicaloric effects in Fe-Rh alloys and FeRh/PZT composites</i>	<i>25</i>
<i>Control of multi-bed active magnetic regenerators in a parallel fluid flow circuit.....</i>	<i>26</i>
<i>Giant Room-Temperature Magnetocaloric effect in low-cost (MnNiSi)_{1-x}(FeCoGa)_x alloys ...</i>	<i>28</i>
<i>Theoretical approach for solid-state refrigeration on spin-crossover compounds.....</i>	<i>29</i>

<i>Thermal hysteresis of caloric materials and its impact on the systems efficiency.....</i>	<i>30</i>
<i>Numerical Investigation of Ferro and its Magnetization behaviour.....</i>	<i>31</i>
<i>Elastocaloric effects in natural rubber.....</i>	<i>32</i>
<i>New refrigeration systems based on force-induced reversible gas-liquid phase transition in elastic nanoporous carbon materials</i>	<i>33</i>
<i>Effect of Doping on Structural and Magnetocaloric Properties of Fe₂P-based Materials</i>	<i>34</i>
<i>Guided Discovery of Magnetocaloric Materials</i>	<i>35</i>
<i>Modeling and Optimal Design of a Novel Solid-State Thermo-Magneto Generator Utilizing Low-Temperature Geothermal Fluid Resources</i>	<i>36</i>
<i>A dynamic active elastocaloric regenerator.....</i>	<i>37</i>
<i>Magnetocaloric properties and cooling performance analysis of the</i>	<i>38</i>
<i>composite materials (1-x)La_{0.6}Ca_{0.4}MnO₃/xMn₂O₃</i>	<i>38</i>
<i>Magnetocaloric effect in cyclic magnetic fields: search for near-perfect refrigerant.....</i>	<i>39</i>
<i>Signal-to-noise: experimental challenges characterizing</i>	<i>40</i>
<i>magnetocaloric materials in active regenerator cycles</i>	<i>40</i>
<i>Direct electrocaloric properties measurements on lead-free Samarium doped Barium Titanate ceramics.....</i>	<i>41</i>
<i>Compact, Low-Cost Magnet Designs for Magnetic Refrigeration</i>	<i>42</i>
<i>Numerical and experimental study of a thermomagnetic generator.....</i>	<i>43</i>
<i>for energy conversion</i>	<i>43</i>
<i>Cycle Analysis and Performance Study of Pulsed Magnetic Refrigeration.....</i>	<i>44</i>
<i>Designing a hydraulic management system for a large scale magnetic refrigerator.....</i>	<i>45</i>
<i>Can Gadolinium compete with La-Fe-Co-Si in a thermomagnetic generator?</i>	<i>46</i>
<i>Bending: a smart way to actuate elastocaloric effect</i>	<i>47</i>
<i>Purely electronic mechanism for first-order ferromagnetic transitions: an itinerant electron positive feedback and Fermi surface topological change</i>	<i>48</i>
<i>Experimental Research on the Time Sequence Matching of Magnetic Field and Flow Field in Active Magnetic Regenerator</i>	<i>49</i>
<i>Experimental validation of 2D-Multiphysics numerical simulations applied to long time AMR cycles</i>	<i>50</i>
<i>Updated design of an active elastocaloric regenerator.....</i>	<i>52</i>
<i>Mastering the magnetic properties of magnetocaloric Ni-Mn-(In,Sn) Heusler compounds</i>	<i>53</i>
<i>Segregation and Functional Properties of Ni-Mn-based Heusler alloys</i>	<i>54</i>

<i>Additive Manufacturing Methods for the Production of Magnetocaloric Heat Exchanger Geometries.....</i>	<i>55</i>
<i>Wide-range magnetocaloric properties of $(\text{Gd,Tb})_6(\text{Fe,Mn})\text{Bi}_2$.....</i>	<i>56</i>
<i>Numerical investigation of an active elastocaloric regenerator refrigerator with enhanced heat transfer structures</i>	<i>57</i>
<i>Spatial and Temporal Characterization of Magnetocaloric Materials with First Order Phase Transitions</i>	<i>59</i>
<i>USING MACHINE LEARNING TO DESIGN A LARGE-SCALE MAGNETIC CIRCUIT</i>	<i>60</i>
<i>Mechanical strengthening of Ni-Mn-In-(Co) Heusler alloys for multi-stimuli caloric cooling ..</i>	<i>61</i>
<i>The influence of the frequency of the cyclic magnetic field on the magnetocaloric effect in manganites</i>	<i>62</i>
<i>Study of cyclic stability of magnetocaloric effect in magnetic field for $\text{La}_{1-x}\text{Pr}_x\text{Fe}_{13.7}\text{Si}_{1.3}\text{-H}_2$ with extra Fe</i>	<i>63</i>
<i>Influence of cycling on the hysteresis of $\text{Gd}_5\text{Si}_2\text{Ge}_2$.....</i>	<i>64</i>
<i>Cabinet Temperature Control Logic in a Magnetic Refrigerator</i>	<i>65</i>
<i>Phase _eld model for ferromagnetic domain evolution during martensitic transformation of Heusler alloys.....</i>	<i>66</i>
<i>Heat driven elastocaloric cooling system</i>	<i>68</i>
<i>Effect of geometric compatibility on the magnetocaloric measurement protocols in shape memory Heusler alloy.....</i>	<i>69</i>
<i>Relaxation Phenomena in Adiabatic Temperature Changes Near Magnetostructural Transitions in Heusler Alloys</i>	<i>70</i>
<i>Tuning Transition Temperature of Magnetocaloric $\text{Mn}_{1.8}\text{Fe}_{0.2}(\text{P}_{0.59}\text{Si}_{0.41})_x$ Alloys for Cryogenic Magnetic Refrigeration</i>	<i>71</i>
<i>Direct electrocaloric measurements via ThermoReflectance</i>	<i>72</i>
<i>Long-term stability of elastocaloric material in a new system approach</i>	<i>73</i>
<i>Integrated design of a large-scale magnetic refrigerator.....</i>	<i>74</i>
<i>Magnetically-activated thermal switch without moving parts for fully solid state magnetic refrigeration.....</i>	<i>75</i>
<i>Effect of composition and hydrostatic pressure on the magnetocaloric properties of Pt doped Ni_2MnGa Heusler alloy.....</i>	<i>76</i>
<i>Performance evaluation of a novel microchannel magnetic regenerator</i>	<i>77</i>
<i>Modeling and optimization of a Samarium doped Barium Titanate multilayer capacitor for electrocaloric refrigeration</i>	<i>78</i>

<i>An AMR Lumped Model for Magnetic Refrigerator System Simulation</i>	<i>80</i>
<i>Performance Assessment of a Magnetic Wine Cooler Prototype</i>	<i>81</i>
<i>Reduction of transient refrigeration time by modulation of fluid displacement ratio and operating frequency of a magnetocaloric device</i>	<i>82</i>
<i>Evolutionary optimization of Hamiltonian model for study of magnetocaloric materials</i>	<i>84</i>
<i>Numerical study of heat transfer between fluid and magnetocaloric bed excited with time-varying magnetic field</i>	<i>85</i>
<i>Shaping LaFe₁₃-xSix-based Materials: Novel Strategies for Developing Metallic Matrix Magnetocaloric Composites.....</i>	<i>86</i>
<i>NiMnCuGa alloy pulverized via ultrasonic atomization.....</i>	<i>87</i>
<i>Applying Materials Informatics Insights to Magnetocaloric Materials Screening and Discovery</i>	<i>88</i>
<i>Enhanced magnetocaloric effect in multi-dimensional Ni-Mn-based alloys through size effect</i>	<i>89</i>
<i>Giant ECE at ultra-low fields</i>	<i>90</i>
<i>Magnetocaloric effect in rare-earth compounds for magnetic refrigeration and gas liquefaction</i>	<i>91</i>
<i>Advanced characterization of multicaloric materials in pulsed magnetic fields</i>	<i>92</i>
<i>Microstructural investigation of large magnetocaloric effects in bulk Ni-Co-Mn-Ti Heusler alloys</i>	<i>93</i>
<i>Scale-up of magnetocaloric NiCoMnIn Heuslers by powder metallurgy for room temperature magnetic refrigeration</i>	<i>94</i>
<i>Characterization and Use of Parameterized Material Property Variation in Magnetocaloric Materials</i>	<i>95</i>
<i>Performance of an Electrocaloric Air-Conditioner</i>	<i>96</i>
<i>Magnetic Pumping - Key Enabler For A Magnetocaloric Fluid Based Refrigerator With No Moving Parts.....</i>	<i>97</i>
<i>Barocaloric Effects in MnNiSi(1-x)Fe₂Ge(x) Alloys</i>	<i>98</i>
<i>Barocaloric effects in metal-organic frameworks</i>	<i>99</i>
<i>Numerical modelling of hysteresis in caloric materials for solid-state cooling</i>	<i>100</i>
<i>Performance Upgrade of a Magnetocaloric Heat Pump.....</i>	<i>101</i>
<i>Fatigue-resistant high-performance elastocaloric materials via additive manufacturing</i>	<i>102</i>
<i>Development of the Magnetocaloric Part of a Hybrid Multisource Heat Pump.....</i>	<i>103</i>
<i>Soft caloric materials for new heat-management technologies</i>	<i>104</i>

<i>Soft caloric materials for new heat-management technologies</i>	<i>105</i>
<i>Experimental investigation of the influence of synchronization profiles between magnetic field and fluid flow on the performance of a magnetic refrigerator</i>	<i>106</i>
<i>Giant Barocaloric effect and Refrigeration capacity in CrI₂(depe)₂</i>	<i>107</i>
<i>Swirl generator design for tubular absorber of vapour absorption refrigeration system</i>	<i>108</i>
<i>Magnetocaloric Effect of Gometrical Frustrated Tb 1 x Y x Ni Al for Hydrogen Liquefaction ..</i>	<i>109</i>
<i>Colossal rotating magnetocaloric effect in highly textured HoNiSi polycrystal with strong magnetocrystalline anisotropy</i>	<i>111</i>
<i>Magnetocaloric effect in GdNi₂ studied in magnetic fields up to 10 T</i>	<i>112</i>
<i>Heat switch for the magnetic refrigerator operating at cryogenic temperatures of 20-77K .</i>	<i>113</i>
<i>The prototype of a cryogenic magnetic refrigerator based on a cryomagnetic system with a 10 T superconducting coil</i>	<i>114</i>
<i>High-throughput computational search of MM'X alloys for magnetocaloric applications....</i>	<i>115</i>
<i>A lead-free and antiferroelectric materials as electrocaloric coolants</i>	<i>116</i>
<i>Study of a self oscillating Thermo-Magnetic Generator; towards a fully autonomous system</i>	<i>117</i>
<i>A thermoacoustically driven thermomagnetic electrical generator system without mechanical moving parts</i>	<i>118</i>
<i>A Generalized Locally Analytical Model for Energy Conversion of Active Caloric Regenerator</i>	<i>119</i>
<i>Unconventional magnetocaloric wine cooler initial performance</i>	<i>120</i>
<i>Stefano Dall'Olio, Urban Tomc, Katja Klinar, Simon Nosan, Andrej Kitanovski</i>	<i>120</i>
<i>Comparison of magnetocaloric properties and hydrogen stability in La_{1-z}Rz(Fe,Si,Mn)₁₃H (R = Ce and Pr) compounds</i>	<i>121</i>
<i>Study on Electrocaloric Cooling Performance of Multilayer Ceramic Components</i>	<i>122</i>
<i>Regulation of phase transition and multicaloric effect in magnetocaloric materials.....</i>	<i>123</i>
<i>Barocaloric effects in fluorinated polymers</i>	<i>124</i>
<i>Magnetocaloric properties of HoB₂</i>	<i>125</i>
<i>Machine-learning assisted search for magnetocaloric materials: Discovery of gigantic magnetocaloric effect in HoB₂</i>	<i>126</i>
<i>Magnetocaloric spherical particles for hydrogen liquefaction fabricated by a gas atomization process.....</i>	<i>127</i>
<i>Digital microfluidics in magnetocaloric cooling</i>	<i>128</i>

<i>Active Elastocaloric Regenerator with Staggered Tube Bank Configuration: An Experimental Investigation</i>	<i>129</i>
<i>Durable elastocaloric effect in thin walled Ni-Ti tubes</i>	<i>130</i>
<i>Study on durability of Mn-based magneto-caloric material for Magnetic Heat Pump</i>	<i>131</i>
<i>Thermal switches in solid state magnetic refrigeration: conductivity change requirements and effects</i>	<i>132</i>
<i>Modeling of a High Frequency Thermal Switching Active Regenerator</i>	<i>133</i>
<i>Tuning of magnetic anisotropy during additive manufacturing of magnetocaloric Gd₅Si₄..</i>	<i>134</i>
<i>Study of electrostatic actuation for electrocaloric cooling devices</i>	<i>135</i>
<i>Impact of epoxy blockage on the AMR performance of La(Fe,Mn,Si)13Hz regenerators</i>	<i>136</i>
<i>Near-net-shape production of LaFeSi micro-channel regenerators.....</i>	<i>136</i>
<i>A multicaloric approach to cool magnetocaloric wires.....</i>	<i>138</i>
<i>Evaluation of the TEWI in the Electrocaloric Materials</i>	<i>139</i>

Comparing Caloric Cooling Systems Sensibly

L. Griffith¹, J. Slaughter¹, A. Czernuszewicz¹, and V. Pecharsky^{1,2}

¹Ames Laboratory of the US Department of Energy, Iowa State University Ames, IA 50011 ²Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011

Caloric cooling consistently stands out as one of the most promising alternatives to vapor-compression [1], however, comparing performance and efficiency of different materials employed in different devices remains challenging. Typically, comparisons are based on temperature span and associated cooling power, coefficient of performance, and second law efficiency. These metrics allow cooling devices to be paired with the requirements of various applications, however, they give little sense of room for growth in the various technologies. For magnetocaloric devices, the specific exergetic cooling power [2] combines the cooling power and temperature span and normalizes the result by system-specific volume of active material and magnetic field. Though this is useful for economic analysis, it does not scale well for devices using different magnetic fields and does not account for differences in operating frequency. It is also unclear how to extend this normalization to other heat pumping technologies.

Recently, we defined the exergetic power quotient as the ratio of the exergetic cooling power to the power available from the driving field [3] and showed that many different magnetocaloric cooling prototypes using Gadolinium achieved similar values of the exergetic power quotient, despite their different designs and operating conditions. Additional results from magnetocaloric devices using other materials will show how improved materials can increase the performance of caloric cooling. The ease with which the exergetic power quotient can be extended to other cooling methods is demonstrated. We introduce the generalized exergetic power quotient to compare magnetocaloric, elastocaloric, electrocaloric, and vapor-compression cooling systems and discuss how well demonstrated devices using these technologies ultimately convert the driving field into cooling. Both the opportunities and strategies for improving each technology will be discussed together with the tradeoffs in operating a direct cooling device vs a regenerative device. Finally the close relationship between the exergetic power quotient and the second law efficiency will highlight potential advantages of caloric cooling. This work is carried out with joint funding from the Advanced Manufacturing Office and the Building Technologies Office of the Office of Energy Efficiency and Renewable Energy of the United States Department of Energy (USDOE). The research was performed at the Ames Laboratory. Ames Laboratory is operated for the USDOE by Iowa State University under contract No. DE-AC02-07CH11358.

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Adoption of adsorption material and phase change cold storage material for air processing in extremely hot and humid spaces

Rang TU(a), Jiaqi LI(a), Lanbin LIU(a)
(a) University of Science and Technology Beijing
Beijing, 100083, China, turang@ustb.edu.cn
EXTENDED ABSTRACT

In extremely hot and humid spaces and traditional air conditioning systems cannot be effectively used, such as underground mine, it is urging to provide efficient air dehumidification and cooling methods for thermal comfort and health of workers.

Currently, space ventilation or water-air exchangers are used for thermal environment control of underground mine. There are problems of cold loose, pipelines installation, transportation costs, environment control quality, etc. This paper proposes an air processing device that adopts multi-stage adsorption plates made with adsorption material and cold storage plate with phase change material for air dehumidification and air cooling, respectively. The multi-stage configuration made capacity of this device adjustable. The cold storage plates only handle sensible heat of air. Therefore, phase change temperature is around 10~20°C, which makes it possible to use natural cooling methods and high-evaporating temperature chiller. The adsorption beds deal with latent heat of air. It can be regenerated with thermal energy, Therefore, it is possible to use solar energy, geothermal, heat pumps and waste heat from production

processes, which are abundant in mining fields. The storage of humid and release of cold happen at the occupant room. While the release of humid and storage of cold happen around the heat and cold sources. Therefore, these processes are decoupled, making the energy systems more flexible and variable. As compared with traditional

air conditioning, cold-lost as well as power consumption of fans and pumps during transportation can be eliminated. Moreover, this method controls only the spaces around people instead of all-space cooling, therefore, cooling capacity can be reduced.

In this paper, the system principle is introduced first. Then, possible cooling and heating sources as well as the adoption potentials are analyzed based on a typical mining field. Next, design parameters, such as dimensions of adsorption beds and cold storage beds, phase-change temperature, cold storage density, processed air volume, supply air temperature and humidity ratio, etc, of the air processing device are discussed. It is aiming to realize good cooling and dehumidification performance in a long running period. Lastly, energy efficiency of this device is discussed, considering different cooling sources and heating sources under typical ambient conditions of a year. In this part, heat pump systems, solar energy, and geothermal are considered as heating sources. Direct and indirect evaporative cooling, high evaporating temperature chiller, and ambient air are considered as cooling sources.

Keywords: cold-storage, phase change material, adsorption dehumidification; renewable energy

Cryogenic Magnetic Cooling for Natural Gas Liquefaction: Materials, Challenges and Prospective

Sergey TASKAEV(a), Konstantin SKOKOV(b), Vladimir KHOVAYLO(c), Maxim ULYANOV(a), Dmitriy BATAEV(a), Daniil PLAKHOTSKIY(a), Mikhail BOGUSH(a), Dmitriy KARPENKOV(c), Alexey KARPENKOV(d), Tino GOTTSCHALL(e), Eduard BYKOV(e), Wei LIU(b), Oliver GUTFLEISCH(b)

(a) Chelyabinsk State University

Br. Kashirinykh str. 129, 454001 Chelyabinsk, Russia

(b) TU Darmstadt

Karolinenplatz 5, 64289 Darmstadt, Germany

(c) NUST MISIS

Leninskiy ave., 4, 119049 Moscow, Russia

(d) Tver State University

Zhelyabova str. 33, 170100 Tver, Russia

(e) HZDR – Helmholtz-Zentrum Dresden-Rossendorf

Bautzner Landstrasse 400, 01328 Dresden, Germany

ABSTRACT

Natural gases are one of the main sources of energy nowadays and in the near future. Currently, there is an upward trend of the production and consumption of this type of energy in all market segments including methane, hydrogen, oxygen etc. For the storage and transportation of this type of energy, liquefaction is needed, but this process requires complex energy-intensive compressor devices operating at cryogenic temperatures. However, the efficiency by traditional liquefaction methods is quite low at temperatures below 150 K, yet there is a fundamentally different approach to liquefy gases as a storehouse of future energy - the emerging magnetic cooling technology. Taking into account the recent progress in the development of superconducting magnets with magnetic fields up to 15 – 22 T, this type of cooling at cryogenic temperatures can make 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 temperature region of interest from 15 to 150 K. This makes it possible to initiate the efficient liquefaction of almost any natural gas in the same type of magnetic cooling machine.

This is certainly the heart of any magnetic cooling device transferring the heat from the low to the high temperature reservoir. The most interesting compounds are ferromagnetic materials operating near their Curie temperature, because in its vicinity the greatest magnetocaloric effect is observed.

In this work, we examine different rare earths (RE) based alloys in a form of Laves phases and other intermetallic compounds such as RE-Al₂, RE-Ni₂ and RE₅Si₄. Combining different 4-f elements in the rare earth sublattice of an alloy one can easily tune Curie point and as a consequence create a set of magnetocaloric materials which exhibit a large magnetocaloric effect at low temperatures from one hand and could be utilized in a wide temperature range from other hand by stacking different alloys in AMR device. The possible application of synthesized alloys is in LNG liquefying devices as a magnetocaloric refrigerants.

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Empirical laws for the performance for magnetic refrigeration

D. Benke^{1,2}, T. Sirman^{1,2}, K. Rahnamarad^{1,2}, T. Gottschall^{1,3}, O. Gutfleisch^{1,2}, M. Fries^{1,2}

1) MagnoTherm Solutions GmbH, Darmstadt, Germany

2) TU Darmstadt, Funktionale Materialien, Darmstadt, Germany

3) Dresden High Magnetic Field Laboratory (HLD-EMFL), Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany

Magnetic cooling technology is considered as a potential replacement to gas vapour compression refrigeration and has been studied for many years in the framework of many industrial and scientific research programs. Yet, there is still a lack of prototypes which are comparable in power output and performance compared to conventional cooling technologies [1]. We believe, that one of the reasons is an insufficient understanding of the materials behaviour when implemented into a magnetic cooling device.

Magnotherm Solutions GmbH is a spin-off from the functional materials group of TU Darmstadt which aims to close the gap between system builders and material experts. We are working on several magnetic cooling prototypes operating around room temperature [2]. Within this framework we have analysed the loss mechanisms of the device in detail and found some empirical laws that serve as an upper limit for the performance of a magnetic cooling device.

An important point during the development of a cooling device is a thorough analysis and quantification of the losses. Knowledge of the loss mechanisms combined with the proposed empirical laws allows an estimation whether the magnetic cooling cycle is implemented correctly and working. By comparing the actual performance with the theoretical upper limit of performance, it is possible to assess the quality of implementation and hence compare different setups and predict the performance of future setups.

In this talk we will present these laws and how they are useful in the development of a magnetic cooling device as well as how they correlate with the performance of our own cooling device.

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Analysis of the critical components for a magnetic cooling device

M. Fries^{1,2}, J. Faulhaber², L. Koch², T. Sirman^{1,2}, K. Rahnamarad^{1,2}, T. Gottschall^{1,3}, O. Gutfleisch^{1,2}, D. Benke^{1,2}

1)MagnoTherm Solutions GmbH, Darmstadt, Germany 2)TU Darmstadt, Funktionale Materialien, Darmstadt, Germany 3)Dresden High Magnetic Field Laboratory (HLD-EMFL), Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany

Magnetic heat pumping is an emerging technology in the refrigeration sector which offers many advantages over vapor compression refrigeration, which is the most widely used cooling technology above 100 K [1].

Most magnetic cooling prototypes presented nowadays are based on the AMR (Active Magnetic Regenerator) cycle which allows an operation of a magnetic cooling device with a temperature span larger than the adiabatic temperature change of the magnetocaloric material [2].

In order to design and operate an efficient magnetic cooling device, many parameters need to be taken into account starting from the selection of the best material in the desired power and temperature range and to ensure a good heat transfer and longevity. Furthermore, efficient components like an efficient drive and pumping system need to be implemented in order to show an overall efficiency of a magnetic cooling device higher than that of a compressor systems. In addition to the complex engineering and physics problems, the economics of the device will play a large role when compared to existing technologies [3].

We at MagnoTherm Solutions GmbH, a spin off from the functional materials group at TU Darmstadt have analyzed many of these parameters on our prototypes and will in this contribution show how we have optimized an existing permanent magnet design in terms of performance, raw materials cost and ease of implementation.

Furthermore, we will show results on various AMR designs and how they compare in terms of performance. From this we will derive a magnetocaloric figure of merit comparing these different designs. Additionally, we will also show the performance of Gd and LaFeSi-based AMRs.

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Giant electrocaloric materials energy efficiency in highly ordered lead scandium tantalate

Youri Nouchokgwe^{1,2*}, Pierre Lheritier¹, C.-H. Hong³, Alvar Torelló^{1,2}, Romain Faye¹, Wook Jo³, C. R. H. Bahl⁴ & Emmanuel Defay^{1*}

¹*Materials Research and Technology Department, Luxembourg Institute of Science and Technology, 41 rue du Brill, L-4422 Belvaux, Luxembourg*

²*University of Luxembourg, 2 avenue de l'Université, L-4365 Esch-sur-Alzette, Luxembourg*

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

⁴*Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, 2800 Kgs. Lyngby, Denmark*

Abstract

Electrocaloric materials are promising working bodies for caloric-based technologies, suggested as an efficient alternative to the vapour compression systems¹. However, their materials efficiency² defined as the ratio of the exchangeable electrocaloric heat to the work needed to trigger this heat remains unknown. Here, we show by direct measurements of heat and electrical work that a highly ordered bulk lead scandium tantalate (PST) can exchange more than a hundred times more electrocaloric heat than the work needed to trigger it. Besides, our material exhibits a maximum adiabatic temperature change of 3.7 K at an electric field of 40 kV cm⁻¹, which represents an increase of 60% compare with previous studies on less ordered PST³. These features are strong assets in favour of electrocaloric materials for future cooling devices⁴.

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Optimization of regenerator design with respect to geometric and operational parameters for solid-state caloric cooling using 1-D transient system model

Minwoong Kang(a), Stefan Elbel(a),(b)

(a) Air Conditioning and Refrigeration Center, Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 1206 West Green Street, Urbana, IL 61801, USA (b) Creative Thermal Solutions, Inc., 2209 North Willow Road, Urbana, IL 61802, USA

EXTENDED ABSTRACT

Many researchers have actively investigated solid-state cooling because it has theoretically high efficiency and does not require the use of refrigerants. While most of the research has focused on developing new materials which have higher caloric effect and lower cost, little work on heat transfer phenomena in the regenerator has been conducted. Therefore, this paper considers the underlying heat transfer characteristics of the regenerator in detail and explores performance effects of different regenerator geometries and operating conditions.

This paper incorporates hydrodynamic and thermal developing regions into the model for solid-state caloric cooling. Many papers neglect the thermal developing region and some papers consider only the thermal developing length for the purpose of obtaining heat transfer coefficients along the length of the regenerator. However, by incorporating both developing regions as well as transient characteristics, the model developed in this paper is more accurate in terms of heat transfer coefficients and friction factors. The thermal developing region changes periodically as a consequence of the cyclic behavior and flow direction changes within the regenerator of solid-state cooling systems. The system model considering developing regions has significantly increased cooling capacity and COP especially at high cycle frequencies.

In addition, this paper establishes a new method to find optimal regenerator geometries and operating conditions. For a plate-type of regenerator with 0.3mm hydraulic diameter, the design with 200mm length, 0.45Hz cycle frequency and 0.5 porosity delivers the highest COP of 2.3 to generate 100W/kg cooling capacity for a temperature lift of 20oC operating between 5oC and 25oC. The detailed understanding of heat transfer phenomena in the regenerator is very important to effectively utilize the caloric effect of current and new materials. In addition, this method can be easily applied to other geometry types of regenerators or operating conditions for all kinds of solid-state caloric cooling cycles. Keywords: magnetocaloric cooling; caloric regenerator; heat transfer and pressure drop; heat exchanger design; optimization; hydrodynamic and thermal developing region.

Improving performance of solid-state cooling cycles using two-phase zeotropic heat transfer fluids

Minwoong Kang(a), Stefan Elbel(a),(b)

Air Conditioning and Refrigeration Center, Department of Mechanical Science and Engineering,
University of Illinois at Urbana-Champaign, 1206 West Green Street, Urbana, IL 61801, USA (b) Creative
Thermal Solutions, Inc., 2209 North Willow Road, Urbana, IL 61802, USA

EXTENDED ABSTRACT

For the past few decades, numerous researchers and companies have been actively developing solid-state cooling technology. However, the study on heat transfer fluids used in caloric regenerators is very limited, even though heat transfer between the magnetocaloric material and the heat transfer fluid used in the regenerator determines system performance. Therefore, this paper has applied different working fluids to a solid-state caloric cooling system and compares the performance achieved to a baseline system using water.

When single phase water is used as heat transfer fluid in the solid-state caloric cooling system, the flow is found to be laminar. Therefore, the heat transfer coefficient cannot be improved for a fixed regenerator hydraulic diameter, because the Nusselt number is constant for fully developed laminar flow. However, when a zeotropic blend is used as the heat transfer fluid, it is expected that Nusselt number increases and temperature gradient appears in the regenerator. Therefore, the authors have chosen an ethane/isobutane mixture (50/50% by mass) as heat transfer fluid due to its high temperature glide during condensation and evaporation. Unlike in conventional vapor compression systems that aim to use blends with low temperature glides, the higher glides in caloric system can be helpful in increasing the temperature lift of the system.

Optimized conditions were chosen for both cases to compare the solid-state caloric system using a zeotropic mixture with the baseline using single phase water. Using the zeotropic mixture increases the Nusselt number 2.4 times and the temperature difference between hot and cold reservoir tanks by 9.6%. In return, cooling capacity and COP increased by simultaneously by 22 and 34%. This is mainly because the zeotropic system requires lower mass flow rate compared to the water system to reach the optimal displacement ratio of the fluid within the regenerator. This is caused by the difference in density between both heat transfer fluids and the optimized aspect ratio. Therefore, the heat capacity of the heat transfer fluid entering and exiting the regenerator during one blow period is lower in the zeotropic system. Consequently, the temperature of the heat transfer fluid during hot and cold blow periods, respectively, increases and decreases in the zeotropic system. Ultimately, this leads to an increase in the temperature difference of the heat transfer fluid between cold and hot sides in regenerator, cooling capacity and COP.

No prior study has described the application of two-phase zeotropic blends to a caloric refrigeration system before. The results are intriguing and demonstrate that it is possible to expand the application of caloric cooling systems due to the use of high-glide zeotropic mixture.

Keywords: magnetocaloric cooling; caloric regenerator; heat transfer fluid; zeotropic blend, temperature glide; efficiency and capacity

Caloric effects in liquid crystals

G. F. Nataf(a), Y. Bernstein(a), E. Stern-Taulats(a), J. Bermúdez-García(a), A. Avramenko(a), P. Lloveras(a),(b), M. Barrio(b), J. Ll. Tamarit(b), X. Moya(a)

(a) Department of Materials Science & Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, UK, gn283@cam.ac.uk (b) Departament de Física, EEBE, Campus Diagonal-Besòs and Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, Eduard Maristany, 10-14, 08019 Barcelona, Catalonia, Spain

Abstract

Current refrigeration technologies rely on pressure-driven gas-to-liquid phase transitions in volatile fluids that are harmful for the environment. Here, we suggest a shift in paradigm by investigating benign liquid crystals for cooling applications, which exhibit large latent heats associated with order-disorder phase transitions and low hysteresis. In particular, I will discuss the potential of liquid crystals as mechanocaloric materials, and report large pressure-driven thermal changes close to those observed in commercially exploited fluid refrigerants.

Keywords: liquid crystals, barocaloric materials

Revisiting thermal penetration depth for caloric cooling system

Lifen Yuan, Jianlin Yu, Suxin Qian*

Department of Refrigeration and Cryogenic Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, China, 710049

* Corresponding Author: qiansuxin@xjtu.edu.cn

Thermal penetration depth is a physical quantity identifying the distance that heat can diffuse through the domain material, which has been widely adopted for thermoacoustic cryocoolers in the past. According to the derivation of thermal penetration depth based on the analytical solution of transient heat conduction to semi-infinite region, the diffusive thermal resistance is the only dominating factor for gaseous refrigerant. The same concept may be applied for caloric cooling devices. If the thermal penetration depth is more than the thickness of the caloric regenerator, it implies that the majority of the caloric effect is absorbed by the heat transfer fluid. For caloric cooling devices, however, the convective thermal resistance on the surface of the caloric material can be on the same magnitude compared with that of the diffusive thermal resistance inside the caloric material. In addition, the slab made of solid refrigerant in the caloric cooling devices is different from semi-infinite region. Consequently, the conventional definition of thermal penetration depth cannot be directly adopted for caloric cooling devices without introducing significant uncertainty that may cause overestimation of heat transfer performance of the caloric regenerator.

In this study, based on the approximate fitting formula proposed by Campo, which was used to describe the temperature of a slab with the Newton boundary condition, we derived a modified thermal penetration depth when considering both the diffusive thermal resistance inside the caloric material and the convective thermal resistance on the surface of the caloric material. Comparison indicates that the conventional thermal penetration fails to accurately represent the thermal diffusion characteristics in the caloric material. To further validate and compare the significance of the modified thermal penetration depth, one-dimensional CFD simulation studies are carried out for different Biot number. We show the approximate fitting formula agrees well with CFD prediction. The quantities involved are dimensionless, including dimensionless temperature, dimensionless length, Biot number and Fourier number. Biot number represents the influence of the diffusive thermal resistance and convective thermal resistance, which correspond to the thermo-physical properties of caloric material and convective heat transfer coefficient in the caloric cooling device. Fourier number represents the influence of the heat-transfer time, which corresponds to the operating frequency. We chart the Biot number and Fourier number and analyze a few typical cases from literature. The results show the cases on the top right of the chart perform better. Therefore, from the perspective of the thermal penetration depth, a modest combination of these two dimensionless numbers can enhance the heat transfer performance of the caloric cooling device, which is conducive to the design and construction of caloric cooling devices.

SUSSTAIN-EL: the design of the first Italian elastocaloric device

Adriana Greco(a)*, Assunta Borzacchiello(b), Claudia Masselli(a)

(a) University of Naples Federico II, Piazzale Tecchio 80, Naples, 80125, Italy, adriana.greco@unina.it

(b) IPCB-CNR, Viale J.F. Kennedy 54, Naples, 80125, Italy

Abstract

Nowadays about 20% of the worldwide energy consumption is attributable to refrigeration that is almost entirely based on vapor compression refrigeration. Such data derives in a driving force towards the research and development of new cooling techniques that could become an alternative to the vapor compression, meeting the requirements of environmental and energy sustainability.

In the general framework of the various emerging proposals, in the scientific literature noteworthy is the class of solid-state cooling techniques based on the caloric effects. In the field of caloric cooling, the scientific community has devoted the attention specifically toward magnetocaloric and toward elastocaloric refrigeration, in recent times.

Elastocaloric refrigeration is based on the latent heat associated with the transformation process of the martensitic phase, found in Shape Memory Alloys (SMA) when they are subjected to uniaxial stress cycles of loading and unloading. SMAs are characterized by the mechanical property of being able to return to the initial form once the uniaxial stress has been removed. By exploiting this effect in a reverse regenerative thermodynamic cycle called "Active elastocaloric regenerative refrigeration cycle (AeR)", a satisfactory cooling effect is achievable. The prototypes of elastocaloric cooler developed so far in the world are less than ten units and they are still in a "pre-competitive development activity-phase", not close to the industrialization and commercialization, yet. Italy has not presented its first prototype of elastocaloric cooler to the scientific community, yet.

This contribution presents the design processes and the steps of development of the first Italian elastocaloric device: SSUSTAIN-EL. This research is part of a bigger Italian project, called SUSSTAINABLE, that involves three units: University of Naples Federico II, University of Genoa and the National Research Council. The aim of research group of the University of Naples Federico II is the developing of a demonstrative prototype of an elastocaloric cooler, which can therefore be the first Italian elastocaloric device and that can represent a fundamental step as "proof of concept". The basic project provides for a device with a very simple and minimal design as its primary purpose is the possibility to testing in different configurations, aimed at investigating the feasibility of the elastocaloric effect for refrigeration applications at room temperature.

Keywords: Elastocaloric, experimental device, project design.

Giant Barocaloric Effects in Fast-ion Conductors: A Promising Route Towards Ambient Solid-State Cooling

Claudio Cazorla *School of Materials Science and Engineering, UNSW Sydney, Sydney, NSW 2052, Australia* E-mail: c.cazorla@unsw.edu.au Solid-state cooling is a sustainable and energy efficient refrigerant technology that exploits field-induced reversible transformations in materials. Solid-state cooling is a promising alternative to traditional refrigeration technologies based on compression cycles of greenhouse gases, which in addition to their obvious environmental threats cannot be scaled to small sizes (e.g., microchip dimensions). Nevertheless, most caloric materials known to date (ferroelastic, ferroelectric, and magnetic compounds) display only modest refrigeration performances and/or operate at temperatures far from ambient conditions. Recently, we have predicted by means of computer simulation methods that giant caloric effects occur in fast-ion conductors [1-3], a class of materials exhibiting high ionic conductivity below their fusion points which commonly are exploited in electro-chemical devices. The giant caloric effects disclosed in fast-ion conductors can be understood in terms of field-driven changes on their ionic conductivity, which are highly reversible and responsive. A giant cooling effect of ~20 K has been just measured directly in the archetypal superionic compound AgI [4]. We argue that solid-state cooling could benefit immensely from the intensive research already undertaken on solid-state batteries and oxide fuel cells. [1] **C. Cazorla** and D. Errandonea, *Nano Letters* 16, 3124 (2016) [2] A. K. Sagotra, D. Errandonea, and **C. Cazorla**, *Nature Communications* 8, 963 (2017) [3] A. K. Sagotra, D. Chu, and **C. Cazorla**, *Nature Communications* 9, 3337 (2018) [4] A. Aznar, P. Lloveras, **C. Cazorla** et al., *Nature Communications* 8, 1851 (2017)

Achieving Directional Heat Flow by Complete Silent Operation for Electrocaloric Heat Pumping

Farrukh Najmi¹, Dr. Lorenzo Cremaschi², Dr. Wenxian Shen³, Dr. Zhongyang Cheng¹

¹ fzn0006@auburn.edu, PhD Student, Materials Engineering, Auburn University, Auburn, AL 36849

² lzc0047@auburn.edu, Associate Professor, Mechanical Engineering, Auburn University, Auburn, AL 36849

³ wenxish@auburn.edu, Professor, Mathematics and Statistics, Auburn University, Auburn, AL 36849

¹Materials Research and Education Center, Auburn University, Auburn, AL 36849, USA

²Department of Mechanical Engineering, Auburn University, Auburn, AL 36849, USA

³Department of Mathematics and Statistics, Auburn University, Auburn, AL 36849, USA

Electrocaloric effect (ECE) is a reversible temperature change of a dielectric material when it is subjected to an external electric field. Therefore, it is interesting to use the ECE to develop all-solid-state cooling and heat pumping devices. However, the development is hindered by the involvement of additional mechanism to achieve directional heat flow from source to sink. These additional mechanisms involve regeneration through working fluids or thermal diodes/switches that not only reduce the efficiency and reliability of the device but also limit their applications in microscale level due to bulky designs. In this work, a novel design of two-layered solid-state heat pump is introduced, in which two layers of electrocaloric material (ECM) are sandwiched between source and sink. The electric field applied on the two layers is independently controlled with different phases. Therefore, a directional heat flow is achieved from source to sink without involvement of any moving parts or additional mechanisms. All bodies in the heat pump remain in contact throughout the thermal cycle, which results in a high reliability. The working principle involves the application of an alternative electric field cycle on ECM layers in such a way that it achieves a directional heat flow in a system of bodies (sink/ECs/source) that are in thermal equilibrium. The transient solution of the heat pump model is solved analytically to find the temperature profiles and heat flux through the interfaces. The determination of the heat flux gives promising results, especially for the cases in which interfaces having lower contacting coefficients. This design can be used for the thermal management of high-power electronics and temperature maintenance in portable medical devices.

Monte-Carlo Simulation of first-order Magnetocaloric Materials

**Radia HAMANE(a), Michel RISSE(b), Anna LEONTEVA(c),
Vincent HARDY(a)**

(a)CRISMAT-ENSICAEN, Caen, 14050, France, radia.hamane@ensicaen.fr

(b)Ubiblue, Entzheim, 67960, France

(c)CSTB-ICube, Strasbourg, 67000, France

Abstract

The compounds of the $\text{LaFe}_{13-x}\text{Si}_x$ series constitute one of the most promising families of magnetocaloric materials for applications in magnetic refrigeration (MR). These alloys exhibit a magneto-structural transition. The Si content changes the interatomic distances of $\text{La}-(\text{Fe}, \text{Si})$, and changes as well as the nature of the magnetic transition which is intimately related to the magneto volume effect.

Optimizing the design of MR devices needs models able to reliably account for the physical properties of these materials. The main properties involved in the simulation of MR devices are the field and temperature dependent magnetization, heat capacity and magnetocaloric effect (Risser et al., 2012). Our goal is to build a model yielding data consistent with the experimental measurements of these properties.

Several theories have previously been developed to study and attempt to simulate magnetic properties. Nevertheless, modeled behaviors remain different from experimental measurements, especially on some first-order samples. In this context, we denote the broadening of the magnetic transition under the presence of an applied magnetic field, and the peak shape of the heat capacity which is symmetric for the most experimental measurements. These features are directly related to the analytical nature of the solution, the physical models and the methods used.

We present a theoretical model which combines the magnetic and structural behaviors around the first-order magnetic phase transition. The generalized Hamiltonian consists of three contributions: magnetic, structural, and magneto-structural coupling. For the first one, we used ferromagnetic Ising interaction $S_i = \pm 1$ defined on the cubic lattice site ($i = 1, \dots, N$). Blume Emery Griffiths model was used in order to incorporate the mutual influence of magnetic ordering and structural transition. It describes the high entropy of vibrations of deformed phase at high temperature (Buchelnikov et al., 2011). A variable σ_i was introduced representing the deformation state near each site of the spin lattice ($i = 1, \dots, N$). The states $\sigma_i = +1$ and $\sigma_i = 0$ represent the distorted and undistorted sites, respectively. Free parameters are introduced for tuning the intensities of interactions. Their numerical values are sought to obtain theoretical MC data set in good agreement with experimental observed behaviors.

Our model is solved by Monte Carlo simulations. The optimization of the free parameters of the Hamiltonian model is performed with an evolutionary algorithm (Ouskova-Leonteva et al., 2020). We describe the physics associated with the coupled magnetostructural first order transition for LaFeSi compounds, and phase diagrams are discussed. The results of the model are in good agreement with the experimental measurements for the magnetization and the heat capacity.

Keywords: Monte Carlo simulation, magnetocaloric materials, first order magnetic transition.

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Experimental investigations for annular effect in a regenerator-exchanger of magnetocaloric heat pump

Tianjiao Li(a)(b), Mickaël Perrin(b), Ali Ismail(b)(c), Antony Plait(b), Alexandre Meunier(a), Laurent Girardot(b), Jean-Claude Roy(b), David Ramel(b), Thierry de Larochelambert(b), Stefan Giurgea(b), Yannick Bailly(b)

(a)Next°PAC, Seingbouse, 57455, France, tianjiao.li@nextpac.fr,

(b)FEMTO-ST Institute, Energy Department, University Bourgogne Franche-Comté, Belfort, 90000,

France, **(c)**FEMTO-ST Institute, Applied Mechanics Department, University Bourgogne Franche-Comté, Besancon, 25000, France

Abstract

Magnetocaloric refrigeration system is identified as a candidate to replace the conventional devices. In this kind of system, the active magnetic regeneration (AMR) cycle is usually applied for magnetizing/demagnetizing magnetocaloric materials (MCM), and oscillating flow is used to realize the heat transfer between coolant and MCM. Various studies on magnetocaloric device mainly focus on the system designs, such as utilization of magnetocaloric materials and distribution of magnetic field, to maximize the temperature span and cooling power. However, the oscillating flow behavior, which is less studied, plays another significant role that could affect the performance of caloric devices. In this flow, a particular phenomenon named annular effect could appear in the boundary layer. It creates a maximal flow velocity gradient near the fluid-solid interface. This irregular velocity gradient could potentially increase the heat transfer efficiency even the COP of heat pump.

Therefore, this article presents an experimental investigation for visualization of annular effect. The experimental bench is composed of two main parts: a quartz duct of square cross section made for the observation area, and the fluidic system, which generates the oscillating flow via two synchronized electromagnetic valves and a circulator pump. To determine the velocity profile, Laser Doppler Velocimetry (LDV) method is used to measure the sparkling frequency of micro particles.

Figure below shows the near wall velocity profile as function of the phase. The comparison between experimental results and numerical simulation will be realized. The further study about the heat transfer in oscillating flow could be expected in the case that the modification of experimental bench could be completed.

Keywords: Caloric device, Heat pumping, Refrigeration, Oscillating flow, Visualization, Laser Doppler Velocimetry, Annular effect.

Multicaloric effects in Ni-Mn-In-(Co) Heusler compounds

Lukas PFEUFFER(a), Adrià GRÀCIA-CONDAL(b), Tino GOTTSCHALL(c), Andreas TAUBEL(a), Franziska SCHEIBEL(a), Konstantin P. SKOKOV(a), Lluís MAÑOSA(b), Antoni PLANES(b) and Oliver GUTFLEISCH(a)

(a) Technische Universität Darmstadt

64287 Darmstadt, Germany

(b) Universitat de Barcelona

08028 Barcelona, Spain

(c) Helmholtz-Zentrum Dresden-Rossendorf

01328 Dresden, Germany

Ni-Mn-In-(Co) Heusler compounds exhibit outstanding magnetocaloric properties as high isothermal entropy changes ΔS_T and adiabatic temperature changes ΔT_{ad} upon the discontinuous application of moderate magnetic fields [1]. However, the large thermal hysteresis accompanying the martensitic transformation hinders the applicability in cyclic operation [2]. To overcome this limit, we recently proposed a new multicaloric cooling process, the so-called exploiting hysteresis cycle [3]. In contrast to conventional magnetic refrigeration, our concept takes benefit from the large thermal hysteresis of Heusler compounds and enables the utilization of the material's maximum magnetocaloric effect. Applying this novel cycle, the material is trapped in the ferromagnetic austenitic state after the magnetic field application and subsequently transformed back to its initial paramagnetic martensite state by a stress stimulus. Hence, the active material should provide a conventional elastocaloric effect with a high mechanical fatigue resistance next to a large inverse magnetocaloric effect.

We investigated the multicaloric response of suction-cast Ni-Mn-In and Ni-Mn-In-Co by means of elasto- and magnetocaloric measurements. By constant stress thermal cycling experiments, a ΔS_T near room temperature of 6.5 J/kgK for Ni-Mn-In and 11 J/kgK Ni-Mn-In-Co was obtained in only 37.5 MPa. Significant training effects of the martensitic transformation could be observed, resulting in an increase of ΔS_T by 40 % for Ni-Mn-In. However, Ni-Mn-In-(Co) suffers from high fatigue during thermomechanical cycling. We detected a failure mechanism in these compounds, significantly differing from the one in NiTi [4]. Interestingly, the fatigue is strongly reduced when the martensitic transformation is induced solely by stress, which is of importance for our exploiting hysteresis approach. The magnetocaloric characterization by magnetic isofield measurements revealed a comparable ΔS_T of 16-18 J/kgK for the studied Ni-Mn-In-(Co) samples, which are close to the maximum ΔS_T obtained from DSC measurements. For the direct determination of the maximum ΔT_{ad} pulsed field measurements up to 10 T were performed on a Ni-Mn-In sample showing a cooling of 4.5 K in 2 T and of 9 K in 5 T and 10 T. We demonstrate, that the maximum ΔT_{ad} can be increased by more than 10 % in the exploiting hysteresis cycle when the second-order transition at the Curie temperature of the austenite is utilized. Our study gives a detailed insight into the multicaloric behavior of suction cast Ni-Mn-In-(Co). A high susceptibility to both stimuli, stress and magnetic field, makes this material class highly attractive for the exploiting hysteresis cycle.

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Study of the Performance of Layered Active Magnetic Regenerators Using a Semi-Analytical Model

Ali Ismail(a,b), Mickaël Perrin(a), Tianjiao Li(a,c), Yannick Bailly(a), Stefan Giurgea(a), Thierry Barrière(b), Jean-Claude Roy(a), David Ramel(a), Raynal Glises(a), Thierry De Laroche Lambert(a)

(a)FEMTO-ST Institute, Energy Department, University Bourgogne Franche-Comte, Belfort, 90000, France, ali.ismail@univ-fcomte.fr.

(b)FEMTO-ST Institute, Applied Mechanics Department, University Bourgogne Franche-Comte, Besançon, 25000, France. (c)Next°PAC, Seingbouse, 57455, France.

Abstract

One of the nowadays challenges in magnetic refrigeration (MR) is to increase the performance of the active magnetic regenerator (AMR). This improvement of the efficiency may be achieved by many techniques such as enhancing the heat transfer between the fluid and the magnetocaloric material (MCM), amplifying the magnetocaloric effect (MCE) of the MCM by increasing the internal magnetic field in the MCM, designing layered regenerators composed of several different MCM with different Curie transition points, tuning frequency, modifying geometry, etc.

The use of layered regenerators with increasing Curie points range from the cold to the hot side leads to higher MCE efficiency of each segment, enhancing thermal power, thanks for larger operating temperature range and larger temperature span between the cold and hot sources as shown in the figure below. These advantages have been pointed out experimentally and numerically in many references.

However, the number of layers that should be used to reach the highest temperature span at a given operating temperature range is still unknown. In this work, a flexible unidimensional semi-analytical model is used to assess the effect of layers' number on the performance of a rectangular micro-channel AMR. The Curie points' difference between lateral layers is settled while varying the number of layers in order to characterize the global regenerator's behavior during AMRR cycles (adiabatic temperature span, temperature's rate of change, cooling and heating power in different functioning modes, efficiency).

Finally, this work will be a part of the ISITE-BFC CompoMag project aiming to design optimal rectangular regenerators made of highly charged thermoplastic magnetocaloric nanocomposites.

Keywords: rectangular AMR, layered regenerator, layers' number, temperature span, efficiency.

Multicaloric effects in Fe-Rh alloys and FeRh/PZT composites

Abdulkarim Amirov(a),(b), Alexander Kamantzev(a),(c), Alisa Chirkova(d), Akmed Aliev(b), Konstantin Skokov(d)

(a) Immanuel Kant Baltic Federal University, Kaliningrad, 236013 Russian Federation

(b) Amirkhanov Institute of Physics of Daghestan Scientific Center Russian Academy of Sciences, Makhachkala, 367003 Russian Federation

(c) Kotel'nikov Institute of Radioengineering and Electronics, Moscow, 125009 Russian Federation

(d) Materials Science, TU Darmstadt, Darmstadt, 64289 Germany

amiroff_a@mail.ru

Abstract

The caloric and multicaloric effects in Fe-Rh alloys and magnetoelectric composites based on them were studied under ordinary and combined external stimulus: magnetic field, hydrostatic pressure and uniaxial strain. The maximum of caloric effects around was observed around antiferromagnetic-ferromagnetic transition temperature around 310 K, which shifts in depends on values combined external fields. Electric voltage-controlled magnetocaloric effect was observed in FeRh/PZT magnetoelectric composite in 310-320 K temperature range.

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

Key Results

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

- 1) By combination two external forces – magnetic with hydrostatic pressure and magnetic field with uniaxial strain
- 2) Through the fabrication of magnetoelectric composites, where voltage induced strain/stress on piezoelectric component mechanically is acted to FeRh.

The Fe-Rh alloys with compositions Fe₄₈Rh₅₂, Fe₄₉Rh₅₁ were fabricated and magnetocaloric (MCE), barocaloric (BCE) and elastocaloric (EICE) in them were studied. It was observed maximum adiabatic temperature changes and isothermal entropy changes around AFM-FM transition temperature ~310 K, induced by the magnetic field, pressure and, uniaxial strain. The combination of elastic strain and magnetic field shift transition temperature to lower temperatures, while magnetic field and pressure play opposite effect and depends on values of combined external fields.

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

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Control of multi-bed active magnetic regenerators in a parallel fluid flow circuit

Kurt ENGELBRECHT(a), Jierong LIANG(a), Marvin MASCHÉ(a), Christian BAHL(a)

(a)Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, 2800 Kgs. Lyngby, Denmark, kuen@dtu.dk

EXTENDED ABSTRACT

Multi-bed active magnetic regenerators (AMR) can be connected hydraulically in serially or in parallel. Serially connected devices usually consist of two AMR beds that share a common cold reservoir with flow provided by reciprocating displacers. Some examples of series connection devices include Refs. [1]-[3]. The advantage of a serially connected devices is that flow in each bed is equal in both directions, provided there is no internal leakage, and the flow can be calculated from geometry. AMR beds connected in parallel generally consist of a fluid circulator with constant unidirectional flow that is connected to a set of flow manifolds, with Ref. [4]-[6] as examples. Individual AMR beds are connected hydraulically in parallel with all other beds via the flow manifolds, and flow to each bed is controlled by a set of valves. Advantages of the parallel flow circuit are a more compact system and less expensive construction due to better utilization of the magnetic field. However, the parallel connection between beds means that the flow in each bed is not necessarily equal. Additionally, the total fluid flux in the hot-to-cold direction and the cold-to-hot direction in each bed is not necessarily equal, giving the possibility of unbalanced flow, which has been shown to drastically reduce AMR performance [7].

DTU has built a parallel fluid flow AMR with computer-controlled solenoid valves whose timing can be changed in real time. The regenerator consists of 13 fixed AMR beds filled with 10 layers of LaFeSiMnH materials and is coupled to a rotating, two-pole magnet [8]. The device is fitted with a gage to measure the torque applied to rotate the magnet and the temperature exiting each regenerator at the cold side is monitored, in addition to other AMR system parameters, such as frequency, system temperatures, and flow rate. We have measured that the outlet temperatures of individual beds can vary by several degrees, even when the device has an overall temperature span of less than 15 K. As the temperature of a single bed decreases, it becomes more magnetic and thus more attracted to the high-field regions of the rotating magnet. Especially with first order magnetic transition regenerator beds, the coldest beds cause a sharp increase in the torque required to rotate the magnet away from the cold regenerator and increase the time that the coldest regenerators are inside the magnetic field because the motor cannot rotate as quickly under the increased load. Because the flow control is position based, the coldest beds thus receive the most flow in the cold-to-hot direction, which further cools the beds. We found that reducing the valve opening angles in the cold-to-hot direction and/or increasing the valve opening angles in the hot-to-cold direction for beds that are colder than average improved AMR performance and reduced torque oscillations in the motor. Controlling valve timing based on the cold side fluid exiting temperature from individual valves has been shown to improve AMR performance when the flow circuit is connected in parallel.

Keywords: magnetic refrigeration, magnetocalorics,

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Giant Room-Temperature Magnetocaloric effect in low-cost $(\text{MnNiSi})_{1-x}(\text{FeCoGa})_x$ alloys

Subrata Ghosh(a)*, Arup Ghosh(b), Pintu Sen(c) and Kalyan Mandal(a)

(a) Department of Condensed Matter Physics and Material Sciences, S. N. Bose National Centre for Basic Sciences, Block-JD, Sector-III, Salt Lake, Kolkata 700106, India*Email: subrataghosh728@bose.res.in

(b) Condensed Matter Physics Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700064, India

(c) Physics Group, Variable Energy Cyclotron Centre, 1/AF Bidhannagar, Kolkata 700064, India

Abstract

Magnetic and structural transitions are found to coincide at around room-temperature in transition metal based $(\text{MnNiSi})_{1-x}(\text{FeCoGa})_x$ ($x = 0.15 - 0.17$) alloys which essentially leads to a coupled first-order magnetostructural transition (MST) from high temperature paramagnetic hexagonal structure (Ni₂In-type) to a low-temperature ferromagnetic orthorhombic structure (TiNiSi-type) and as a result, giant magnetocaloric effect (MCE) is observed in these alloys [1]. The alloys with $x = 0.15, 0.16$ and 0.17 exhibits isothermal magnetic entropy change (ΔS_M) as large as $\sim 25 \text{ J/kg-K}$ at 323 K, $\sim 31.1 \text{ J/kg-K}$ at 281 K, and $\sim 23.8 \text{ J/kg-K}$ at 213 K respectively due to field change of $\Delta H = 50 \text{ kOe}$ which is shown in **Fig. 1**. These materials may be considered as promising candidates for magnetic refrigeration due to their giant magnetocaloric properties with significantly large relative cooling power ($\text{RCP} = 191.8, 209.6$ and 139.2 J/kg respectively for $x = 0.15, 0.16$, and 0.17 due to $\Delta H = 50 \text{ kOe}$). Magnetocaloric response has been analyzed using Maxwell relation following both heating and cooling protocols and we observed that cooling mode is preferred to determine the ΔS_M precisely which is confirmed by the measured ΔS_M value using the Clausius-Clapeyron equation, from the analysis of universal scaling behavior of the calculated ΔS_M data and the calorimetry study of MCE.

Keywords: Magnetocaloric, Isothermal Magnetic Entropy change, Measurement protocols.

Theoretical approach for solid-state refrigeration on spin-crossover compounds

Bruno P. ALHO (a), Paula O. RIBEIRO (b), Rafael M. RIBAS (b), Vinicius S. R. DE SOUSA (b), Eduardo P. NOBREGA (b), Pedro J. VON RANKE (b)

(a) Instituto de Física Armando Dias Tavares, UERJ

Rio de Janeiro, 20550-013, Brazil, e-mail: brunoalho@gmail.com

(b) Instituto de Aplicação Fernando Rodrigues da Silveira, UERJ

Rio de Janeiro, 20260-232, Brazil.

The solid-state refrigeration comes as an alternative to the low efficiency and environmental unfriendly gas-compression refrigeration systems, due to an increase necessity, of saving energy consumption in cooling processes, as well as, of finding new environmental friendly materials to act as refrigerant. In order to describe the caloric refrigeration potential of a solid material two thermodynamic quantities are used: the entropy change in an isothermal process and the adiabatic temperature change, both calculated or measured upon applied external field variation.

Recently, spin crossover compounds, which usually shows a transition from a diamagnetic ($S = 0$) low spin (LS) state to a paramagnetic high spin (HS) state, were reported to present a high barocaloric potential [1, 2] which can be ascribed to the activation of the vibration quantum states in spin crossover transition.

In this work, we give an overview of our recent theoretical developments on spin crossover compounds focusing on its application to the solid-state refrigeration. In the last few years, we constructed a Hamiltonian to describe the microscopic interactions in spin crossover compounds. Our theoretical entropy includes the lattice, electronic and configurational coupled-contributions. In addition, we proposed an indirect method to measure, by means of a proper Maxwell relation for spin crossover compounds, the interested thermodynamic quantities [3]. We obtained, for some compounds [4], a huge caloric effect, which is ascribed to the coupling interactions between the crystal lattice (phonons) and the order parameter that describes the molar fraction of high spin molecules.

Acknowledgements:

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Thermal hysteresis of caloric materials and its impact on the systems efficiency

K. Bartholomé(a), T. Hess(a), L. Maier(a), P. Corhan(a), O. Schäfer-Welsen (a)

(a) Fraunhofer-Institut für Physikalische Messtechnik IPM, Thermische Energiewandler, Heidenhofstr. 8, 79110 Freiburg, Deutschland, kilian.bartholome@ipm.fraunhofer.de

Abstract

Cooling with caloric materials has the potential to replace compressor-based cooling systems in many applications in the future. In addition to the advantage of avoiding hazardous coolants, caloric materials promise a higher efficiency compared to compressor-based systems. However, prediction of potential efficiencies of caloric systems derived from basic material data can hardly be found in the literature. The aim of this work is to assess the efficiency potential of cooling systems using first-order caloric materials. Therefore, a relation between thermal and field hysteresis is theoretically derived. Based on this relation the performance of hysteretic first-order material can be predicted in a Carnot-like cycle and conclusions regarding the systems efficiency can be made.

As a main result a direct relation between thermal hysteresis and the expected maximum exergy or second-law efficiency of a caloric cooling device is presented. It is shown that the thermal hysteresis of caloric materials needs to be smaller than a certain fraction of the adiabatic temperature change in order to be able to compete with the efficiency of compressor based systems.

Keywords: Magnetocaloric, Material, Hysteresis, Efficiency

Numerical Investigation of Ferro and its Magnetization behaviour

Shubham Dalvi¹, Theo H. van der Meer¹, Mina Shahi¹

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

Magnetic Fluids or Ferrofluids (FF) are being widely used as the primary choice for transport medium in energy conversion devices based on MagnetoCaloric Effect (MCE). Owing to the stable, mono-disperse, colloidal suspensions of magnetic particles, the FF exhibit distinct hydrodynamic behaviour when exposed to an external magnetic field (H). Such unique characteristics are mainly attributed to the different magnetization (M) responses offered by the magnetic particles. These small particles contribute macroscopically to the various volumetric forces experienced by the FF such as Kelvin Force density (F_K) and the MCE as shown in Equation 1. Thus, to optimize a FF based energy transport device, it becomes essential to have in depth understanding of this multi-scale response, and its variation with respect to the different system variables. This can be achieved with the help of a robust numerical model which can precisely predict the M of FF and ultimately help in improving the overall performance of a system.

Using Computational Fluid Dynamics (CFD) approach, different discretization methods can be used to closely interpret the complex interplay between various hydro-thermal and magnetic parameters. In the present work, a numerical model is developed using Finite Volume Method in a C++ based open-source CFD framework OpenFOAM [1]. The conventional hydrodynamic equations (continuity equation, Navier - Stokes equation) and the Maxwell's Equation of 1

magneto-statics are solved along with an additional equation to model the magnetic response of FF. This magnetization behaviour can be replicated in several ways based on particle volume fraction (ϕ), FF viscosity (μ_{eff}), flow vorticity (ω), and H , with each having their own limitations as well as advantages [2]. Thus, for the present study, based on the comparisons available in the literature [3], an appropriate magnetization equation known as Debye relaxation mechanism is used and is shown in Equation 2.

The validity and accuracy of the above set of equations are then confirmed by comparing the results from the present work with the published literature (Papadopoulos et al. [4]) as shown in Figure 1. This validated numerical model is then used for analysing the FF performance under the field of solenoid as shown in Figure 2. The cylindrical geometry is intentionally selected as it is practically relevant for many energy transport devices. With the help of aforementioned numerical model, it is possible to locally visualize the internal distributions of pressure, velocity, temperature, and magnetization. This results in improved understanding of overall system and eventually in their enhanced functioning.

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Elastocaloric effects in natural rubber

M. Kaminski, G. F. Nataf and X. Moya

Department of Materials Science, University of Cambridge
Cambridge, CB3 0FS, 27 Charles Babbage Rd, Cambridge, UK

Natural rubber displays large elastocaloric effects when stretched/unstretched using small forces. Moreover, it is non-toxic and inexpensive, making it a promising candidate for new environmentally friendly and energy efficient solid-state cooling devices. However, before any applications can take place, it is important to understand in full the mechanistics of its elastocaloric response, and optimise it. Here, we combine infra-red imaging, Raman spectroscopy and finite-element modelling to explain elastocaloric effects in natural rubber, both on loading and unloading. This understanding should lead to the improvements in the elastocaloric response of natural rubber, and of elastic polymers in general.

New refrigeration systems based on force-induced reversible gas-liquid phase transition in elastic nanoporous carbon materials

Author: Hirotomo Nishihara,^a Masanori Yamamoto,^a Keita Nomura,^a Masashi Ito,^b Masanobu Uchimura,^b

Affiliation: ^aTohoku University, Japan, ^bNissan Motor Co., Ltd., Japan

Keywords: force-driven phase transition, elastic nanosponges, nanoporous materials, isotherms

Abstract (The abstract should be no longer than 500 words)

The electricity used for cooling, heat pumping, and refrigeration accounts for a large scale of energy consumption of mankind, and therefore, their improvement in the efficiency is of great importance in relation to the urgent energy problems. In addition, typical refrigeration systems use halocarbons as the refrigerants, and the greenhouse effects of fluorinated gases are our serious concern in relation to the environmental issues. As such, highly efficient refrigeration systems with water or alcohols as environmentally-friendly refrigerants are highly desired. Refrigeration systems containing porous adsorbents such as zeolites allow use water as the refrigerant, but their sizes are relatively large. Herein we report a new concept of refrigeration based on the gas–liquid phase-transition upon the mechanical deformation of elastic nanosponge materials (*Nat. Commun.* **2019**, *10*, 2559) such as zeolite-templated carbons (*Chem. Commun.* **2018**, *54*, 5648–5673; *Chem. Eur. J.* **2013**, *19*, 13009–13016) and graphene mesosponges (*Adv. Funct. Mater.* **2016**, *26*, 6418–6427), in which endothermic desorption and exothermic adsorption of refrigerants occur upon the mechanical deformation of the elastic materials. The gas–liquid phase transition of the green refrigerants has been reversibly controlled using the elastic nanosponges, and the significant cooling upon the compulsive phase transition has also been demonstrated. The theoretical investigation showed that the coefficient of performance (COP) is proportional to the reciprocal of the Young's modulus of the nanosponge materials, and is comparable to or even potentially higher than those of conventional air conditioners. These will provide new refrigeration systems with high efficiency and with no use of fluorinated refrigerants that cause the greenhouse effects.

Effect of Doping on Structural and Magnetocaloric Properties of Fe₂P-based Materials

Ivan BATASHEV(a), Gilles A. de WIJS(b), Niels H. van DIJK(a), Ekkes H. BRÜCK(a)

(a) Fundamental Aspects of Materials and Energy, TU Delft.

Delft, 2629JB, The Netherlands, I.Batashev@tudelft.nl

(b) Institute of Molecules and Materials, Radboud University.

Nijmegen, 6525AJ, The Netherlands, G.deWijs@science.ru.nl

EXTENDED ABSTRACT

Properties of extensively studied (Fe,Mn)₂(Si,P) system, well-known for its promising magnetocaloric qualities, are greatly influenced by the crystallographic parameters of this hexagonal system, particularly by c/a ratio. Doping results in different equilibrium volumes and c/a ratios leading to changes of the exchange interactions between the two magnetic sublattices present in this system. In this work, first-principles calculations are used to determine the site preferences and optimal lattice parameters for the substitutions with elements from 2nd, 3rd and 4th periods. We demonstrate the effect of these substitutions on the Curie temperature, magnetic properties, and electronic structure of the Fe₂P-based compounds for different amounts of each dopant element. Understanding the effect of doping gives the ability to fine-tune magnetocaloric properties and create better materials for practical applications, both for cooling and energy conversion purposes.

Keywords: magnetocaloric materials, Curie temperature, ab-initio calculations, Fe₂P.

Guided Discovery of Magnetocaloric Materials

Nikolai A. Zarkevich(a), Duane D. Johnson(a,b)

(a) Ames Laboratory, U.S. Department of Energy, Ames, IA, 50011-3020, USA, e-mail: zarkev@ameslab.gov; (b) Iowa State University, Ames, IA, 50011, USA

Abstract

Accelerated discovery and design of novel caloric materials in the caloric materials consortium - CaloriCool® - is based on the theoretical and computational methods that serve as a guide for experimental efforts. We investigate the computational methods that provide thermodynamic properties in relevant phases at or near a reversible diffusionless solid-solid phase transition, accompanied by the caloric effect. We apply those methods for the high-throughput screening of the dominant caloric contributions. The outcomes of the CaloriCool® approach include discovery of several novel classes of materials with a giant magnetocaloric response.

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Modeling and Optimal Design of a Novel Solid-State Thermo-Magneto Generator Utilizing Low-Temperature Geothermal Fluid Resources

Mingkan Zhang(a), Ayyoub M. Momen(a), Kyle Gluesenkamp(a)

(a) Oak Ridge National Laboratory

Oak Ridge TN, 37930, United States, zhangm1@ornl.gov

Abstract

The importance of the direct use of the low temperature geothermal heat is recognized in the recent geothermal vision study. Electricity generation from geothermal resources occurs predominantly at high-temperature ($>150\text{ }^{\circ}\text{C}$) and more efficient electricity generation technologies are still required at lower temperatures (below $150\text{ }^{\circ}\text{C}$) to make lower temperature geothermal resources economically viable to produce. In this study, a novel solid-state thermo-magneto generator is introduced to transfer low-grade thermal energy directly to electricity. The solid-state thermo-magneto generator is based on the phenomenon that the magnetic permeability of a magnetocaloric material (MCM) is tunable according to the change of temperature. The permeability change results in the magnetic field change leading to the electricity generation. Therefore, by control the MCM temperature, it is possible to generate electricity. A model has been developed using COMSOL to investigate the performance of the solid-state thermo-magneto generator. Based on the model, an experimental design is conducted to obtain the optimal design of the prototype.

Keywords: magnetocaloric materials; generator; low-grade energy; modeling.

A dynamic active elastocaloric regenerator

David CATALINI(a), Suxin QIAN(b), Yunho HWANG(a), Reinhard RADERMACHER(a), Ichiro TAKEUCHI(c)

(a)Center for Environmental Energy Engineering, Department of Mechanical Engineering, University of Maryland, College Park, Maryland, 20742, United States, yhhwang@umd.edu, (b)Xi'an Jiaotong University, Department of Refrigeration and Cryogenic Engineering, Xi'an, Shaanxi, 710049, China, (c)Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, 20743, United States

Abstract

Current designs for active elastocaloric regenerators operate in a stepwise operation. The main steps in the cycle are: applying stress to the elastocaloric regenerator, rejecting the latent heat to the heat sink, relieving the stress, and absorbing heat from the heat reservoir (and thus supplying cooling). For these heat exchange steps, a heat transfer fluid (HTF) is used as an intermediary between the elastocaloric regenerator, sink, and reservoir. The temperature difference that can be established between the heat sink and reservoir, the temperature lift and the cooling capacity are dependent on the operating conditions and system characteristics. Operating conditions include HTF flow rate, duration of the heat transfer steps, and total cycle time. System characteristics include the amount of elastocaloric material in the regenerator and its specific geometric characteristics like length and wall thickness. Operating conditions and system characteristics are very much coupled and currently the way to increase cooling capacity has been increasing the amount of elastocaloric material. With this, larger driving systems are required, capable of either providing a larger force or a larger displacement. In this work, we investigated another way to increase the cooling capacity without increasing the amount of elastocaloric material: increasing the operating frequency. As the frequency increases, the operation approaches a quasi-continuous operation. By operating continuously, another concept of mechanical resonance phenomena allowing dynamics to take up some of the loading and decrease the loading requirements of the driver could be realized. This system concept is equivalent to a spring-mass-damper system. The spring and the damper are represented by the elastocaloric material (through non-linear superelastic behaviour and the transformation hysteresis), and a new component, an oscillating mass, acts as a medium to periodically store and release kinetic energy and assist the dynamic loading process. A unique fixture was built to test the dynamic behaviour of the elastocaloric material and extract the stiffness and damping coefficients experimentally. We determined that the dissipated energy does not make the system overdamped and it was calculated that the dynamic amplification factor at the natural frequency is approximately 4, which means that if operated in resonance, the load required to actuate the system with respect to the static operation is close to 4 times smaller. This continuous operation mode also requires a different heat transfer fluid flow control strategy as compared to the discontinuous operation. As a starting point for the analysis, a sinusoidal flow rate function was used in a numerical study of the performance of the system. It was determined that there is an optimal phase shift between the flow rate function and the strain function of 3.45 rad. A set of design parameters were studied to determine the feasibility of such a design and an estimation of the potential benefits of synergy in a system tuned for optimal thermal and mechanical behaviour.

Keywords: Elastocaloric, Regenerator, Resonance.

Magnetocaloric properties and cooling performance analysis of the

composite materials $(1-x)\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3/x\text{Mn}_2\text{O}_3$

A. El Boukili(a, b, *), O. Mounkachi(a), M. Hamedoun(b), A. Benyoussef(a, b, c),
M. Ballid and H. Ez-Zahraouy(a)

(a) LaMCScl Laboratory, B.P. 1014, Faculty of science-Mohammed V University, Rabat, Morocco.

(b) Materials and Nanomaterials Center, MASclR Foundation, B.P. 10100-Rabat, Morocco.

(c) Hassan II Academy of Science and Technology, Rabat, Morocco.

(d) LERMA, ECINE, International University of Rabat, Parc Technopolis, Rocade de Rabat-Salé, 11100, Morocco.

*Email address: ezahamid@fsr.ac.ma; elboukiliaicha@gmail.com

Abstract

Perovskite manganite $(1-x)\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3/x\text{Mn}_2\text{O}_3$ ($x=0, 0.05, 0.1, 0.15, 0.20$) composites were prepared by solid state reaction method. X-ray diffraction measurements were used to confirm the crystal structure and the average crystallite size of samples. Their magnetic, magnetocaloric and heat capacity properties display a second order magnetic phase transition at 260 K. The maximum magnetic entropy change was found to be 5.33 J/kg K for $x=0.1$ of Mn_2O_3 under 5T. The relative cooling power (RCP) was found (235 J/kg) to largely exceed the reported experimental values in early works and enhanced with more than 20% compared with RCP of the mother compound under 32 kOe without changing the curie temperature. AMR-numerical analysis has been carried out aiming to get more insight on the thermodynamic performance of investigated composite. The implementation of $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ material as a refrigerant and the mixture water/EG as the coolant in a 1T-AMR (Active Magnetic Refrigeration) device would enable us to generate a maximum no-load temperature span of about 13.75 K and a maximum cooling power of 16 W for low operating frequency of 0.5 Hz.

Keywords: Magnetocaloric, COP, AMR cycle, Composite, Solid state reaction.

Magnetocaloric effect in cyclic magnetic fields: search for near-perfect refrigerant

Akhmed Aliev(a), Adler Gamzatov(a), Nurizhat Abdulkadirova(a), Piotr Gębara(b) Kazimir Yanushkevich(c) and Gennady Govor(c)

(a) Amirkhanov Institute of Physics of Daghestan Federal Research Centre of Russian Academy of Sciences, Russian Federation, Makhachkala, 367015, Russia, lowtemp@mail.ru (b) Institute of Physics, Częstochowa University of Technology, Częstochowa, 42-200, Poland

(c) Scientific-Practical Materials Research Centre of the National Academy of Sciences, 220072 Minsk, Belarus

Abstract

There are many requirements for materials that will be used in magnetic cooling technology; the main one is that the material should have a giant magnetocaloric effect (MCE) at room temperature. In fact, this requirement should be clarified and strengthened. Namely, the MCE should be giant and stable under the long-term effects of a cyclic magnetic field and weakly dependent on the frequency of change of the magnetic field. Most of the promising magnetocaloric materials are first-order magnetostructural phase transition materials. Due to the structural changes that are characteristic of these materials, accompanied by large changes in the volume of the lattice and hysteresis phenomena, the stability of the magnetocaloric properties in such materials is not obvious.

This work presents the results of direct measurements of the magnetocaloric effect in $\text{La}_{0.9}\text{Pr}_{0.1}\text{Fe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1}$ alloy. Direct measurements of the adiabatic temperature change (ΔT_{ad}) were carried out in cyclic magnetic fields with a frequency of up to 30 Hz. The maximum ΔT_{ad} values were 2.8 K, 6.71, and 8.63 K at temperatures of 265, 268.5, and 270 K in magnetic fields of 1.8, 5, and 8 T in amplitude, respectively. Studies in heating and cooling run in a 1.8-T field show that the width of the temperature hysteresis is small and does not exceed 0.5 K. The width at a half-maximum of the ΔT_{ad} (T) curve reached 20 K in a magnetic field of 1.8 T and almost 40 K in a magnetic field of 8 T.

The value of the effect at a frequency of 1 Hz was 1.18 K and 1.13 K at a frequency of 22 Hz, i.e., the decrease in effect was less than 5%. The width of the effect was almost unchanged and amounted to 12 K at the half-maximum of the effect that means that the upper limit of the operating frequencies of magnetic refrigerators was not limited to 22 Hz in terms of the value effect when using $\text{La}_{0.9}\text{Pr}_{0.1}\text{Fe}_{11.2}\text{Co}_{0.7}\text{Si}_{1.1}$ alloy as a refrigerant.

Studies the temporal dependences of the MCE under a continuously applied cyclic magnetic field showed a complete absence of MCE degradation in the alloy in both strong and weak cyclic magnetic fields.

For comparison, the results of the study of MCE in MnAs compounds, in which a giant MCE is also observed, are presented. In contrast to the first composition, the effect of long-term exposure to a cyclic magnetic field is noticeable in these compounds: near the temperature of the magnetic phase transition, the phenomenon of MCE degradation is observed, and above the transition temperature, the phenomenon is strong, it becomes weaker at the temperature of the maximum of the effect, and hardly manifests itself below the transition temperature.

The study was supported by RFBR-BRFBR (Project No. 20-52-00047).

Keywords: Magnetocaloric effect, cyclic magnetic fields, field dependence, degradation

Signal-to-noise: experimental challenges characterizing

magnetocaloric materials in active regenerator cycles

Rowe, Andrew(a), Christiaanse, Theo(a), Trevizoli, Paulo(b)

(a) Institute for Integrated Energy Systems, University of Victoria, Victoria, V8W2Y2, Canada, arowe@uvic.ca, (b) Federal University of Minas Gerais, Belo Horizonte, 31270-901, Brazil

Abstract

Caloric materials offer new technology options for cooling, heating, and heat-to-work transformations. As with most energy conversion devices, material science is the foundation on which these devices are created (Fähler et al., 2012). Bridging the divide between property measurements and commercialization of caloric devices requires experimental characterization of materials undergoing repeated cycling with coupled transfer of heat. No standard instrument exists, the design space is vast, and ultimately, bespoke experiments are often constrained by cost (Trevizoli et al., 2016). Here we review some of the challenges we have faced regarding the fabrication and experimental characterization of active regenerators. Many active materials are available in limited quantities and shapes. Materials with first order phase transitions have narrow active ranges, highly non-linear properties, and hysteresis. In the case of permanent magnet magnetocaloric systems, material volumes are limited by magnet structure, peak field, and spatial distribution of flux. The impacts of these many constraints can lead to the well-known problem where the response of dependent variables due to changes in independent parameters is difficult to resolve i.e. poor signal-to-noise. This may be due to low device sensitivity, or systemic errors in an experiment. With low-power devices (typical for generic test devices) and imperfect thermal isolation, transient response should be considered when reporting cyclic-steady state conditions (Christiaanse et al., 2016). Sometimes this is difficult to determine, or it is ignored. In addition to itemizing various challenges with experimental characterization of active regenerators, we provide examples arising in our experimental investigations (Christiaanse et al., 2019). Collectively, poor signal-to-noise in experiments impacts model confidence and the results of model-based design optimization.

Keywords: Magnetocaloric, systems, experimental characterization.

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Direct electrocaloric properties measurements on lead-free Samarium doped Barium Titanate ceramics

Miriam ACHKAR, Eliane BSAIBESS, Said BELLAFKIH, Didier FASQUELLE, Abdelhak HADJ SAHRAOUI, Stéphane LONGUEMART

Unité de Dynamique et structure des Matériaux Moléculaires, Université de Littoral Côte d'opale, Dunkerque, 59140, France.

miriam.p.achkar@gmail.com

Keywords: Electrocaloric, ceramics, ferroelectrics, calorimetry.

Vapor compression refrigeration is the most common refrigeration technology. However, it uses refrigerants that are harmful to the environment. As alternative solutions, several technologies based on solid state refrigeration are being developed. One of these alternatives is Electrocaloric (EC) refrigeration, which has attracted a growing interest in recent years upon discovery of a significant electrocaloric effect in lead-based thin film. Electrocaloric effect (ECE) is a physical phenomenon present in polar materials and requires the application and removal of external electric field. This, results in an adiabatic reversible change of temperature or an isothermal variation of entropy [1].

Nowadays, the majority of the studied electrocaloric materials are ferroelectric, because they have a very important EC effect near phase transition. These materials may be divided into two categories: normal ferroelectrics and relaxor ferroelectrics. Relaxor ferroelectrics seem to be more attractive than normal ferroelectrics since they allow to exploit the ECE over a wider temperature range [2].

ECE is largely studied in ceramics because they are easy to manufacture. The most studied ceramics are of the perovskite (ABO_3) type, in particular lead-based materials. Since the use of lead is being prohibited in a growing number of countries, for example in Europe by the European Restriction of Hazardous Substances (RoHS) directive, these materials can be substituted by perovskite materials based on barium titanate ($BaTiO_3$), which are among the most well-known lead-free ferroelectric materials having excellent dielectric and ferroelectric properties [3].

Works on ECE of doping $BaTiO_3$ with samarium (BTO-Sm) are very rare. To our knowledge, a single electrocaloric study on this compound has been reported with a single concentration of samarium (4%) [4]. In this work BTO-Sm was synthesized using sol-gel method. Here, samarium was incorporated into the A site for obtaining the composition $Ba_{1-x}Sm_xTiO_3$, with x from 0 to 0.06. Structural characterizations (XRD, SEM), impedance spectroscopy and photo-thermal methods for electrical and thermal properties measurements have been carried out. For the electrocaloric properties, a direct method implying the use of an adiabatic calorimeter has been employed. Results shows that the substitution leads to a decrease in the temperature at which the maximum EC effect occurs and a widening of the temperature range where the EC effect may be exploited, making (BTO-Sm) ceramics good candidates for EC refrigeration.

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Compact, Low-Cost Magnet Designs for Magnetic Refrigeration

J. Slaughtera, L. Griffith¹, A. Czernuszewicz¹, and V. Pecharsky^{1,2}

¹Ames Laboratory of the US Department of Energy, Iowa State University Ames, IA 50011,

julies1@ameslab.gov ²Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011

Abstract

Adoption of magnetocaloric refrigeration technology has been impeded by high costs of permanent magnet assemblies (Russek and Zimm 2006). Numerous studies on magnet design largely focused on minimizing magnet volume needed to generate high fields (Bjørk et al. 2010) without accounting for use of the magnet in a system. We present specific metrics of a compact magnet for Gd-based regenerators targeting magnetic fields of less than 1.0 T (Gottschall et al. 2019).

One well-known figure of merit for permanent magnets relates field strength, B , and volume of magnetic field, Vf , to the remanence, Br , and volume of permanent magnet, Vm :

$M = \int B^2 dV / \int Br^2 V_m dV$ with $M \leq 0.25$ (Jensen and Abele 1996). In a system with stationary regenerator(s) and magnets rotating with a constant angular velocity, a regenerator ideally spends equal time in highest and lowest (zero) magnetic fields to maximize performance. We use a figure of merit that has a value of 1 for equal time in high and low fields with lower values indicating an imbalance.

$$b = \frac{1}{2} - \frac{|\theta_{low} - \theta_{high}|}{\theta_{total}} \leq 1$$

The transition between low and high fields should be as narrow as possible since regenerator performs no useful work in this transition period. A simple ratio of the portion of the cycle spent in the high and low fields to the total circular path provides a good metric of the transition width.

$$a = \frac{\theta_{low} + \theta_{high}}{\theta_{total}} \leq 1$$

The figure shows a particular field profile as a function of rotation angle for a permanent magnet assembly. θ_{high} is taken as the period when $B > 0.9 B_{max}$; θ_{low} is the period when $B < 0.1 B_{max}$. For this particular magnet design, $b = 0.985$ and $a = 0.906$, indicating good balance of high and low fields and a narrow transition between high and low fields. M for this magnet is 0.109 which compares favorably with other designs (Bjørk et al. 2010) and has a relatively small magnet volume. It also has desirable features such as low rotary inertia, low-cost block-shaped magnets, and high magnetic permeability materials making up the remainder of the magnetic circuit.

This work is carried out with joint funding from the Advanced Manufacturing Office and the Building Technologies Office of the Office of Energy Efficiency and Renewable Energy of the United States Department of Energy (USDOE). The research was performed at the Ames Laboratory. Ames Laboratory is operated for the USDOE by Iowa State University under contract No. DE-AC02-07CH11358.

Keywords: Magnetocaloric, magnet design, permanent magnet.

Figure: Simulated magnet design showing fractions used for figures of merit.

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Numerical and experimental study of a thermomagnetic generator for energy conversion

Michel Risser(a), Sergiu Lionte(a), Radia Hamane(b), Anna Ouskova-Leonteva(c), Nicolas Brochard(a), Christian Muller(a)

(a) Ubibblue, Entzheim, 67960, France, michel.risser@ubibblue.com

(b) CRISMAT-ENSICAen, Caen, 14050, France

(c) CSTB-ICube, Strasbourg, 67000, France

Abstract

Climate and energy challenges require reducing our energy consumptions, working on the efficiency of energy conversion systems and stopping the release of greenhouse gases. Energy conversion from low temperature levels represents a promising market for magnetocaloric (MC) systems suitable for renewable heat sources or waste-heat recovery.

Previous experimental results obtained in real operating conditions provided us feedbacks for the design of MC machines in the field of refrigeration, as presented by Lionte et al., (2018) for small-scale systems, or by Chaudron et al., (2018) for a large-scale remote cooling system. These MC refrigeration system designs are proving to be appropriate candidates to produce reversible machines targeting energy conversion.

In this paper, we present a theoretical and experimental study of a thermomagnetic (TM) energy conversion system, which is coupled with an electric generator. This system is designed to be adapted to low temperature levels: hot source from 50 to 60°C and cold source at room temperature.

We use a multi-physics and multi-scale numerical model of Active Magnetic Regenerator (AMR) simulation. Theoretical data sets based on experimental measurements are required for good energy conservation in the simulations, and therefore a reliable assessment of the energy conversion yield (Risser et al., 2012) for the TM system. The MC material data of FeSiLa-based compounds are measured experimentally for few Curie Temperatures (T_c). These data can then be reproduced on demand, using a theoretical model of magnetic materials (Hamane et al., 2020) on the entire T_c range of the required temperature span.

The numerical model of the MC system is used as an evaluation function for an evolutionary optimization algorithm. This stochastic optimization method makes it possible to automate and to speed up the research process of the optimal system design, related with given specifications (Ouskova-Leonteva et al., 2019).

A specific TM system thus dimensioned has been manufactured. Its performances have been mapped and compared with calibration simulations through behaviour maps. A parametric study based on the optimization, from the point of view of both the energy efficiency and the power density, is also presented in this work. The results show that such TM systems could represent good candidates for waste heat recovery or renewable heat sources energy conversion.

Keywords: Energy conversion, Waste heat recovery, Evolutionary algorithm, Magnetocaloric materials.

Cycle Analysis and Performance Study of Pulsed Magnetic Refrigeration

Xiao Tong(a), Limei Shen(a), Liang Li(b), Huilin Li(a), Huanxin Chen(a), Jiaqi Xu(a),

Yiliang Lv(b), Zhang Tu(b)

(a) School of Energy and Power Engineering, Huazhong University of Science and Technology
Wuhan, 430074, China, ep_shenlimei@hust.edu.cn

(b) Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology
Wuhan, 430074, China, Liangli44@mail.hust.edu.cn

EXTENDED ABSTRACT

To avoid the greenhouse gas emission caused by vapor compression refrigeration, alternative refrigeration technology is receiving more and more attention. Magnetic cooling is one of the most promising alternatives to vapor compression refrigeration with the characteristics of high efficiency and environmental friendliness. Nevertheless, magnetic refrigeration is still limited in cooling capacity and temperature span due to the influence of magnetic material properties, magnetic field strength and heat transfer mechanism, etc. The existing magnetic refrigeration systems are mostly based on permanent magnets, which have the problems of low magnetic field intensity, uneven magnetic field distribution and relative motion between magnet and magnetocaloric materials to complete magnetization and demagnetization. In view of the above problems, this paper proposes the application of pulse magnetic field to magnetic refrigeration innovatively based on the advantages of pulse magnetic field. The cyclic mechanism of pulsed magnetic refrigeration is qualitatively analyzed, and its performance is studied by numerical simulation.

The magnetocaloric effect of gadolinium under high magnetic field strength is calculated by the average molecular field theory. And a numerical model based on the transient energy equations is present to simulate the steps of pulse magnetic refrigeration cycle and evaluate the performance of the system in terms of cooling capacity, heat release, power consumption and the Coefficient of Performance (COP). The effects of heat transfer time, fluid velocity, pulse magnetic field intensity, waveform, pulse width and pulse interval on the performance of pulsed magnetic refrigeration system are studied with this model. The numerical results indicate that heat transfer time and fluid velocity have significant effects on cooling capacity (Q_c) and heat release (Q_h) of pulsed magnetic refrigeration system. The refrigeration capacity and heat release increase with the increment of pulse magnetic field intensity and the maximal Q_c of 1.85 kW/kg and Q_h of 1.98 kW/kg are obtained with the magnetic field of 60 T, which are 14.9 times and 20.9 times respectively at 1 T. The results show better performance when compared to traditional magnetic refrigeration system under the same working condition.

Keywords: pulse magnetic field; Magnetic refrigeration; cycle; performance study; numerical simulation

Designing a hydraulic management system for a large scale magnetic refrigerator

Diego DOS SANTOS, Sergio L. DUTRA, Marcelo C. RIBEIRO, Anderson M. LORENZONI,

Gabriel M. DO ROSÁRIO, Maria C. R. SILVA, Gislaine HOFFMANN,

Guilherme F. PEIXER, Jaime A. LOZANO(a), Jader R. BARBOSA Jr.

POLO – Research Laboratories for Emerging Technologies in Cooling and Thermophysics,

Department of Mechanical Engineering, Federal University of Santa Catarina

Florianópolis, SC, 88040-900, Brazil

(a)e-mail: jaime@polo.ufsc.br

The overall performance of caloric devices is strongly dependent on the working frequency and on the fluid flow rate through the active caloric regenerator (ACR). Usually, these operating parameters are set by the hydraulic management system (HMS), which controls the alternating fluid flows through the ACR. Typical HMS operate over narrow ranges, so other subsystems such as the magnetic circuit (MC) and the ACR are generally oversized. Since these subsystems contain the most expensive components of the device, the design of the HMS becomes key to simplify the remaining components, leading to an increase of the system compactness, reducing the overall cost of the device. Thus, this work aims to present the development of an HMS for a magnetic refrigeration unit (MRU) that will operate an air conditioner. The project requirements demand an HMS capable of providing alternating fluid blows for 16 active magnetic regenerators (AMRs) with a mass flow rate of up to 1000 kg/h per regenerator and an AMR frequency of 5 Hz. The main HMS

design constraint is a maximum pressure drop of 1 bar, aiming for a low power consumption.

Several works in the literature have proposed different HMS configurations for magnetic refrigerators; some researchers have developed personalized HMS systems, such as rotary valves, while others have adopted electronically-actuated valves, such as solenoid valves. In this work, an experimental apparatus (Figure 1) has been developed to evaluate both, a personalized mechanically-actuated HMS system, composed of valves actuated by cams, and commercially available solenoid valves. Both HMS systems are evaluated by three different experimental analyses to verify which system will fit best the requirements of the MRU application, such as operating at high frequencies with an adequate fluid flow management and with low power consumption.

Firstly, a single valve test analysis is carried out to investigate the flow restriction, sealing, leakage, delay, and actuation load with respect to defined geometric characteristics of the valve body, seat, and spring. Then, a unitary valve system test analysis is performed, where a set of valves were actuated simultaneously, either by a cam or by a logical system, and the relation between the valve position and the fluid flow profiles were evaluated. The final test consists of operating the complete system in a condition similar to that of the application in the MRU, where system dynamics, recirculation effects, and the overall operating parameters are evaluated to verify the HMS performance.

To date, both systems have performed satisfactorily in single and unitary tests for operating frequencies up to 5 Hz and fluid flow rates larger than 1000 kg/h (Figure 2). Other experimental tests are being performed to verify the pressure drop and power consumption of each HMS system.

Keywords: caloric devices; magnetic refrigeration, hydraulic management.

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Can Gadolinium compete with La-Fe-Co-Si in a thermomagnetic generator?

Daniel DZEKAN(a,b), Anett DIESTEL(a), Dietmar BERGER(b), Kornelius NIELSCH(a,b), Sebastian FÄHLER(a)

(a) Leibniz IFW Dresden

Dresden, 01069, Germany, d.dzekan@ifw-dresden.de

(b) TU Dresden

Dresden, 01069, Germany

EXTENDED ABSTRACT

A thermomagnetic generator is a promising technology to harvest low temperature waste heat and convert it into electricity. To make this technology competitive with other technologies for energy harvesting near room temperature, the optimum thermomagnetic material is required. Here we compare the performance of a state of the art thermomagnetic generator using Gadolinium and La-Fe-Co-Si as thermomagnetic material, which exhibit strong differences in thermal conductivity and type of magnetic transition. Gadolinium is the established benchmark material for magnetocaloric cooling, which follows the reverse energy conversion process as compared to thermomagnetic energy harvesting. Surprisingly, La-Fe-Co-Si outperforms Gadolinium in terms of voltage and power output. Our analysis reveals the differences in thermal conductivity are less important than the particular shape of the magnetization curve. In Gadolinium an unsymmetrical magnetization curve is responsible for an uncompensated magnetic flux, which results in magnetic stray fields. These stray fields represent an energy barrier in the thermodynamic cycle and reduce the output of the generator. Our detailed experiments and simulations of both, thermomagnetic materials and generator, clearly reveal the importance to minimize magnetic stray fields. This is only possible when using materials with a symmetrical magnetization curve, such as La-Fe-Co-Si.

Keywords: Thermomagnetic energy harvesting, Gadolinium, Thermomagnetic generator, Magnetocaloric materials, Thermomagnetic materials

Bending: a smart way to actuate elastocaloric effect

Agata Czernuszewicz(a), Lucas Griffith(a), Alexander Scott(a), Julie Slaughter(a), and Vitalij Pecharsky(a,b)

(a) Ames Laboratory of the US Department of Energy, Iowa State University, Ames, IA 50011, U.S.,
acz@ameslab.gov

(b) Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, U.S.

Abstract

Development of elastocaloric heat pumps for near room temperature applications suffers from high force requirements and low fatigue life of active materials in which elastocaloric effects are actuated by either tensile or compressive forces. Generally, stresses required to achieve useful strains and adiabatic temperature changes in tension (Wu, Ertekin, and Sehitoglu 2017) are relatively low, yet materials under tension are susceptible to crack propagation (Hou et al. 2018) and early failure. While less destructive, axial compression is limited to bulk shapes resistant to buckling. Both tension and compression can be realized in thin layers, e.g., strips, sheets, and plates, by bending, where the inner side of the deflection curvature is under compression, while the outer side is under tension. Thus, simple bending of elastocaloric materials does not prevent early failures.

To overcome these issues and allow actuating elastocaloric effect by bending, while ensuring that active material is entirely in either compression or tension, we arrange elastocaloric layers into composite structures with polymer supports. The force needed to achieve a certain strain in the elastocaloric layer is lower than the force required to axially actuate the material. Different configurations of the composite structures were designed, manufactured, and tested with NiTi (nitinol) strips as active material and PEEK (polyetheretherketone) as support. For tension, elastocaloric strips were clamped to the support beams; for compression the elastocaloric strips were framed into the support beams. Maximum adiabatic temperature changes demonstrated to date are 19 K at 5% strain in tension and 8 K at 2.5% strain in compression with the forces reduced over 50% when compared to axial tension and compression. When properly manufactured, composite structures withstand repeated loading without failure.

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Keywords: Elastocaloric cooling, NiTi, Solid-state refrigeration, Superelasticity.

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Purely electronic mechanism for first-order ferromagnetic transitions: an itinerant electron positive feedback and Fermi surface topological change

Eduardo Mendive Tapia(a,b), Durga Paudyal(c), Leon Petit(d), and Julie B. Staunton(b)

(a) Department of Computational Materials Design, Max-Planck Institut für Eisenforschung GmbH, Düsseldorf, 40237, Germany, mendive@mpie.de, (b) Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom, (c) The Ames Laboratory, U. S. Department of Energy, Iowa State University, USA, (d) Daresbury Laboratory, Warrington, WA4 4AD, United Kingdom

Abstract

Refrigeration and air conditioning are crucial in modern life and in adapting to climate change. In this context, the behavior of magnetic materials around discontinuous phase transitions has great promise for new, energy efficient, and environmentally friendly solid-state cooling technologies. Huge exploitable field-induced entropy and temperature changes typically result from the coupling between a material's spin polarized interacting electrons and the crystal structure, i.e. a magnetostructural effect (Bean and Rodbell, 1962). However, magnetostructurally driven cooling responses are nearly always degraded by hysteresis. We present a first-principles disordered local moment theory (Gyorffy et al., 1985 and Mendive-Tapia and Staunton, 2019) able to find mechanisms for first-order magnetic phase transitions which are purely electronic in origin, thus avoiding the need for a magnetostructural coupling. We show that this electronic mechanism arises from a mutual feedback between magnetic ordering, associated to different orientational arrangement of local magnetic moments, and the electronic structure. In particular, the theory presented is used to explain the hysteresis-free giant cooling properties recently measured in a ferromagnetic divalent rare earth orthorhombic compound Eu₂In (Guillou et al., 2019), as shown in panels (a) and (b) in the figure below. It is demonstrated that a topological change of the itinerant electron Fermi surface produces a positive feedback on the magnetic interactions, which in turn generates a discontinuous character for the paramagnetic-ferromagnetic phase transition of Eu₂In (see panel (c) of the figure below). Results will be compared with the hexagonal Gd₂In counterpart, which exhibits a second order ferromagnetic transition instead and so it will serve to illustrate and contrast our results. First principles magnetic free energies, heat capacities, Fermi surfaces, density of states, and magnetic local moment interactions, and their crucial dependence on ferromagnetic order underlying the mechanism, will be shown. This work lays down a groundwork to investigate why discontinuous phase transitions of this sort are non-hysteretic as well as to search for new materials.

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Experimental Research on the Time Sequence Matching of Magnetic Field and Flow Field in Active Magnetic Regenerator

HAI Peng¹, LI Zhenxing^{1,2*}, LI Ke¹, HUANG Hongmei^{1,2}, ZHENG Wenshuai^{1,2},
GAO Xinqiang¹, DAI Wei^{1,2}, SHEN Jun^{1,2}

Since the first magnetic refrigeration prototype in 1976[1], room temperature magnetic refrigeration, as an emerging refrigeration technology, has received more and more attention due to its environmental protection, potential high efficiency, and safe and reliable operation. Although the current magnetic refrigerators have obtained a higher refrigeration capacity, for example, in 2015, Li Zhenxing et al. [2] obtained a cooling capacity of 47W / kg at a temperature span of 7K., it is still necessary to optimize and improve magnetic refrigerators to obtain better performance. In the improved research, the time sequence matching of magnetic field and flow field is one of the important factors affecting the performance of the prototype. In recent years, scholars from Brazil, Slovenia, and Canada [3-5] have carried out related studies. The experimental results show that [4] in the continuous magnetic field profile, the operation strategy of low flow time ratio has obtained a larger cooling temperature span. The long flow time accounts for a lower pressure loss. Based on the developed magnetic refrigerator with nested concentric Halbach magnets [2], this paper conducts experimental research on two different operating strategies (intermittent operation and continuous operation of magnet). Two timing strategy diagrams are shown in Figure 1. The regenerator in the platform is filled with 352.6 g gadolinium spheres, and the nested concentric Halbach magnet array can provide an average magnetic field strength of 0.06-1.40 T. In the intermittent timing study, the platform obtained a cooling temperature span of 24.1 K at a frequency of 0.5 Hz and a utilization factor of 0.52, which is 2.5 K higher than the temperature span of the continuous timing strategy. In the follow-up frequency conversion research, the prototype obtained a maximum cooling temperature span of 26.6 K at 0.75 Hz, and a cooling capacity of 20 W at a temperature span of 16.9 K. Compared with the continuous sequence, the intermittent sequence can obtain a larger temperature span, and the prototype runs less smoothly and consumes more power. The dependence of temperature span and power consumption on utilization factor under no heat load condition is shown in Fig. 2.

Key words: active magnetic regenerator; intermittent sequence; continuous sequence; temperature span; power

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Experimental validation of 2D-Multiphysics numerical simulations applied to long time AMR cycles

Antony Plait, Thierry de Larochelambert, Stefan Giurgea, Christophe Espanet

FEMTO-ST Institute, Univ. Bourgogne Franche-Comté, CNRS, Belfort, 90000, France

antony.plait@gmail.com

Abstract

The Energy Department of the FEMTO-ST Institute is developing large theoretical and experimental research on high efficiency magnetocaloric refrigeration for several years. The analysis of the active magnetic regenerative (AMR) cycles for different waveforms of both the magnetic field and the fluid velocity is an essential tool for designing and implementing efficient heating and cooling applications based on the magnetocaloric effect.

Our laboratory developed first a powerful electromagnet as magnetic source composed of four coils wound on a soft ferromagnetic eight-shaped yoke, which induces 1 T magnetic field short pulses inside a 21 mm air gap. The fluidic device is a hydraulic cylinder producing precise flow sequences through a specific Plexiglas® case housing a built-in magnetocaloric regenerator and two 316L steel micro-heat exchangers. This module is inserted and positioned at the air gap center. The magnetocaloric regenerator consists of 14 pure gadolinium plates, spaced 0.5 mm apart, through which Zitrec™ flows as a cooling fluid.

The waveform of both the magnetic field and the fluid velocity is an important control means for obtaining optimum results (temperature gap, cooling power, etc.). For this purpose, a Hall effect sensor is glued on one polar piece of the electromagnet, and a magnetic position transducer measures the instantaneous piston displacement of the hydraulic device. Precise control and synchronization of both the applied magnetic field and the fluid flow are obtained by choosing operating frequencies as well as fluid displacement ratios in a LabVIEW™ parametric controlled regulation and monitoring program. Besides, in order to investigate the phenomena occurring in the regenerator, thermocouples and pressures sensors are immersed in the fluid at both ends of the regenerator and the two micro-heat exchangers (Figure).

The modelling of the multi-physics phenomena inside the active magnetocaloric regenerator requires the coupling of magnetostatic (Plait et al, (2019)), magnetocaloric and thermo-fluidic models. The 2-D semianalytical multi-physics model calculates also the internal magnetic field and magnetic flux density (magnetostatic phenomena), magnetization and magnetocaloric power density (magnetocaloric phenomena), heat capacity, temperature and velocity (thermo-fluidic model).

The evolution of the temperatures on both sides of the regenerator obtained experimentally is compared with the numerical simulations for different control parameters. For example, the Figure presents a comparison between experimental measurements and simulation results for a frequency 0.5 Hz and a fluid displacement ratio (A_0) 56 %. The fluid temperature span at steady state between two tanks (Figure) is around 6.9 K, in adequation with the numerical results (7.4 K).

Different operation cases are studied and shown in the Table. The different fluid temperature spans between the hot and cold tanks are obtained for different fluid displacement ratios at constant cycle frequency (0.5 Hz). Experimental and simulated results are in good agreement as exposed in the Table. These first experimental results provide a good validation of the developed 2-D semi-analytical

multiphysics model. More explanation of the multiphysics model and the experimental device is given in (Plait et al (2021)).

PAPER ID: 190

Keywords: Magnetic refrigeration, magnetocaloric device, experimental results, theoretical results.

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Updated design of an active elastocaloric regenerator

Lucia Ianniciello(a), Jaka Tušek(b), Kurt Engelbrecht(a)

(a)Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, 2800 Kgs. Lyngby, Denmark, luciann@dtu.dk, (b) Faculty of Mechanical Engineering, University of Ljubljana, Aškerčeva cesta 6, SI-1000 Ljubljana, Slovenia

Abstract

Elastocaloric cooling could be an alternative to classic cooling systems, as they represent a way to cool more efficiently and being more environmentally friendly. Several shape memory alloys have been investigated for this purpose, either Cu-based, Fe-based or Ni-based. Ni-Ti was selected in this study to build an elastocaloric regenerator. A stack of nine plates has been tested in a cooling system to evaluate its performances. The plates are dog-bone-shaped. The Ni-Ti alloy is composed 49.1 at.% Ti and has an austenite finish temperature of approximately 270 K. The edges of the plates were hand polished with sandpaper and wax compounds, and a buffing wheel. Microscopy imaging was done on the edges of the plate after polishing. The sample was trained up to 120 cycles at 6% of strain, a strain rate of $1.10 \cdot 10^{-4} \text{ s}^{-1}$ and 60 s of waiting time between loading and unloading using a Zwick/Roell testing machine to stabilize the material behavior. The flow system is composed of two loops, one to extract the heat and the second to cool the load. Water was used as the heat transfer fluid. The hot loop contains a heat exchanger and a hot reservoir whereas the cold loop contains a heater to simulate a cooling load. The adiabatic temperature change of the regenerator were measured using an IR camera for different strain amplitudes. To assess the performances of the system different strain amplitudes, different waiting times at the end of loading and unloading and different straining speed were tested.

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

Key results

The regenerative elastocaloric setup that has previously been tested was modified to improve flow system control and to add a heater to the cold end. The updated setup is shown in Fig. 1. The latest NiTi regenerator that will be tested on the updated system is shown in Fig 2 and 3.

Mastering the magnetic properties of magnetocaloric Ni-Mn-(In,Sn) Heusler compounds

Francesco Cugini(a,b), Simone Chicco(a), Greta Cavazzini(a,b), Fabio Orlandi(c), Vincenzo Vezzoni(a), Markus Gruner(d), Giuseppe Allodi(a), Lara Righi(e), Simone Fabbri(b), Franca Albertini(b), Massimo Solzi(a,b)

(a) Department of Mathematical, Physical and Computer Sciences, University of Parma, Parma, Italy

(b) IMEM-CNR Institute, Parma, Italy

(c) ISIS Facility STFC, Rutherford Appleton Laboratory, Didcot, UK

(d) Department of Physics and Center for Nanointegration, CENIDE, University of Duisburg-Essen, Duisburg, Germany

(e) Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parma, Italy

E-mail of corresponding author: francesco.cugini@unipr.it

Abstract

The lattice of Ni₂MnX Heusler compounds (X= Ga, In, Sn, Sb...) allows, by changing composition, the development of different crystallographic and magnetic structures. The possibility of fine tailoring the critical temperatures and the magnetic states makes this class of compounds very promising as active elements in thermomagnetic devices, like magnetic refrigerators and wasted heat thermomagnetic harvesters. However, though this class of materials was diffusely investigated in the last decades, a full comprehension of the factors affecting their structural and magnetic properties, pivotal to design materials with demanded functionalities, has not been achieved yet.

The aim of this work is the comprehension of the physical mechanisms that control the magnetic structure of the austenitic phase in (Ni,Mn)-based Heusler compounds. A series of Ni₄₈Mn₃₆In_{16-x}Sn_x (x = 0-16) alloys was investigated by combining magnetometry, X-rays diffraction, neutron diffraction and solid-state ⁵⁵Mn nuclear magnetic resonance (NMR) experiments. All the compounds show a cubic austenitic phase down to 2 K with a Curie transition slightly above room temperature, at which a fully reversible magnetocaloric effect is associated. Both the critical temperature and the saturation magnetization of the ferromagnetic phase follow a not linear trend with the In to Sn ratio (Figure 1). First-principles DFT calculations suggested that the non-monotonous behaviour of the Curie temperature is related to the modification of the electronic band structure of the compound (Cavazzini et al. 2019). Instead, neutron diffraction experiments combined with NMR results revealed the key role of the excess Mn, sited in the mixed site, to control the saturation magnetization. These results demonstrate that different mechanisms separately control the main magnetic properties of the austenitic phase of these alloys, thus opening new possibilities in the design of new functional Heuslers. Moreover, from an application point of view, this work demonstrates the possibility to replace up to 50% of In with the cheaper and less critical Sn, by substantially keeping constant the magnetocaloric performances of the compound.

Keywords: Magnetocaloric Materials, Heusler Compounds, Thermomagnetic Energy Conversion, DFT Calculations, Neutron Diffraction

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Segregation and Functional Properties of Ni-Mn-based Heusler alloys

Olga Miroshkina(a,b), Vladimir Sokolovskiy(b), Vasiliy Buchelnikov(b), Peter Entel(a), Markus Gruner(a)

(a) University of Duisburg-Essen, Duisburg, 47057, Germany, olga.miroshkina@uni-due.de

(b) Chelyabinsk State University, Chelyabinsk, 454001, Russia

Abstract

Ni-Mn-based Heusler alloys have attracted the attention of the scientific community during the last decades due to their unique properties, which – depending on the composition – include a significant magnetocaloric effect (MCE), large magnetic-field-induced strains, and magnetoresistive properties. Many of these applications require single phase materials or even single crystals, while in recent times also intriguing new phenomena like shell-ferromagnetism (Çakır et al., 2016) have been discovered, which affect the shape of hysteresis in a magnetic field cycle and are ascribed to micro-segregation. In this respect, it appears essential to gain a systematic understanding of the interplay between the tendency of off-stoichiometric Ni-Mn-based Heusler alloys to decompose into mixtures of stable binary and ternary components and their intrinsic functional properties in the entire composition range. In this work, we evaluate from first-principles the propensity for segregation and relevant magnetocaloric properties for Ni-Mn-based Heusler alloys with particular emphasis on the Ni-rich series $\text{Ni}_2\text{xMn}_{1-\text{x}}\text{Ga}$. This paradigmatic system exhibits a coupled magnetostructural phase transition between ferromagnetic (FM) martensite and paramagnetic austenite for compositions between $0.18 \leq x \leq 0.27$, which is accompanied by a considerable MCE (Khovaylo et al., 2005; Buchelnikov et al., 2010). The Figure illustrates the dependence of mixing energies on composition for $\text{Ni}_2\text{Mn}_{1+\text{x}}\text{Ga}_{1-\text{x}}$ and $\text{Ni}_2\text{xMn}_{1-\text{x}}\text{Ga}$ as a function of Ni content, which we obtain from total energy calculations in the framework of Density Functional Theory carried out in a 16 atom super-cell (Sokolovskiy et al. 2019, Entel et al., 2017). Our calculations reveal that in particular FM martensitic $\text{Ni}_2\text{xMn}_{1-\text{x}}\text{Ga}$ compositions are stable against decomposition when Ni-excess concentration is smaller than $x < 0.7$, while in the Mn-rich system, off-stoichiometric compositions exhibit a tendency to segregate at low temperatures. For stable compositions found from the described above calculations, the magnetocaloric properties are modeled with the help of a phenomenological mean-field approach based on Malygin theory of the smeared phase transitions (Malygin, 2001), Bean-Rodbell theory of the first-order phase transitions (Bean, Rodbell, 1962). From the temperature dependencies of magnetization and magnetic entropy change, we identify the compositions with optimum MCE and refrigeration capacity.

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Keywords: magnetocaloric effect, Heusler alloys, first-principle calculations, segregation

Additive Manufacturing Methods for the Production of Magnetocaloric Heat Exchanger Geometries

Christina Breitzke(a), Sandra Wieland(a)

(a) Fraunhofer IFAM, Bremen, 28359, Bremen, christina.breitzke@ifam.fraunhofer.de

Abstract

Thin walled structures with regular channels providing fast heat exchange and low fluid pressure drop are one key factor to achieve efficient magnetocaloric AMR systems. During the last years, Additive Manufacturing (AM) methods have shown to be especially advantageous for the production of tailored heat exchanger structures for different applications, providing high geometrical flexibility combined with low material waste rates. However, nowadays there is a broad spectrum of AM methods, with each of them holding specific advantages and disadvantages for different materials and applications.

Laser Powder Bed Fusion (LPBF) is one of the most advanced AM methods, and has recently been successfully applied for magnetocaloric La(FeSi)₁₃-alloys (Wieland et al., 2020). Latest results on LPBF manufacturing of samples with cascaded Curie-Temperature as well as experiences from tests of these samples in prototype systems will be presented.

Opposed to LPBF, Metal Binder Jetting (MBJ) is not yet as established as an AM technology, but is attracting increasing interest due to its potential to achieve high productivity and process even brittle, non-weldable materials. For magnetocaloric heat exchangers, the low thermal stresses, adjustable porosity and higher surface quality of MBJ compared to LPBF could be favourable. The presentation will give an in-depth comparison of both manufacturing methods as well as first results on MBJ of La(FeSi)₁₃.

Keywords: Magnetocaloric, Additive Manufacturing, Laser Powder Bed Fusion, Metal Binder Jetting

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Wide-range magnetocaloric properties of $(\text{Gd,Tb})_6(\text{Fe,Mn})\text{Bi}_2$

A. Herrero^(a), A. Oleaga^(a), A. Salazar^(a), A.V. Knotko^(b), V. O. Yapaskurt^(c), A.V. Morozkin^(b)

alberto.oleaga@ehu.es^(a) Departamento de Física Aplicada I, Universidad del País Vasco UPV/EHU, Bilbao, Spain ^{(b) (c)} Department of Chemistry, Moscow State University, Moscow, Russia Department of Petrology, Geological Faculty Moscow State University, Moscow, Russia

Abstract

The intermetallic family of Fe_2P -type $(\text{Gd,Tb})_6(\text{Fe,Mn})\text{Bi}_2$ (space group P-62m, N 189, hP9) has been studied as a prospective magnetocaloric material in a very wide and tunable temperature range. The substitution of Gd by Tb (Gd_6FeBi_2 , $\text{Gd}_3\text{Tb}_3\text{FeBi}_2$, Tb_6FeBi_2) tunes T_c in the range 350-250 K and favors the apparition of a metamagnetic transition at very low temperature from a magnetic state with a marked antiferromagnetic component to a ferromagnetic one, as well as a spin reorientation transition below $T_m = 72$ K. An important inverse magnetocaloric effect (IMCE) appears below 20 K and a relevant direct magnetocaloric effect (DMCE) appears over a wide temperature span between T_c and T_m with maxima at those temperatures. The partial substitution of Fe by Mn in $\text{Tb}_6\text{Fe}_{0.5}\text{Mn}_{0.5}\text{Bi}_2$ shifts these effects upwards in temperature while expanding the region of the DMCE. Tuning this family allows to locate the magnetocaloric effect in different regions of interest. The critical behavior of the PM-FM transitions has been studied obtaining the critical exponents α , β , γ , δ and checking that the respective magnetocaloric effects also scale with the critical parameters n and δ ; finally, the master curves for the magnetocaloric effect have been obtained. The transition in Gd_6FeBi_2 has been found to belong to the Heisenberg universality class with deviations due to magnetocrystalline anisotropies; the critical exponents for $\text{Gd}_3\text{Tb}_3\text{FeBi}_2$ suggest the presence of long range order magnetic interactions, as the critical parameters agree quite well with the Mean Field model, while Tb_6FeBi_2 and $\text{Tb}_6\text{Fe}_{0.5}\text{Mn}_{0.5}\text{Bi}_2$ present an unconventional critical behavior aligned with long range order interactions.

Keywords: Magnetocaloric, Critical behavior, Rare earth compound, Intermetallics

Numerical investigation of an active elastocaloric regenerator refrigerator with enhanced heat transfer structures

Yuxiang ZHU (a), Jun HUR (a), Weihong LI (a, b), Qingping SUN (a), Shuhuai YAO (a) *

(a) Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong, 999077, China

(b) HKUST Jockey Club Institute for Advanced Study, The Hong Kong University of Science and Technology, Hong Kong, 999077, China

*Corresponding author: meshyao@ust.hk

Abstract

Elastocaloric cooling exhibits extraordinary potential as an alternative cooling technology due to its environmentally friendly nature. Previous studies have achieved highly efficient elastocaloric cooling by applying compression or tension to Nickel Titanium alloy (Ni-Ti) and adopting active regeneration with water as a heat transfer fluid (HTF) (Qian et al., 2016; Tušek et al., 2016). An active elastocaloric regenerator was developed in which cyclic tension loading was applied to bundles of Ni-Ti thin plates that facilitated convective heat transfer (Tušek et al., 2016). However, insufficient structural fatigue limits its application for long-term operation (Tušek et al., 2018). To improve the fatigue life, compression is identified as a promising alternative, and yet the integration of thermally efficient structures with compressive loading mode is challenging due to material and structural instability. The upgrading of the heat transfer component and its adequate coupling with the elastocaloric materials are required to achieve high cooling performance of compressive loaded elastocaloric cycles.

The performance of an elastocaloric system is normally presented by specific cooling power (SCP). Numerical modelling of the elastocaloric system serves as a powerful tool to predict the thermodynamic efficiency and evaluate the system design. The state-of-the-art numerical models are based on relatively simple structures, for instance, single or a bundle of tubes (Qian et al., 2017; Tušek et al., 2015). Here we present a quasi-1D model for an active elastocaloric regenerator system with efficient heat transfer components, aiming to achieve higher SCP without compromising the fatigue life of the elastocaloric materials in compressive loading cycles.

As illustrated in Figure 1, a Ni-Ti tube is supported by mechanical structures inside the tube to avoid buckling. The latent heat of the Ni-Ti tube is transferred by the structures surrounding the tube, which include copper enclosure and fluid passages. The fatigue of the design is not affected since the whole heat transfer enhancement structure remains stress-free. In our simulations, we examined several designs of fluid passages, e.g., porous medium, mini-channels, or thin film fins. With the heat transfer area extended by these structures, we expect that heat transfer by convection can be largely enhanced. The model is applicable for investigating the performance of different heat transfer enhancement structures at various operating conditions including frequency, properties of heat transfer fluid, and temperature difference, etc., as shown in Figure 2. The results demonstrate that these novel structures are effective designs for enhancing the heat transfer efficiency and improving SCP of refrigerators. The newly developed model may provide us a useful tool to optimize and develop compressive elastocaloric refrigerators.

Keywords: Elastocaloric, Specific cooling power, Porous medium, Heat transfer enhancement.

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Spatial and Temporal Characterization of Magnetocaloric Materials with First Order Phase Transitions

Florian ERBESDOBLER, Christian R.H. BAHL, Rasmus BJØRK, Kaspar K. NIELSEN

Department of Energy Conversion and Storage Technical University of Denmark

Copenhagen, 2800, Denmark, floe@dtu.dk

EXTENDED ABSTRACT

We present a device capable of measuring the magnetocaloric effect and phase transitions of milligram magnetocaloric materials by means of infra-red (IR) thermography. Thereby, both the temporal and spatial temperature response upon change in applied field is investigated at a frequency up to 150 Hz and with 320x256 pixels, each pixel corresponding to 20x20 μm^2 .

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

In order to explore the functionality of the device we present measurements of Gadolinium and La(Fe,Si,Mn)H with stoichiometry variation to gain different transition temperatures. We compare the results with literature and point out that first order magnetocaloric materials can exhibit spatially distributed phase transitions due to variations in Curie temperature. Hence, temperature ramps reveal a time shifted activation of different sample parts.

Keywords: spatial, characterization, phase, transition.

USING MACHINE LEARNING TO DESIGN A LARGE-SCALE MAGNETIC CIRCUIT

Fábio P. FORTKAMP (a), Luís Felipe P. CATTELAN, Guilherme F. PEIXER, Jaime A. LOZANO, Jader R. BARBOSA JR.

POLO - Research Laboratories for Emerging Technologies in Cooling and Thermophysics, Department of Mechanical Engineering, Federal University of Santa Catarina
Florianópolis, 88040900, Brazil
(a) fabio@polo.ufsc.br

In the design of caloric devices for the kilowatt range, integrated simulations of many numerical models are required to deal with the complex interactions between the system components. Of particular interest to the focus of this work, Magnetic Circuit (MCI) models based on the Finite Element Method (FEM) are useful in predicting the magnetic profile applied on the Active Magnetic Regenerators (AMR). However, to determine the cooling capacity and the coefficient of performance of the system, one needs to integrate magnetic waveforms and fluid flow profiles in mathematical models that describe the thermal and magnetic interactions in the AMR. Although global optimization methods can combine multiple numerical models, it is impractical to run FEM simulations at every iteration. In this work, we train regression models using MCI simulation data to be used as a continuous mathematical function in the analysis of other components.

The MCI model developed by our group solves Maxwell's Equations in a magnetic circuit composed of two concentric cylinders: an internal laminated iron stator and a rotor composed of permanent magnet wedges and magnetic steel segments. In a hybrid and novel approach (validated against experimental data), the remanence directions of each segment are optimized for a target magnetic profile using a linear two-dimensional model. The angles are used as input in a more realistic 3D model that considers magnetic saturation and edge effects and returns the 3D magnetic profile surface.

In the special case of designing a large-scale magnetic circuit, but using the same topology, we simulate this model over a wider range of parameters. By varying the high level of the magnetic field in the target function until the optimized angles stop changing, it is possible to determine the highest level of magnetic field achieved as a function of radii, widths and thickness of each part. The data can be regressed using two approaches: (i) a nonlinear function that considers physical characteristics as features (e.g. ratio of gap to magnet volumes, ratio of soft to hard materials volume, rotor aspect ratio); and (ii) a polynomial model that considers all input variables as features.

We compare these two approaches, evaluating the residuals and model adequacy of each one. The influence of train dataset sizes and other regression parameters are shown, in order to develop a configuration that can be used as a reliable design tool for large-scale devices. The first approach allows a clear visualization of the effect of each physical feature, which can help guide the direction of design improvements, in particular by identifying the trade-offs between permanent magnet, soft material and air volumes. In the polynomial approach, smaller residuals can be obtained, leading to narrower prediction intervals for future points, but this approach is more sensitive to overfitting. With careful analysis and selection of the regression parameters, the polynomial regression method is preferred as a design tool.

Keywords: permanent magnet, magnetic circuit, regression, machine learning, numerical Simulation

Mechanical strengthening of Ni-Mn-In-(Co) Heusler alloys for multi-stimuli caloric cooling

Franziska Scheibel (a), Wei Liu (a), Andreas Taubel (a), Lukas Pfeuffer (a), Tino Gottschall (b), Konstantin Skokov (a), and Oliver Gutfleisch (a)

(a) Technische Universität Darmstadt, Material Science, Functional Materials, Alarich-Weiss-Str. 16, 64287 Darmstadt, Germany

(b) Dresden High Magnetic Field Laboratory, Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany

The concept of multi-stimuli caloric cooling uses a magnetic field and a mechanical pressure as external stimuli to induce a first-order magnetostructural transition [1]. By using second stimuli, the otherwise disadvantageous thermal hysteresis can be actively used to induce a fully reversible phase transition. Ni-Mn-X-(Co) Heusler alloys are a potential material for multi-stimuli cooling. Due to their magnetostructural phase transition from martensite to austenite, these alloys have good magneto-caloric and elastocaloric properties as well as a sufficiently broad and designable thermal hysteresis [2, 3, 4].

However, Heusler alloys are often very brittle which is problematic for multi-stimuli cyclic application requiring fatigue resistance. One possibility of mechanical strengthening is precipitation hardening. In the case of Ni-Mn-In-(Co) Heusler alloys, such precipitates can be produced e.g. by doping with small amounts of Gd [5]. By optimizing the processing route, we were able to generate Gd-rich precipitates in a pure Ni-Mn-In-(Co) matrix. Energy-dispersive X-ray spectroscopy shows that Gd is exclusively located in the precipitates, surrounded by a Ni-Mn-In-(Co) matrix. The comparison of a Ni₅₀Mn₃₅In₁₅ alloys with and without Gd-rich precipitates shows only a slight increase of the thermal hysteresis by 8.3 K and the steepness of the phase transition, the magnetization changes of 83 Am²kg⁻¹ is for both samples the same. An isothermal entropy change of 11 Jkg⁻¹K⁻¹ (un-doped) and 9 Jkg⁻¹K⁻¹ (Gd-doped) in 2 T has been measured in isofield protocol. Despite the precipitates, an adiabatic temperature change of 4 K could be measured in the Gd-doped sample in 2 T field change.

Stress-strain measurements show that the Gd-doped Ni-Mn-In (Co) alloy exhibits an improved mechanical stability and two times larger compressive strain than the un-doped alloy. The analysis of the microstructure shows a comparable grain size in the austenite phase for both alloys, but the doped alloy shows a much finer microstructure in the martensite phase. The influence of the precipitates on the microstructure of the martensite phase is currently being investigated.

Our study of Gd-doped Ni-Mn-In-(Co) Heusler alloys could show that the mechanical stability of those Heusler alloys could be improved while the magnetocaloric properties remain nearly unchanged and the method can be used to design efficient caloric materials for multi-stimuli caloric cooling.

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The influence of the frequency of the cyclic magnetic field on the magnetocaloric effect in manganites

A.G. Gamzatov^{1,*}, A.M. Aliev¹, D.-H. Kim², M.-H. Phan³

¹*Amirkhanov Institute of Physics, Daghestan Federal Research Centre, RAS, 367003 Makhachkala, Russia*

²*Chungbuk National University, Cheongju, South Korea*

³*University of South Florida, Tampa, Florida, USA*

E-mail: *gamzatov_adler@mail.ru

Experimental study of the frequency dependences of the magnetocaloric effect (MCE), when the applied field varies according to the law $\Delta H = H_0 \sin(\omega t)$ have been started relatively recently [1-3] and are of great interest due to the fact, that the investigation of MCE in cyclic fields is as close as possible to the actual operating conditions of the magnetic cooling device. Depending on the phase transition nature and the type of magnetic ordering, the MCE behavior can strongly depend on the frequency of the field change [3]. In addition, the cyclic action of the magnetic field causes irreversible effects leading to MCE decrease and degradation of the magnetocaloric material [2], which requires further research also.

Different compositions of manganite are one of the promising materials for the magnetic cooling technology. In this paper, we studied several compounds of manganites. Frequency dependences of the MCE were measured in $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{16}\text{O}_3$, $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{18}\text{O}_3$, $\text{La}_{0.75}\text{Ag}_{0.125}\text{MnO}_3$, $\text{La}_{0.7}\text{Ag}_{0.15}\text{MnO}_3$, $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ and $\text{Pr}_{0.7}\text{Sr}_{0.2}\text{Ca}_{0.1}\text{MnO}_3$ manganites.

Our experimental results show that the MCE value for all samples strongly depends on the frequency of the magnetic field (both for samples with magnetostructural transitions and for samples with magnetic transitions). Dependence of ΔT_{max} on frequency f near TC for all samples is well described by the expression [4]:

$$\Delta T(f) = \Delta T_{f=0} - B f^n, \quad (1)$$

where $\Delta T_{f=0}$, the MCE value at low frequencies ($f=0$ or at $f \leq 0.3$) and B [K/Hz n] – independent of temperature parameter (depending on the nature of the sample). The exponent of n in the formula (1) for some samples is ~ 0.5 and for others ~ 1.5 . Obviously, the parameter B in expression (1) will determine the dissipation processes of the energy of the magnetic system in the lattice, which are characterized by their relaxation times, i.e., where τ is the relaxation time. To date, we do not know any theoretical works about low-frequency (0.3-30 Hz) relaxation processes in magnetic materials that could be used to interpret our experimental results. As is well known, inhomogeneities contribute significantly to the dissipation of magnetic oscillations. Inhomogeneities lead to additional scattering of magnons – the contribution of this mechanism can exceed by several times the self-spin-spin relaxation. Moreover, if we are talking about polycrystalline manganites, in which intergranular effects, which lead to a slowing of energy dissipation, participate along with pronounced Jahn-Teller distortions in this process, all this will lead to a significant increase in τ . However, as we see from equation (1), the relaxation processes in this case will not be described by the usual exponentially decaying functions of the type $M(t) \sim \exp(-t/\tau_0)$ with one characteristic relaxation time τ_0 , but rather will have a more complex form with several different relaxation processes. To understand these phenomena, it is necessary, under the same conditions, to measure the magnetization, which would shed light over the observed frequency effects. At present, creation of an experimental setup for studying magnetization in cyclic magnetic fields is in process.

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Study of cyclic stability of magnetocaloric effect in magnetic field for $\text{La}_{1-x}\text{Pr}_x\text{Fe}_{13.7}\text{Si}_{1.3}\text{-H}_2$ with extra Fe

A.G. Gamzatov^{1,*}, H.B. Zhou², A.M. Aliev¹, N. Abdulkadirova¹, J. Wang², Feng-xia Hu^{2*}, B.G. Shen²

¹Amirkhanov Institute of Physics, Daghestan Federal Research Centre, Russian Academy of Sciences, 367003

Makhachkala, Russia

²State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China

E-mail: *gamzatov_adler@mail.ru, fxhu@iphy.ac.cn

Despite the fact that the process of creating solid-state magnetic refrigerators goes to the practical plane (created and described dozens of types of refrigeration machines with different characteristics, with different working magnetic samples, different designs, etc. [1]), the technology of magnetic cooling has faced many problems requiring further research. As is known, the prototypes of magnetic refrigeration machines created to date operate at relatively low frequencies of 4-10 Hz. Moreover, one of the main problems hindering the beginning of mass production of magnetic refrigerators is the lack of an experimental basis for the study of the properties of magnetic materials in conditions of long-term cyclic influence of the magnetic field. In addition, such studies are of great interest from a fundamental point of view. The study of the influence of the cyclic magnetic field on the magnetic and magnetocaloric properties, is currently carried out by single groups in the world [2-4].

This paper presents the influence of magnetic field frequency (up to 20 Hz) and the long-term cyclic effect of magnetic fields (0.62, 1.8 and 8 T) on the magnetocaloric performance of $\text{La}_{1-x}\text{Pr}_x\text{Fe}_{13.7}\text{Si}_{1.3}\text{-H}_2$ with extra Fe [5] by directly measuring the adiabatic temperature change (ΔT_{ad}). It is shown that most samples had strong frequency dependence in the magnetic field 0.62 T. For some compositions, such as $x = 0.3$, the ΔT_{ad} decreases by more than 3 times at $f=20$ Hz. In magnetic fields of 1.8 and 8 T, the degradation of ΔT_{ad} under long-term cycles were further studied for $\text{La}_{0.8}\text{Pr}_{0.2}\text{Fe}_{13.7}\text{Si}_{1.3}$ and $\text{La}_{0.8}\text{Pr}_{0.2}\text{Fe}_{13.7}\text{Si}_{1.3}\text{H}_2$ (more than 1000 cycles of magnetic field on/off). The results showed that in the field 1.8 T, after 1044 cycles, the ΔT_{ad} is slightly degraded by $\Delta T=0.13$ and 0.57 K, for $\text{La}_{0.8}\text{Pr}_{0.2}\text{Fe}_{13.7}\text{Si}_{1.3}$ and $\text{La}_{0.8}\text{Pr}_{0.2}\text{Fe}_{13.7}\text{Si}_{1.3}\text{H}_2$, respectively, while the maximum ΔT_{ad} is equal to $\Delta T_{\text{max}}=5.6$ K and 4.3 K at $H=1.8$ T. Turning off the field for 30 minutes and overheating and cooling the sample did not restore the effect. This indicates long-term relaxation processes in these samples. In a magnetic field of 8 T up to 1000 cycles, the ΔT_{ad} shows good stability. The maximum ΔT_{ad} reaches $\Delta T_{\text{max}}=12.69$ K and 10.91 K with degradation only about 1-2% at $H=8$ T for $\text{La}_{0.8}\text{Pr}_{0.2}\text{Fe}_{13.7}\text{Si}_{1.3}$ and $\text{La}_{0.8}\text{Pr}_{0.2}\text{Fe}_{13.7}\text{Si}_{1.3}\text{H}_2$, respectively. The relevant mechanism involving microstructure and phase transition dynamics are still under way.

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Influence of cycling on the hysteresis of Gd₅Si₂Ge₂

Yaroslav Mudryk(a), Anis Biswas(a), Arjun K Pathak(a,b), Lin Zhou(a,c),
Vitalij K Pecharsky(a,c)

(a) Ames Laboratory, US Department of Energy, Iowa State University, Ames, Iowa, 50011-3020, USA,
slavkomk@ameslab.gov

(b) Department of Physics, SUNY Buffalo State, Buffalo, New York 14222, USA

(c) Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-2300,
USA

Abstract

Knowing how a promising material exhibiting the giant magnetocaloric effect (GMCE) responds to a repetitive magnetic field cycling through a magnetostructural transition is critical because potential changes in thermal behaviors may affect how such material is employed in a magnetic refrigeration device. Yet, up to now, it was unknown how the magnetocaloric performance of Gd₅Si₂Ge₂, the original giant magnetocaloric material (Pecharsky and Gschneidner, 1997), would respond to cycling, either thermal or magnetic.

Managing hysteresis and irreversibilities while preserving the GMCE constitutes another critical need in the development of high-performance magnetocaloric materials. Hysteresis in Gd₅Si₂Ge₂, can be reduced and even completely eliminated by chemical substitutions, but at the cost of reducing the magnetocaloric effect by a factor of two or more due to the destruction of the first-order magnetostructural transition responsible for GMCE.

We address both of the issues mentioned above, and show that magnetic field cycling is actually beneficial for the magnetocaloric properties of Gd₅Si₂Ge₂ because cycling reduces hysteresis without diminishing the magnetocaloric performance (Figure 1). The *in situ* cycling measurements were performed on a small bulk polycrystalline sample using Quantum Design DynaCool PPMS-VSM. The sample remains intact at the end of the experiment, after ~400 cycles, indicating no drastic deterioration of mechanical integrity. Our study suggests that the formation and retention of a small amount of the trapped ferromagnetic orthorhombic Gd₅Si₂Ge₂ phase even after the complete magnetic field removal is responsible for the reduction of hysteresis.

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Keywords: Magnetocaloric, Cycling, Hysteresis, Gd₅Si₂Ge₂.

Cabinet Temperature Control Logic in a Magnetic Refrigerator

Gislaine HOFFMANN, Alan T. NAKASHIMA, Guilherme F. PEIXER,

Jaime A. LOZANO(a), Rodolfo C. C. FLESCHE, Jader R. BARBOSA JR.

POLO – Research Laboratories for Emerging Technologies in Cooling and Thermophysics,

Department of Mechanical Engineering, Federal University of Santa Catarina

Florianópolis, SC, 88040-900, Brazil,

(a)e-mail: jaime@polo.ufsc.br

With the evolution of magnetic refrigeration systems and prototypes for near room-temperature applications, a need has emerged for temperature and cooling capacity control. To regulate the temperature inside the refrigerated compartment (cabinet) of a magnetic refrigerator, one can change the following input parameters: fluid flow rate (FFR), magnetic cycle frequency (MCF), and fan speed. In this work, we demonstrate experimentally that, using appropriate control strategies, the temperature pull-down time can be decreased, cabinet temperature disturbances due to external events, such as door openings or ambient temperature oscillations, can be quickly eliminated, and the system thermodynamic efficiency can be improved. In our experimental analysis, a 40-liter thermally insulated cabinet (see Figure 1) was coupled to the active magnetic regenerator (AMR) system originally developed by Trevizoli et al. (2016), which was adapted with electronic valves and fansupplied tube-fin heat exchangers. The influence of the operating variables on the cabinet temperature behavior was experimentally quantified and the results were employed in the development of different control techniques. Static and dynamic characterization results show that, among all the controlled variables, the FFR has the highest influence on the cabinet temperature. Also, by changing either the MCF or the FFR it is possible to reach equivalent cabinet temperatures, but the former has a larger impact on the system power consumption (PC), and shows slower transients. Based on the characterization results, a closed loop proportional-integral (PI) controller was designed to manipulate the FFR in order to obtain the desired cabinet temperature (see Figure 2). The dynamic behavior of the system was approximated by a first-order transfer function at the desired operating condition to perform the tuning of the controller. The PI controller was tested with three different MCFs and managed to maintain the cabinet temperature around its desired reference within ± 0.1 °C at steady state and eliminate disturbances due to external events in all of them. The shortest pull-down time was obtained with a MCF of 0.75 Hz. In order to improve system efficiency, an event-driven PC minimization logic was proposed to operate as an external loop to the PI controller. The system operates at a frequency of 0.75 Hz until it reaches the temperature set-point and then both MCF and fan speed of the hot heat exchanger are reduced according to the proposed logic. These reductions are made gradually to verify if the PI controller is still able to maintain the desired temperature inside the cabinet and if they result in a lower PC; otherwise, the control logic returns the setup to the previous configuration. If a disturbance is detected, the control system returns to its default configuration until the cabinet temperature reaches its reference value again. The addition of this logic reduced the PC by 70% and increased the COP in 350%, while keeping the cabinet temperature around the reference value, when compared to the case which considers only the PI controller.

Keywords: caloric devices; control logic; magnetic refrigeration system, cabinet, proportional-integral controller; cooling, heat pumping; refrigeration.

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Figure 2: Experimental temperature, FFR and PC data.

Phase-field model for ferromagnetic domain evolution during martensitic transformation of Heusler alloys

Dominik Ohmer, Min Yi, Bai-Xiang Xu, and Oliver Gut

Institute of Materials Science, Technische Universität Darmstadt, Germany

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As the energy consumed by cooling systems is expected to increase over the next decades, magnetocaloric cooling

systems are of high interest as they are promising more energy efficient alternative to conventional vapor compression

refrigerators.^{1,3} Heusler alloys show large magnetocaloric effects and are therefore of high interest for possible application in magnetocaloric cooling devices.^{4,5} They exhibit a magnetostructural transition, which results in larger entropy changes ΔS and therefore in larger adiabatic temperature changes ΔT_{ad} . We propose a phase-field model based on Landau theory to simulate the magnetic domain evolution during the martensite formation in, e.g. Heusler alloys. With our model, we are able to simulate field- and pressure-induced phase transitions, including the martensite and magnetic domain evolution. This is of high interest for a multicaloric cooling cycle, as proposed by Gottschall et al.⁶ The model takes into account three order parameters η_1 , η_2 , and η_3 , which represent the three martensite variants in a cubic to tetragonal phase transition. The energy of the martensite transformation is described by a Landau-type formulation from Cui et al.⁷ and is coupled with micromagnetic formulations for the description of the magnetic domain evolution. The three-dimensional finite-element implementation of this model is straightforward and has been performed within the MOOSE framework.^{8,9} The model is shown to be capable of reproducing the formation and evolution of domains in magnetic materials under external magnetic field, e.g. as in Fig. 1, or mechanical loading.

Modeling field- and pressure-induced transformation aims at investigating pressures and fields used in a multicaloric cooling cycle. By the finite-element implementation of this model, it is also possible to investigate the influence of microstructure on the magnetocaloric effect.

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FIG. 1: The figure on the left shows the stable microstructure for the martensite at zero field. The arrows indicate

the magnetization, which is parallel to the x-axis for martensite variant η_1 and parallel to the y-axis for η_2 .

Applying an external magnetic field H , the magnetization rotates and aligns with the magnetic field. The martensite variant η_2 starts transforming to η_1 in order to reduce the anisotropy energy, resulting in a single domain

and single phase microstructure.

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Heat driven elastocaloric cooling system

Jianming Tan^{1,2}, Yao Wang³, Shijie Xu³, Xiaojie Lin⁴, Huaican Liu^{1,2}, Suxin Qian^{3*}

¹State Key Laboratory of Air-Conditioning Equipment and System Energy Conservation, Zhuhai, Guangdong, China, 519070

²GREE Electric Appliances Inc., Zhuhai, Guangdong, China, 519070

³Department of Refrigeration and Cryogenic Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, China, 710049

⁴College of Energy Engineering, Zhejiang University, Hangzhou, China, 310027

* Corresponding Author: qiansuxin@xjtu.edu.cn

Elastocaloric cooling utilizes the latent heat during the unloading phase transformation process in super-elastic alloys. To provide the cyclic loading and unloading force, a mechanical driver is required, which is usually oversized to provide sufficient loading force. Consequently, the mass ratio of the driver to refrigerant is usually higher than 500 to 1.

In this study, we propose to use a shape memory heat engine as a driver to overcome this gap. In the new system, the mechanical driver which consumes electricity is replaced by the shape memory actuator that consumes low grade thermal energy. When pumping hot water into the shape memory actuator, the wire bundle shrinks when the hot water's temperature becomes higher than the martensitic phase transformation temperature, thus provides tensile force to drive the transformation of the super-elastic refrigerant. When unloading of the super-elastic refrigerant is needed, water at ambient temperature flows through the wire bundle to induce the reverse transformation to the shape memory actuator. The cycle and configuration of the super-elastic refrigerant in the heat driven system is identical to that of a mechanical driven elastocaloric cooling system.

A heat driven elastocaloric cooling demonstrator is currently under development, using four sets of 1mm Ni-Ti actuator wire bundle with a transformation temperature of 60°C as the driver. The refrigerant consists of two 0.5mm thick Ni-Ti sheets at a transformation temperature of 0°C. This demonstrator has a mass ratio of 3.2. Water is used as the heat transfer fluid, whereby the flow rate, blowing time and blowing sequences can be adjusted in the demonstrator. The geometric parameters and operating parameters of the demonstrator are determined by a numerical model. The length ratio and cross-sectional area ratio between the refrigerant and the actuator are two critical parameters determining the system performance. Using the numerical model, we show that low grade thermal energy at 70°C is capable to drive the new system. Such hot water can be produced by solar thermal collector or by engine jacket coolant, which indicates potential application such as solar driven refrigerator or solar driven air-conditioner for this new technology. The prototype assembly is constructed and is currently under initial tests.

Effect of geometric compatibility on the magnetocaloric measurement protocols in shape memory Heusler alloy

Krishna K. DUBEY(a), P. DEVI (b, c), Anupam K. SINGH (a), Sanjay SINGH(a)

(a) School of Materials Science and Technology, Indian Institute of Technology (BHU), Varanasi-221005, India

(b) Max Planck Institute for Chemical Physics of Solids, Nothnitzer Str. 40, Dresden, 01187, Germany

(c) Ames Laboratory, US Department of Energy, Iowa State University, Ames, Iowa 50011, USA

ABSTRACT

We present here the effect of the geometric compatibility of the austenite and martensite phase on the magnetocaloric measurement protocols in Ni-Pt-Mn-In shape memory Heusler alloy. The elements of phase transformation matrix are calculated using the lattice parameters of the high temperature austenite phase and low temperature martensite phase obtained from the refinement of the x-ray diffraction data. The middle eigenvalue of the transformation matrix is found to be very close to 1 suggesting the reversible phase transformation. The isothermal entropy change calculated using indirect measurement protocols suggests the reversibility of the MCE in the current alloy system.

Keywords: Magnetocaloric effect, Geometrical compatibility condition, Reversibility, Phase transformation, Heusler Alloy.

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Relaxation Phenomena in Adiabatic Temperature Changes Near Magnetostructural Transitions in Heusler Alloys

Yuriy Koshkid'ko(a), Sudip Pandey(b), Jacek Cwik(a), Igor Dubenko(b), Anil Aryal(b), Alexander Granovsky(c), Damian Szymanski(a), Shane Stadler(d), Erkki Lähderanta(e), Naushad Ali(b)

(a)Institute of Low Temperature and Structural Research PAS, Wroclaw, 50-422Poland
y.koshkidko@intibs.pl (b)Department of Physics, Southern Illinois University, Carbondale, IL 62901 USA,
(c)Faculty of Physics, Lomonosov Moscow State University, Moscow, 119991 Russia, (d)Department of
Physics & Astronomy, Louisiana State University, LA 70803 USA, (e)Lappeenranta University of
Technology, 53851, Finland

Abstract

The changes in magnetization in a magnetic material induced by external magnetic fields (or other external factors) are described as a multistage process of establishing thermodynamic equilibrium, which is characterized by a relaxation time. The relaxation time can change from 10-14(s) in response to femtosecond laser pulses (Kirilyuk A. et al., 2010), to 102-103(s) in soft magnetic materials due to eddy-currents, magnetic aftereffects, and magnetic aging (Hohler H. et al., 1980 and Tikadzumi S., 1964), to more than 105(s) in spin glasses. In this paper, we study the dynamics of field-induced martensitic transitions under adiabatic conditions in large static magnetic fields up to 14 T generated by a Bitter-type magnet. The experiments were carried out with a unique magnetic setup that facilitates adiabatic temperature change measurements. Samples of Heusler alloys with different values of latent heat of the martensitic transition were selected for this project. It is shown that in the case of the direct of MCE in the vicinity of the second order magnetic phase transition in Ni₄₅Mn₄₃CoSn₁₁ (see the figures below), the changes in temperature under adiabatic conditions nearly follow the application of field. Given that the time resolution in the extraction method is about 0.1 (s) or better, it is reasonable to assume that the characteristic times of the energy redistribution between the magnetic and ionic systems are shorter than this time. The situation is different at the inverse MST since the relaxation times of the adiabatic temperature changes can reach 10 seconds or more, depending on the latent heat of the transition and the initial temperature. It is important to note that, with a significantly large value of the latent heat of transition, the relaxation of the adiabatic temperature change is comparable to the value of the temperature change and, therefore, the measured temperature may be overestimate, when applying pulse techniques. The process of relaxation of the adiabatic temperature changes can be described by the same logarithmic law as that which describes the relaxation of magnetization, but with different parameters. This logarithmic law indicates the presence of a wide range of characteristic relaxation times, but the specific value of the parameters of this law should be justified from microscopic theory.

Tuning Transition Temperature of Magnetocaloric $\text{Mn}_{1.8}\text{Fe}_{0.2}(\text{P}_{0.59}\text{Si}_{0.41})_x$ Alloys for Cryogenic Magnetic Refrigeration

Jiawei Lai, Hossein Sepehri-Amin, Xin Tang, Kazuhiro Hono

Research Center for Magnetic and Spintronic Materials, National Institute of Materials Science, Ibaraki, 305-00470, Japan, H.SEPEHRIAMIN@nims.go.jp

Abstract

Cryogenic Magnetic Refrigeration (CMR) has been developed as a next generation of refrigeration technique since its highly efficiency and environment friendly, which could be utilized for liquefaction of N_2 , H_2 and He.[1] Materials with a giant magnetocaloric effect (MCE) mainly determines the performance of CMR. In the cryogenic magnetic refrigeration region of 90-150K, heavy rare-earth-based alloys, such as DyFeAl , [2] GdCoAl , [3] TbAl_2 , [4] DyIn_2 [5] and $\text{Tb}_5\text{Si}_2\text{Ge}_2$ [6], are the dominant candidates. However, the usage of strategy elements limits the large-scale application. It is therefore necessary to search for alternative materials. The $(\text{Mn}, \text{Fe})_2(\text{P}, \text{Si})$ -based compounds are known to have the combination of outstanding MCE and low material cost. [7] However, these materials are widely studied for room temperature magnetic refrigeration rather than cryogenic applications. In this work, we tuned the composition of $(\text{Mn}, \text{Fe})_2(\text{P}, \text{Si})$ such as Mn to Fe ratio as well as total content of P+Si ratio to reduce the transition temperature to cryogenic applications while maintaining giant magnetocaloric effect. Excellent MCE properties are found in the transition-metal-based Mn-Fe-P-Si alloys with a tuned curie temperature ranging from 99 to 124 K.

Polycrystalline $\text{MnFeP}_{0.605}\text{Si}_{0.33}\text{B}_{0.065}$ and $\text{Mn}_{1.8}\text{Fe}_{0.2}(\text{P}_{0.59}\text{Si}_{0.41})_x$ alloys were prepared by induction melting. Figure 1 shows the magnetization as a function of temperature for $\text{MnFeP}_{0.605}\text{Si}_{0.33}\text{B}_{0.065}$ and $\text{Mn}_{1.8}\text{Fe}_{0.2}(\text{P}_{0.59}\text{Si}_{0.41})_{1.02}$ alloys under 1.0 T. By tuning the Mn to Fe ratio, T_C decreases from 310 to 120 K. Therefore, transition temperature is able to reach the cryogenic region. Then, in order to optimize magnetocaloric effect, annealing time and metal/non-metal ratio are investigated systematically. Firstly, annealing at 1353 K for 5 h is confirmed to be the condition to achieve a largest magnetization. Secondly, total content of P+Si ratio is tuned in $\text{Mn}_{1.8}\text{Fe}_{0.2}(\text{P}_{0.59}\text{Si}_{0.41})_x$ alloys. T_C can be tuned from 99 to 124 K with a thermal hysteresis of 10.0 - 3.0 K. Optimal magnetic entropy change ($-\Delta S_M$) is obtained in the $\text{Mn}_{1.8}\text{Fe}_{0.2}(\text{P}_{0.59}\text{Si}_{0.41})_{1.03}$ alloy. This outstanding $-\Delta S_M$ ascribes to the highest amount of Fe_2P -type phase and optimal metal/non-metal ratio in the matrix. The composition of matrix is $\text{Mn}_{61}\text{Fe}_{42}\text{P}_{21}\text{Si}_{14}$, which has a metal/non-metal ratio of 1.94. For the $\text{Mn}_{1.8}\text{Fe}_{0.2}(\text{P}_{0.59}\text{Si}_{0.41})_{1.03}$ alloy, a giant ΔS_M of 10.6 and 14.0 J/kgK under a magnetic field of 2.0 and 5.0 T is obtained at 117.0 K, which is competitive to another heavy-rare-earth-based alloy, as shown in figure 1 (b).

Keywords: Magnetocaloric; Refrigeration; Mn-Fe-P-Si; Entropy; Microstructure.

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Direct electrocaloric measurements via ThermoReflectance

Layla FARHAT^{1,2}, Mathieu BARDOUX¹, Stéphane LONGUEMART¹, Ziad HERRO², Abdelhak HADJ SAHRAOUI¹

1. Unité de Dynamique et Structure des Matériaux Moléculaires, Université du Littoral Côte d'Opale, Dunkerque, France 2. Laboratoire de Physique Appliquée, Faculté des Sciences, Université Libanaise, Fanar, Liban

Electrocaloric (EC) effect refers to the isothermal entropy or adiabatic temperature changes of a dielectric material induced by an external electric field. This phenomenon has been largely ignored for application because only modest EC effects (2.6 K) have been detected in bulk ceramics materials such as $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.75}\text{Sn}_{0.20}\text{Ti}_{0.05})_{0.98}\text{O}_3$ [1]. The discovery of a giant electrocaloric effect by Mischenko et al.[2] in thin films (up to 12 °C with $E=480 \text{ kV.cm}^{-1}$) renewed interest in electrocaloric materials and related cooling technologies. It is indeed the development of thin structures that has made it possible to obtain high dielectric rigidity and significant electrocaloric effects.

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

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

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

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Long-term stability of elastocaloric material in a new system approach

Nora Bachmann, Andreas Fitger, Andreas Mahlke, David Fink, Olaf Schäfer-Welsen, Kilian Bartholomé

Fraunhofer Institute for Physical Measurement Techniques IPM, Freiburg, 79110, Germany,
nora.bachmann@ipm.fraunhofer.de

Abstract

Elastocaloric materials enable efficient concepts for cooling that eliminate the need for flammable or environmentally harmful refrigerants. Demonstrator systems already prove the functionality of elastocaloric cooling systems. In most of these systems, the load is applied via tensile stress. However, a challenge of these systems is the long-term stability of the materials due to the occurrence of micro-cracks under tensile load.

Elastocaloric systems, in which the material is loaded under compression, promise an increase in long-term stability. However, compression leads to limitations of the aspect ratio of the material, and this in turn leads to smaller surface areas available for heat transfer between material and heat transfer fluid. In the approach presented in this work, experimental results of an elastocaloric system are shown where this heat transfer is realized by evaporation and condensation of the working fluid. The heat transfer coefficient based on condensation and evaporation of a harmless working fluid is significantly higher than, for example, the one based on forced convection or heat conduction.

Thereby very good system performances can be attained for systems with a long-term stability outreaching several million cycles.

Keywords: Elastocaloric, long-term stability, latent heat, new system approach.

Integrated design of a large-scale magnetic refrigerator

Jaime A. LOZANO(a), Guilherme F. PEIXER, Bernardo P. VIEIRA, Fábio P. FORTKAMP, Henrique N. BEZ, Luís. F. P. CATTELAN, Higor F. TEZA, Mayara S. DE OLIVEIRA, Alan T. D. NAKASHIMA, Jader R. BARBOSA JR.

POLO – Research Laboratories for Emerging Technologies in Cooling and Thermophysics, Department of Mechanical Engineering, Federal University of Santa Catarina Florianópolis, SC, 88040-900, Brazil,

(a)e-mail: jaime@polo.ufsc.br

The development of a magnetic refrigeration system is a multidisciplinary task that requires the simultaneous and integrated design of several components. Not only the optimization of every single component but also the integration between them is fundamental for the design of a compact and efficient system. The objective of this work is to present the methodology for the integrated design of the active magnetic regenerator (AMR), magnetic circuit (MC), heat exchangers (HEX) and hydraulic and control systems (HCS) that provide the best performance of a magnetic refrigerator. The integrated design has been applied in the development of a magnetic refrigeration unit (MRU) that aims to operate an air conditioner (AC) with a cooling capacity of 9000 Btu/h (~2.6 kW) for internal and external reservoir temperatures of 22 and 35 °C, respectively. The MRU consists of a magnetic circuit of Nd-Fe-B permanent magnets and solid refrigerants based on La-based alloys.

The design process was done following the lean product development (LPD) using the Toyota kata approach and set-based concurrent engineering (SBCE) strategy in which the development of the MRU was split into four subsystems: MC, AMR, AC and HEX, and HCS. As shown in Figure 1, the design process consists on target-cycles of the design and optimization of the individual components in parallel with integration events carried out periodically. The integration model gathers strategic data from each subsystem to perform a system-level evaluation to include the advances performed in the last cycle in all the components. Then, after coupling the individual data into the integrated model, design feedbacks are given to each subsystem for the following target-cycle of design and optimization of each component.

The models developed for the simulation of the components, especially the AMR and MC, involved the discretization and numerical solution of the governing equations that represent their physical phenomena.

Given the large number of parameters to design the system, the optimization of an MRU in the integration stage is computationally expensive as the number of simulations which arise from the combination of those parameters is extremely high. To overcome that challenge, semi-analytic modeling and artificial intelligence regression methods have been developed for each one of the components and integrated into a single MRU model, turning the simulation of hundreds of thousands of possible MRU candidates achievable within minutes (Figure 2). The system design is improved through a Pareto optimization, seeking to minimize the total MRU mass and power consumption, providing the decision-maker multiple Pareto optimal solutions (orange crosses in Figure 2). These solutions dictate the next target-cycle guidelines for each subsystem, e.g., an increase in the operating frequency for the HCS or an increase in the magnetic field for the MC. After several iterations, a taper down of the project space occurs until the decision-maker defines the best MRU candidate which has successfully fulfilled the project requirements.

Keywords: caloric devices, magnetic refrigeration, integrated design, system optimization.

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Magnetically-activated thermal switch without moving parts for fully solid state magnetic refrigeration

C. RODRIGUES(a), M. M. DIAS(a), L. MARTINS(a), D. J. SILVA(a), J. P. ARAÚJO(a), J. C. R. E. OLIVEIRA(b), A.M. PEREIRA(a), J. O. VENTURA(a),

(a) IFIMUP, Department of Physics and Astronomy, Faculty of Sciences, University of Porto, Porto, 4169-007, Portugal

(b) CFP, Department of Physics Engineering, FEUP, Rua Dr. Roberto Frias, 4200-465 Porto,

With the ever-increasing power dissipation in electrical devices, new thermal management solutions are in high demand to maintain an optimal operating temperature and efficient performance. In particular, recently developed magnetically-activated thermal switches (MATs) provide an alternative to existing devices, using the magnetic and thermal properties of superparamagnetic nanofluids to dissipate heat in a controlled manner [1]. Typically, TSs can be divided into three main categories: active solid-state, passive solid-state and fluidic thermal switches [2]. Active thermal switches need to be externally activated by applying, e.g., a magnetic [3]. Passive solid-state thermal switches, or thermal diodes, function with materials that transfer heat asymmetrically. Fluidic thermal switches remove the problem of the interface between two solids caused by surface roughness that reduces the actual contact area [20]. In fact, by adapting to the contact surface, the interface resistance is decreased. Thus, fluidic thermal switches have been widely reported in the literature [2]. Liquid metal coolants have also been used taken advantage of the electrowetting effect. Nanofluids [4], made of high thermal conductivity nanoparticles suspended in a fluid, display enhanced thermal properties and are more effective in heat removal. In particular, magnetic nanofluids, besides offering enhanced thermal conductivities, can be externally redirected to specific areas on demand by just applying small magnetic fields, which makes them good actuation components for micropumping applications. Thus, they can be moved into localized hot spots where they can absorb heat that is then released at a far away location after the field is removed. However, up to now, magnetic nanofluids have been primarily used as a secondary transport mechanism rather than a primary mean of heat transportation].

In a previous work [4], we have reported a novel magnetically-actuated thermal switch (MATs) relying on the mechanical motion of permanent magnets to move a magnetic nanofluid between two surfaces at different temperatures. Such apparatus allowed the realization of heat transference between hot and cold sides with a remote operation. However, and although with a reliable and efficient performance, the necessity for moving parts is a majority disadvantage, preventing its use in a broad range of systems. Moreover, a recent investigation showed that the unwanted losses which electromagnets produce can be mitigated by using the concept of magnetic energy recovery. Taking this into consideration, we idealized and developed a new design in which all mobile parts are removed and that relies instead on the magnetization/demagnetization processes of a soft magnetic material. With the reported results, we provide the groundwork for future applications of the MATs. This device can also provide a future alternative to the more commonly used phase change materials in thermal management applications or to new fully solid state magnetic refrigerators.

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Effect of composition and hydrostatic pressure on the magnetocaloric properties of Pt doped Ni₂MnGa Heusler alloy

P. Sivaprakasha, S. Esakki Muthua,b, Sanjay Singhc, M. Kannana, Anupam K.Singhc,

S. Muthukumarana, Shampa Guhad, Manoranjan Kard, S. Arumugama,* aCentre for High Pressure Research, School of Physics, Bharathidasan University, Tiruchirappalli 620024, India bDepartment of Physics, Karpagam Academy of Higher Education, Coimbatore 641021, India cSchool of Materials Science and Technology, Indian Institute of Technology (BHU), Varanasi-221005, India dDepartment of Physics, Indian Institute of Technology Patna, Bihta, Patna 801103, India *Corresponding author E Mail Id: sarumugam1963@yahoo.com

The magnetocaloric effect on Ni₂-xPt_xMnGa (x= 0.2, 0.3 and 1.0) shape memory Heusler alloy around martensite transformation temperature (*T_M*) is investigated. The magnetic entropy (ΔS_m) decreases marginally with increasing Pt content at Ni site in Ni₂MnGa for various external applied magnetic field up to 3 T. The effect of hydrostatic on ΔS_m for x = 0.2 i.e Ni_{1.8}Pt_{0.2}MnGa is also investigated. We observed that the application of hydrostatic pressure increases the martensite phase transition temperature (*T_M*) and therefore pressure stabilizes the martensite phase for Ni_{1.8}Pt_{0.2}MnGa with a rate of 0.4 K/ GPa, while with increasing pressure, the ΔS_m is decreases. **Keywords:** Magneto caloric effect, Heusler alloys, Martensite transition

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Performance evaluation of a novel microchannel magnetic regenerator

Jierong Liang(a)*, Kurt Engelbrecht(a), Kaspar K. Nielsen(a), Hugo Vieyra(b), Alexander Barcza(b), Konrad Loewe(b), Christian R.H. Bahl(a)

(a) Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, 2800 Kgs. Lyngby, Denmark, *jilia@dtu.dk

(b) Vacuumschmelze GmbH & Co. KG, 63450 Hanau, Germany

Abstract

A novel microchannel active magnetic regenerator (AMR) prepared by Vacuumschmelze GmbH & Co. has been evaluated with regards to heat transfer, hydraulic resistance, cooling capacity and stability over time. The regenerator is made from the La(Fe,Si,Mn)₁₃Hy based Calorivac-HS shaped into triangular microchannels with a hydraulic diameter of ~200 µm (Figure 1). The AMR testing in an oscillatory flow and periodic magnetic field, results in a cooling performance similar to conventional packed bed AMRs but with a significantly lower flow resistance (Figure 2 and 3). The chemical and mechanical stabilities are validated by comparisons of heat transfer effectiveness, pressure drop and magnetocaloric properties of the regenerator before and after the long-term tests. This novel AMR has a good potential for maximizing the operational coefficient of performance (COP) essential for its application in magnetic refrigeration.

Keywords: Active magnetic regenerator, Microchannel, Heat transfer, Hydraulic resistance, Stability.

Modeling and optimization of a Samarium doped Barium Titanate multilayer capacitor for electrocaloric refrigeration

Miriam ACHKAR, Eliane BSAIBESS, Said BELLAFKIH, Didier FASQUELLE, Abdelhak HADJ SAHRAOUI, Stéphane LONGUEMART

Unité de Dynamique et structure des Matériaux Moléculaires, Université de Littoral Côte d'opale, Dunkerque, 59140, France.

miriam.p.achkar@gmail.com

Keywords: Electrocaloric, ceramics, Sm-doped BaTiO₃, multilayer capacitor modeling

Vapor compression refrigeration is the most common refrigeration technology. However, it uses refrigerants that are harmful to the environment. As alternative solutions, several technologies based on solid state refrigeration are being developed. One of these alternatives is Electrocaloric (EC) refrigeration, which has attracted a growing interest in recent years upon discovery of a significant electrocaloric effect in lead-based thin film. Electrocaloric effect (ECE) is a physical phenomenon present in polar materials and requires the application and removal of external electric field. This, results in an adiabatic reversible change of temperature or an isothermal variation of entropy [1].

Nowadays, the majority of the studied electrocaloric materials are ferroelectric, because they have a very important EC effect near phase transition. These materials may be divided into two categories: normal ferroelectrics and relaxor ferroelectrics. Relaxor ferroelectrics seem to be more attractive than normal ferroelectrics since they allow to exploit the ECE over a wider temperature range [2].

The strongest ECE was measured in lead-based materials, thin films or polymers. Since the use of lead is being prohibited in a growing number of countries, for example in Europe by the European Restriction of Hazardous Substances (RoHS) directive, these materials can be substituted by perovskite materials based on barium titanate (BaTiO₃), which are among the most well-known lead-free ferroelectric materials having excellent dielectric and ferroelectric properties [3]. Moreover, in order to reduce the useful electrical voltages, it is necessary to work with low thicknesses. However, to exchange more heat, larger quantities of material are required, that is why the use of a multi-layered material is privileged. Multilayer Capacitor (MLC) overcomes some of the difficulties encountered with bulk ceramics and thin films, while maintaining their respective advantages. For this, they represent the optimal geometry for electrocaloric applications [1]. To date, the main materials used for the manufacture of MLCs are lead-based ceramics such as PZT or PMN-PT. Other oxides based on BaTiO₃ were reported. However, these materials do not exhibit an efficient ECE yield unless they are subjected to high electric fields.

Works on ECE of doping BaTiO₃ with samarium (BTO-Sm) are very rare. To our knowledge, a single electrocaloric study on this compound has been reported with a single concentration of samarium (4%) [4]. In this work BTO-Sm was synthesized using sol-gel method. Here, samarium was incorporated into the A site for obtaining the composition Ba_{1-x}Sm_xTiO₃, with x from 0 to 0.06. Structural characterizations (XRD, SEM), impedance spectroscopy and photo-thermal methods for electrical and thermal properties measurements have been carried out. For the electrocaloric properties, a direct method implying the use of an adiabatic calorimeter has been employed. Results shows that the substitution leads to a decrease in the temperature at which the maximum EC effect occurs and a widening of the temperature range where the EC effect may be exploited, making (BTO-Sm) ceramics good candidates for EC refrigeration. Based on BTO-Sm properties, modeling and optimization of heat transfer in an MLC is realized using COMSOL software to provide a finest MLC geometry.

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An AMR Lumped Model for Magnetic Refrigerator System Simulation

Alan T. D. NAKASHIMA, Guilherme F. PEIXER, Jaime A. LOZANO, Jader R. BARBOSA Jr.

POLO – Research Laboratories for Emerging Technologies in Cooling and Thermophysics, Department of Mechanical Engineering, Federal University of Santa Catarina Florianópolis, SC, 88040-900, Brazil, (a)e-mail: alan.nakashima@polo.ufsc.br

EXTENDED ABSTRACT

Mathematical modeling and numerical simulation are powerful tools for research and development of thermal devices, being widely applied in fundamental physical investigation and practical problem solution in AMR systems. The complexity and depth of a mathematical model are usually determined by a balance between its goal, available resources and previous knowledge of the problem. The majority of AMR models in the literature solve two or one-dimensional differential versions of the governing equations using some type of numerical method, such as finite volume or finite element. Although the computational time of current solutions are acceptable for standalone AMR analysis, full-system optimization using numerical tools would be much more efficient if a simple, yet accurate analytic or semi-analytic model was available. In this sense, one of the first simplified models was proposed by Rowe (2012) and later expanded and validated by Burdiny et al. (2014) and Teyber et al. (2018). The model is based on the solid-fluid thermal equilibrium assumption and, therefore, the energy conservation of the AMR is described by a single equation. Another class of models based on dimensional analysis was introduced in the works of Tagliafico et al. (2013) and Qian et al. (2017). All of these modelling approaches are relatively simple and have been validated for specific conditions. However, an accuracy assessment for broader application ranges is still absent. Thus, the objective of this work is to propose an alternative model for application in AMR system design based on a lumped analysis and application of the regenerator effectiveness equation. Numerical results will be assessed in terms of accuracy for an extensive database of experimental data, which includes single and multi-bed AMR systems. The model will also be integrated with steady-state energy balance of the complete AMR, heat exchangers and cabinet system and the results will be compared to experimental data of a small-scale magnetic refrigerator.

Keywords: AMR system model, Lumped analysis, Regenerator effectiveness.

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Performance Assessment of a Magnetic Wine Cooler Prototype

Alan T. D. NAKASHIMA, Natalia M. DE SÁ, Victor M. A. DOS SANTOS,

Gislaine HOFFMANN, Jaime A. LOZANO, Jader R. BARBOSA JR.

POLO – Research Laboratories for Emerging Technologies in Cooling and Thermophysics, Department of Mechanical Engineering, Federal University of Santa Catarina

Florianópolis, SC, 88040-900, Brazil

(a)e-mail: alan.nakashima@polo.ufsc.br

The challenge of building proof-of-concept magnetocaloric refrigerators was embraced by several researchers of room-temperature magnetic cooling and heat pumping. However, after decades of development, a complete experimental comparison between magnetic and conventional systems at similar operating conditions is still lacking in the open literature. In our laboratory, a working prototype was built to mark the conclusion of the first phase of the ongoing POLOMAG project, whose aim is to develop a compact magnetic refrigeration system capable of controlling the temperature of a 31-bottle wine cooler cabinet between 5 °C and 20 °C for an ambient temperature of 25 °C. In this paper, we present, for the first time, performance results for the device operating the cabinet in a controlled environment. Main components include eight multi-layered AMRs composed of Gd and Gd-Y alloys, a two-pole Halbach cylinder as the magnetic field generator (maximum field of 1 T), a set of eight solenoid valves for flow control (1.5 W of nominal consumption), as well as tubefin heat exchangers operating the hot (ambient) and cold (refrigerated cabinet) sides of the apparatus. The power sources include an induction motor for the magnetic circuit, a gear pump and the solenoid valves for the hydraulic circuit, and axial fans for the cold and hot heat exchangers. Synchronization of magnetic field variation and fluid flow processes is enabled by real-time pressure loss and magnetic field measurements.

Pressure, torque, mass flow rate, voltage, current and temperature transducers are used to calculate the heat transfer rates and power parcels (electric, mechanic and hydraulic). The output variables of this assessment include the cooling capacity, temperature spans, energy consumption and thermodynamic efficiency measured for several mass flow rate and frequency inputs. These results are compared with the data acquired for the conventional vapor compression wine cooler, which was obtained by Dutra (2018). Presentation of such data is the first step in assessing the magnetic refrigeration technology for this niche application, and it will fuel the next steps of the project aiming to build the compact, plug-and-play magnetocaloric wine cooler.

Keywords: Magnetic refrigerator prototype, Conventional system, Efficiency comparison.

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Reduction of transient refrigeration time by modulation of fluid displacement ratio and operating frequency of a magnetocaloric device

Antony Plait, Stefan Giurgea, Thierry de Larochelambert, Christophe

Espanet

FEMTO-ST Institute, CNRS, Univ. Bourgogne Franche-Comté, Belfort, 90000, France

antony.plait@gmail.com

Abstract

In the literature, there are a lot of one-dimensional magnetic refrigeration model developed using less or

more well adapted exchange coefficients. In order to reduce assumptions and approximations, a global twodimensional

(2-D) multiphysics model has been developed for an AMRR magnetocaloric device. It

integrates successively:

- a magnetostatic model based on a semi-analytical modeling of the magnetostatic phenomena, which takes

into account the nonlinear behaviour of the ferromagnetic external circuit as well as the active magnetocaloric material (MCM) properties. The analytical model calculates the values of the internal magnetic field and the internal magnetic flux density at each point of the regenerator volume;

- a magnetocaloric model for calculating the magnetic power density produced in the magnetocaloric material as a result of the magnetic field variation (provided by the magnetostatic model), combined with

the interpolation of the local magnetization of the magnetocaloric material (from experimental data) as a

function of local magnetic field and temperature values;

- a thermo-fluidic model, which solves the energy and momentum equations using an implicit finite difference method. It also calculates the heat capacity and the thermal conductivity of the magnetocaloric

material as a function of temperature and internal magnetic field, allowing to update the new temperatures

of both the fluid and the material.

The capacities and performances of the 2-D multiphysics model (Plait et al. (2021)) are studied by the influence of input parameters on the temperature difference and the time necessary to obtain the steady state in adiabatic mode. The first study consists in calculating the influence of the two main operating parameters – the fluid displacement ratio $A0$ and the AMR frequency f – in order to obtain the maximal temperature difference between the two ends of the regenerator. The fluid displacement ratio ranges from 5 % to 100 % of the channel volume for every specific operating frequency between 0.1 Hz and 1 Hz. The first figure shows the maximal temperature mapping obtained at steady state and permits to observe a maximal span temperature of 16 K, with a combination $\{A0, f\} = \{25 \%, 0.3 \text{ Hz}\}$. However, some other combinations permit to obtain a similar temperature difference (in equipotential zones combining whether lower $A0$ with higher f or combination of higher $A0$ with lower f). This kind of study was realized in the literature (Bahl et al. (2008), Almanza et al. (2015)), which permits to validate this study. Thus, it is interesting to identify which combination permits to reduce the time necessary to obtain these results.

For that, the second study consists in calculating the transient temperature between the start and the stationary regime, allowing to determine the best combination $\{A0, f\}$, which ensures the fastest cooling

rate. The second figure shows the mapping of the time necessary to achieve the steady state. A high frequency combined to a high fluid displacement ratio permits to reduce the time necessary to obtain the steady state. In our configuration the best combination to obtain the maximal temperature difference in a minimal time is {20 %, 0.5 Hz}.

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Keywords: Magnetic refrigeration, multiphysics model, temperature difference, operating frequency, fluid displacement ratio.

Key Results

Figure: Mapping of temperature difference (top); time necessary to obtain steady state (bottom)

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Evolutionary optimization of Hamiltonian model for study of magnetocaloric materials

Anna Leonteva(a), Radia Hamane(b), Michel Risser(c), Anne Jeannin-Girardon(a), Pierre Parrend(a,d), Pierre Collet(a)

(a) CSTB-ICube, Strasbourg, 67000, France, anna.ouskova-leonteva@etu.unistra.fr

(b) CRISMAT-ENSICAen Caen, 14050, France

(c) Ubiblu, Strasbourg, 67000, France

(d) ECAM Strasbourg Europe, France

Abstract

The modeling of magnetic refrigeration systems (MR) for their optimization requires a good simulation of

the Magnetocaloric (MC) alloys behavior. The use of material dataset from theoretical models is necessary to ensure thermodynamic consistency and therefore the perfect energy conservation in the simulation of the MR devices (Risser et al., 2012).

The LaFe₁₃-xSix based compounds show good MC properties and they are real candidates for commercial

applications. Several models have been developed to simulate their magnetic properties, but modeled behaviors (the shape of magnetic transition and heat capacity) differ from experimental measurements. These differences are related to the applied solving methods. For numerical modeling of the physical properties of materials, we use Blume Emery Griffiths – Ising (BEG-I) theoretical model, solved by Monte-Carlo simulation (Hamane et al., 2020), where the generalized Hamiltonian consists of three contributions: magnetic, structural and magneto-structural. Free parameters are introduced into BEG-I Hamiltonian for tuning the intensities of interactions. Their numerical values have to be found to obtain theoretical MC dataset in concordance with experimental observed behaviors.

In order to set up a database of different materials revealing properties of interest, a new numerical approach remains necessary. Existing indirect methods (based on first-principles calculations, machinelearning algorithms and the Mean Field Theory), have serious limitations, like a lack of generalization, strong dependence on experimental database quality/availability or an overestimation of magneto caloric effect. In this paper we present a new time-efficient optimization method for BEG-I model, based on evolutionary optimization approach, applying a single-objective quantum-inspired algorithm (Ouskova Leonteva et al., 2020) to find the free parameters of Hamiltonian. This optimization approach are compared with our previous experiment (Ouskova Leonteva et al., 2021), which was based on the multiobjective algorithm FastEMO (Ouskova Leonteva et al., 2019). Proposed approach not only allows to overcome some drawbacks of existing indirect methods, but also to reduce the search cost to reach the optimal values of free parameters, whose combination returns a micro-state from which flows the shape of the magnetization curve, the transition temperature, the intensity of the heat capacity and the degree of magnetic field dependence. We demonstrate that proposed method makes it possible to describe physics, associated with the magnetostructural transition for LaFe₁₃-xSix compounds. The control simulation results (done with obtained free parameters) are in good agreement with the experimental data of the magnetization, the heat capacity and magnetic entropy change (see Figure 1).
Keywords: Evolutionary Algorithm, Monte Carlo simulation, magnetocaloric materials.

Numerical study of heat transfer between fluid and magnetocaloric bed excited with time-varying magnetic field

Pawel Pluszka(a), Daniel Lewandowski (b) , Ziemowit Malecha(a)

(a) Department of Cryogenics and Aeronautic Engineering, Wroclaw University of Science and Technology, Poland, pawel.pluszka@pwr.edu.pl

(b) Institute of Materials Science and Applied Mechanics, Wroclaw University of Science and Technology, Poland

Abstract

A reliable numerical tool is an essential advantage supporting the design of a solid bed of magnetocaloric cooling devices. An application of a simulation based design can significantly reduce the experimental workload and optimize the main performance outputs: temperature span between hot and cold reservoirs and available cooling capacity of the system. The objective of the presented work is to develop an effective and robust numerical technique that can be successfully used for the design of the magnetocaloric cooling devices.

In the present paper, the CFD based numerical model of the magnetocaloric porous bed was developed. The conjugated heat transfer between solid magnetocaloric particles and working fluid flow was modelled using the Finite Volume Method.

In order to effectively simulate the Active Magnetic Regenerator (AMR) cycle a time-varying magnetic field excitation and the corresponding magnetocaloric effect (MCE) of the bed particles have been implemented.

The article describes the technical aspects of the implementation of the MCE and the corresponding, direction varying, flow of the heating medium. Subsequently, the developed numerical model was used to study the influence of different geometries of the solid bed on the heat transfer performance.

Keywords: OpenFOAM, AMR gadolinium cycle, magnetic refrigeration.

Shaping LaFe_{13-x}Si_x-based Materials: Novel Strategies for Developing Metallic Matrix Magnetocaloric Composites

Marcelo A. ROSA (a), Deise SCHAFFER (a), Henrique NEVES BEZ (b), Cristiano da Silva TEIXEIRA (c), Paulo Antônio Pereira WENDHAUSEN (a)

**(a) MAGMA – Federal University of Santa Catarina
Florianópolis, 88040-900, Brazil**

**(b) POLO – Federal University of Santa Catarina
Florianópolis, 88040-900, Brazil**

(c) Federal University of Santa Catarina, 89036-002, Blumenau, Brazil

EXTENDED ABSTRACT

LaFe_{13-x}Si_x-based alloys are considered one of the most promising candidates for room temperature magnetic refrigeration due to their low cost, environmental friendliness and large magnetocaloric effect when compared to gadolinium-based materials. However, their inherent brittleness offers major challenges regarding both their application and processing into active magnetic regenerator (AMR) devices. Volume change during the first order magnetic transition may lead to failure during thermomagnetic cycling. Moreover, the need to hydrogenate these alloys for Curie temperature tuning further embrittles them, making them available only in a powdered form. Attending geometry requirements for optimal AMR design becomes a difficult task considering the mechanical properties of such alloys. It has been proposed that embedding LaFe_{13-x}Si_x-based magnetocaloric particles in a ductile matrix, either metallic or polymeric, is an effective way of overcoming this mechanical liability. Although polymeric composites are relatively easily processed and mechanically stable, polymer binders are rather thermal insulating, which is detrimental to AMR performance. Metallic binders may offer better thermal performance, but their high melting point demands forming techniques such as hot pressing and hinders their application, since LaFe_{13-x}Si_x hydrides tend to decompose at relatively low temperatures, around 423 K. This work presents two alternative processing routes for obtaining metallic matrix magnetocaloric composites at room temperature. The final material is composed of LaFe_{13-x}Si_x hydride-based particles dispersed in a Sn matrix. We show that it is possible to attain porosities lower than 10%, while preserving the magnetocaloric particles hydrogenated and therefore their thermomagnetic properties unchanged, leading to refrigerants with ~10 J/kg.K isothermal entropy variation at a 2 T applied field. Furthermore, when combining Sn with electroless Cu coated LaFe_{13-x}Si_x hydride-based particles, it is possible to increase compressive strength in 30%, while maintaining aforementioned properties. Thus, either Sn bonding or Sn-Cu bonding processing routes could lead to significant developments regarding the deployment of LaFe_{13-x}Si_x-based AMRs for room temperature magnetic refrigeration applications.

Keywords: LaFe_{13-x}Si_x alloys; AMR; magnetocaloric composites.

NiMnCuGa alloy pulverized via ultrasonic atomization

Rafal Wroblewski(a), Lukasz Zrodowski(a,b), Mateusz Ostrysz(b), Wojciech Lacisz(b), Karolina Pomian(a), Marcin Leonowicz(a)

(a) Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, 02-507, Poland, Rafal.Wroblewski@pw.edu.pl (b) AMAZEMET Ltd., Warsaw, 00-867, Poland

Abstract

Ni-based Heusler alloys exhibit promising magnetocaloric properties (Stadler et al., 2006, Wroblewski et al., 2016), however they are hard to machine. Powder metallurgy, e.g. 3D printing, may be a solution for this problem (Caputo et al. 2018), however producing spherical particles might be challenging. In order to pulverize the NiMnCuGa alloy for further 3D printing or other powder metallurgy technique we have utilized rePowder technology developed by Amazemet Ltd. This innovative patent pending solution allows for pulverisation of the pre-alloyed materials, regardless of the form of the input material, via ultrasonic agitation of the melted metal. Left-hand part of the Figure below shows the basics of ultrasonic atomization, i.e. vibrating sonotrode ejects droplets which crystallize into spherical particles. Right-hand part of the Figure shows the 3D image of the Ni₅₀Mn_{18.75}Cu_{6.25}Ga₂₅ single particle. The diameter is ca. 180 µm and one can easily see dendrites on the surface.

Particles size distribution was determined by a sieve analysis and its results are shown in the Table below. These results are very promising since half of the obtained powder has the particle sizes between 50 and 100 µm which makes it suitable for 3D printing, since bulk density of such powders is very high.

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Applying Materials Informatics Insights to Magnetocaloric Materials Screening and Discovery

A.N. Tantillo,^{1,2} K.G. Sandeman^{1,2}

¹Physics Program, The Graduate Center, CUNY, 365 Fifth Avenue, New York, NY 10016, USA

²Brooklyn College of The City University of New York, Brooklyn, NY 11210, USA

It is over twenty years since the discovery of a giant magnetocaloric effect (GMCE) in Gd-Si-Ge [1], and in that time two low-cost GMCE materials systems have been pursued towards commercialization: Mn-Fe-P-Si [2] and La-Fe-Si [3]. This relatively small number of target room temperature magnetic refrigerants underscores the need for time- and cost-effective magnetocaloric materials discovery projects. The ideal material candidates for magnetocaloric applications must be non-toxic, inexpensive, and readily manufacturable [4]. Highthroughput workflows, guided by machine learning and other statistical methods in material informatics, are essential to streamlining the process of screening new possible materials, making the experimental process as targeted and efficient as possible. This presentation describes two approaches to materials screening based on simulated data.

The first approach is a modification of the screening method of Bocarsly et al. [5], wherein lattice deformation across the magnetic phase transition (magnetic deformation) was computed based on the difference between unit cell dimension lengths with and without magnetic interactions in models based on density function theory (DFT). We add a phenomenological parameter calculated from the electronic density of states available from the Materials Project [6]. The addition of this new parameter can enhance the prediction of magnetic field-induced entropy change, ΔS_m , with nearly 60% better correlation than using magnetic deformation alone.

The second approach is motivated by the relative scarcity of consistent magnetic entropy data for stoichiometric compounds, which limits the ability of researchers to cross-check predicted ΔS_m with experiment. We describe a method of scraping the Materials Project database for DFT results on magnetically ordered compounds [7] using the Pymatgen open-source Python library [8]. By analyzing the electronic density of states, computed unit cell volume and other parameters obtained through the Materials Project database for over 20,000 materials, we compile a data subset which we use to propose directions for magnetocaloric material research.

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Enhanced magnetocaloric effect in multi-dimensional Ni-Mn-based alloys through size effect

Mingfang Qian (a), Xuexi Zhang(a) and Lin Geng(a)

(a) Harbin Institute of Technology, Harbin, 150001, China

mingfang.qian@hit.edu.cn; xxzhang@hit.edu.cn

Abstract

Magnetic refrigeration is of great interest due to its high energy efficiency, environmental friendliness and low cost (O. Gutfleisch et al., 2011). However, bulk magnetic refrigerant materials with first-order character usually possess hysteresis losses and concentrated refrigeration working temperature interval ($\delta TFWHM$), which are detrimental for magnetic refrigeration applications. Recent progress on microstructural design has pointed out a strategy to overcome the problems associated with first-order transition by reducing the grain boundaries, i.e. by creating more free surfaces so that the constraints provided by the neighboring grains can be effectively released (M. Chmielus et al., 2009). On the other hand, Ni-Mn-based Heusler alloys are capable of tunable transformation temperatures through composition adjustment, where the first-order transition temperature (or temperature range) can be adjusted more effectively in alloys with higher ratio of free surfaces, owing to enhanced element evaporation at high temperature (X.X. Zhang et al., 2016). Here, 3D foams, 1D microwires and 0D single crystalline micro-particles were introduced in Ni-Mn-based alloys and the magnetocaloric characteristics were determined and analyzed in detail. Figure 1 displays the typical morphologies of the micro-particles (M.F. Qian et al., 2018), microwires and foams. These structures all increased the specific surface area (SSA) of the alloys when compared with the bulk ones. Reduced hysteresis losses were found (see Figure 2 and Figure 3) due to the high SSA that reduces incompatibility between neighboring grains. On the other hand, tunable magnetocaloric effect owing to different magneto-structural coupling states is realized by (i) composition design and subsequent tuning, which adjusts the temperature difference between the martensite transformation (MT) and the magnetic transition, and (ii) creation of gradient composition distribution state, which manipulates the MT range (M.F. Qian et al., 2018). Reduced hysteresis, enlarged working temperature interval $\delta TFWHM$ and moderate magnetic entropy change gave rise to the enhanced magnetocaloric effect in these materials, as shown in Figure 4.

Keywords: Magnetocaloric effect, Hysteresis, Foams, Microwires, Micro-particles.

Giant ECE at ultra-low fields

Xiaoshi Qian*(a)

(a) Shanghai Jiao Tong University, Shanghai, 200240, China, *xsqian@sjtu.edu.cn

Abstract

The EC solid-state cooling represents a zero-global-warming-potential, high efficient refrigeration alternative. Due to the fact that the electrocaloric materials are mostly wide band-gap, insulating dielectrics, which operate as an electricity-driven capacitor, the electrocaloric working bodies inherent the advantages in the cyclic energy efficiency and the device integration. However, giant ECE is normally excited under high electric field, putting obstacles in material stability and further engineering design for prototypes. It is a counter-intuitive and therefore non-trivial process trying to introduce more dipolar entities in a material without generating large polar-correlation that diminishes the ECE. Here, we demonstrated a molecular-modified high-entropy polymer that exhibit giant ECE ($\Delta T > 7\text{K}$) under 50 MV/m (350% enhancement compared to the well-studied P(VDF-TrFE-CFE)), and can be cycle fatigue-freely up to one million cycles (ten thousand times enhancement). The giant enhancement of the intrinsic ECE in the pristine polymers does not require any type of nano-composition. The results would also facilitate researchers in the related fields to design new EC materials and/or devices for advanced heat pump.

Keywords: Electrocaloric Effect, Low-field Operation, Long-term Cycling, High-entropy Polymer.

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Magnetocaloric effect in rare-earth compounds for magnetic refrigeration and gas liquefaction

Eduard Bykov (a,b) , Tino Gottschall (a), Alexey Karpenkov (c), Konstantin Skokov (d), Sergey Taskaev (e,f,g), Yuri Skourski (a), Jochen Wosnitza (a,b)

(a) Dresden High Magnetic Field Laboratory (HLD-EMFL), Helmholtz-Zentrum Dresden-Rossendorf 01328 Dresden, Germany

(b) Festkörper- und Materialphysik, TU Dresden, 01062 Dresden, Germany

(c) Tver State University, Faculty of Physics, Tver, 170033, Russia

(d) Technische Universität Darmstadt, Material Science, Functional Materials,

Alarich-Weiss-Str. 16, 64287 Darmstadt, Germany

(e) Departament of Physics, Chelyabinsk State University, 454001 Chelyabinsk, Russia

(f) National University of Science and Technology "MISIS", 119049 Moscow, Russia

(g) National Research South, Ural State University, 454080 Chelyabinsk, Russia

Our modern industrial society is dependent on the development of energy-efficient and environmentally friendly gas liquefaction and storage technologies. Magnetic refrigeration is one promising alternative and today there are a number of devices operating at room temperature [1]. In recent years, new materials have been examined that show large magnetocaloric effects below room temperature, including the boiling points for hydrogen, nitrogen and natural gas. Rare-earth compounds, which can be potentially used in layered magnetocaloric heat exchangers, enable to create temperature gradients from room temperature down to the boiling point of hydrogen.

In this work, we will present our recent results in pulsed magnetic fields [2]. The first compound that we studied in direct ΔT_{ad} measurements at low temperatures was $DyCo_2$ with a cubic Laves phase-type crystal structure which distorts to a tetragonal phase at its Curie temperature $T_C = 143$ K. It exhibits ferrimagnetic order between the magnetic Dy and Co ions with antiparallel spin aligned [3]. Another compound with similar crystal structure, $Ho_{0.5}Dy_{0.5}Al_2$, has a transition temperature $T_C = 43$ K and has a non-magnetic Al instead of the magnetic Co ion [4]. Moreover, because of the substitution of Dy by Ho, which has the largest magnetic moment among all elements, we have observed a large magnetocaloric effect over a wide temperature window. Direct measurements show that under 2, 20, and 40 T applied magnetic field, the maximum ΔT_{ad} for $Ho_{0.5}Dy_{0.5}Al_2$ is about 5 K, 21 K and 30 K and for $DyCo_2$ 4 K, 12 K and 16 K near their Curie points. These results agree well with specific heat data and it demonstrates the great potential of these compounds. Especially the usage of $Ho_{0.5}Dy_{0.5}Al_2$ for a final stage of H_2 liquefaction in magnetic refrigerator devices is interesting.

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Advanced characterization of multicaloric materials in pulsed magnetic fields

Tino GOTTSCHALL (a), Eduard BYKOV (a,b), Adrià GRACIÀ-CONDAL (c), Lluís MAÑOSA (c), Antoni PLANES (c), Yurii SKOURSKI (a), Jochen WOSNITZA (a,b)

(a) Dresden High Magnetic Field Laboratory (HLD-EMFL), Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany

(b) Festkörper- und Materialphysik, TU Dresden, 01062 Dresden, Germany

(c) Universitat de Barcelona, Departament de Física de la Matèria Condensada, Barcelona, Catalonia, Spain

t.gottschall@hzdr.de

Solid-state refrigeration is based on materials that exhibit one of the caloric effects - electrocaloric, magnetocaloric, barocaloric or elastocaloric - where the temperature is forced to change under the adiabatic application of an electrical, magnetic, or mechanical field [1]. However, some materials are sensitive to more than one external stimulus and are therefore referred to as multicaloric compounds. This circumstance makes it possible to realize cooling cycles beyond the conventional AMR (active magnetic regenerator), such as the scheme that exploits the thermal hysteresis of materials with first-order transitions [2]. However, research into these coupled phenomena is still in its infancy. Advanced characterization methods must therefore be implemented to learn more about these effects.

Direct measurements of the adiabatic temperature change ΔT_{ad} in pulsed magnetic fields have proven to be a useful tool for the analysis of magnetocaloric materials [3, 4]. In this work, we extend these experiments by a further stimulus, namely a constant uniaxial load that is applied during the magnetic-field pulse. Especially the short pulse duration of only a few dozen milliseconds facilitates the direct determination of the temperature change of the sample that is inevitably in contact with the piston unit. We will present our first results under simultaneous magnetic- and stress-field application on Ni-Mn-based Heusler alloys whereby the multicaloric effects can be described in detail.

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Microstructural investigation of large magnetocaloric effects in bulk Ni-Co-Mn-Ti Heusler alloys

Andreas TAUBEL (a), Benedikt BECKMANN (a), Lukas PFEUFFER (a), Franziska SCHEIBEL (a), Semih ENER (a), Tino GOTTSCHALL (b), Konstantin SKOKOV (a), and Oliver GUTFLEISCH (a)
(a) Technische Universität Darmstadt, Material Science, Functional Materials

Alarich-Weiss-Str. 16, 64287 Darmstadt, Germany
(b) Dresden High Magnetic Field Laboratory (HLD-EMFL),

Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany

The family of Ni(-Co)-Mn-X Heusler alloys with X = Al, Sn, Ga, In shows a first-order magnetostructural phase transition and has been studied intensively in terms of magnetocaloric properties and especially their adiabatic temperature change ΔT_{ad} [1]. Recently, the principle of all-d metal Heusler alloys has been demonstrated by placing Ti on the X site in Ni-Mn-X Heusler alloys [2]. The Ni-Co-Mn-Ti alloy system has been studied as a promising material for multicaloric applications due to its large magnetization and volume change, good tunability of the phase transition and enhanced mechanical properties. The good mechanical stability and the high pressure sensitivity make this material system very suitable for the novel approach of multicaloric cooling cycles, using both magnetic field and mechanical pressure as stimuli [3].

By optimizing the processing route of the novel Ni-Mn-Ti system, we could improve the inverse magnetostructural phase transition from high magnetic austenite to low magnetic martensite in terms of sharpness and magnetization change. Microstructural investigations reveal differences in grain sizes and stoichiometric homogeneity that lead to large differences in the transition width for different heat treatments. A large isothermal entropy change of up to 38 J/kg-K in 2 T has been measured in isofield protocol for the compound Ni₃₇Co₁₃Mn₃₄Ti₁₆. However, the adiabatic temperature change in magnetic field changes below 2 T is significantly lower compared to Ni-Mn-In alloys. A reason for this is the low shift of the transition temperature with applied magnetic field, which accounts to only 1-3 K/T for a transition at room temperature. Maximum adiabatic temperature changes of 3.5 K for the first field application and 0.8 K under cyclic conditions are measured directly for a magnetic field change of 2 T. In order to design an efficiently working magnetocaloric material, the magnetic-field sensitivity needs to be adjusted in order to induce a completed phase transition. For this purpose, we produced sample series of different Co contents in order to study the influences of stoichiometry on the maximum achievable magnetocaloric effect in low and high magnetic fields.

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Scale-up of magnetocaloric NiCoMnIn Heuslers by powder metallurgy for room temperature magnetic refrigeration

Simone FABBRICI(a), Francesco PUGLIELLI(b), Valerio MUSSI(b), Francesco CUGINI (a,c), Nicola SARZI AMADE'(a,c), Massimo SOLZI(a,c), Cecilia BENNATI(a), Franca ALBERTINI(a)

(a) IMEM-CNR

Parma, 43124, Italy

(b) MUSP, Machine Tools and Production Systems Laboratory

Piacenza, 29122, Italy

(a) Department of Mathematical, Physical and Computer Sciences, University of Parma

Parma, 43124, Italy

Ni-Mn based Heusler alloys with metamagnetic martensitic transformation are among the most studied materials for future magnetocaloric applications thanks to the high adiabatic temperature changes 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 (magnetization, volume), caloric effects can be obtained not only by applying magnetic fields but also by stress and pressure, enabling multicaloric applications [2,3].

Up to now the quaternary system Ni-Co-Mn-In has shown the highest values, among all Heuslers, of maximum and reversible adiabatic temperature change in a 2 Tesla field [4] associated to the first order martensitic transformation: adiabatic temperature changes up to 8K (peak) and 3K (reversible) for a 2 Tesla field change have been measured for sample $\text{Ni}_{45.7}\text{Co}_{4.2}\text{Mn}_{36.6}\text{In}_{13.3}$

Magnetocaloric Heusler compounds are usually obtained through melting the single elements; many different techniques can be exploited, but they have only been employed for their production on a laboratory scale, while large scale, reliable methods have not been demonstrated yet. Another important drawback for these materials relies in their poor mechanical properties, which challenge the possibility to machine them in high surface-to-volume ratios.

Both brittleness and small sample mass can be considered as major obstacles for a further development of the materials, in terms of structural reliability and workability. In this sense, the possibility to produce dense samples with reduced brittleness and significant dimensions is a mandatory step that still must be developed.

In this contribution we will present a method for a reliable and large-scale production of polycrystalline $\text{Ni}_{45.7}\text{Co}_{4.2}\text{Mn}_{36.6}\text{In}_{13.3}$ alloy with homogeneous composition and properties. We propose a new approach to increase the mechanical stability of Heusler compounds and to obtain a scalable, cost-effective process. A complete magnetocaloric characterization proved that the materials produced show magnetocaloric properties comparable to the best results available in literature for the same material. A series of thermal treatments proved effective in improving transition sharpness and reversibility of the magnetocaloric effect. The overall results as well as the equipment and reagents employed suggest that this method is

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Characterization and Use of Parameterized Material Property Variation in Magnetocaloric Materials

Michael G. SCHROEDER(a,b), Ellen Brehob(a)

(a) University of Louisville

Louisville, 20292, USA, ellen.brehob@louisville.edu

(b) GE Appliances, a Haier Company

Louisville, 20292, USA, Michael.Schroeder2@GEAppliances.com

EXTENDED ABSTRACT

In the field of magnetocaloric heat pumps much research has been performed around designing prototype and theoretical machines, but little has been researched around practical implementation problems such as variability in material properties. The present work parametrically defines actual magnetocaloric material cascades composed of LaFeSiH and MnFePAs, such that they can be recreated using a split Lorentz function with normally distributed parameters. Cascades with variation parameters and typical peak defining parameters are used as input for a model to assess lower limit cooling power density and efficiency as functions of material variation level and temperature span for a high performing microchannel design in a household refrigerator application. Performance drops substantially between the benchmark material variation level observed in available materials and zero material variation, the ideal case. Design considerations are discussed at a high level from the perspective of an appliance manufacturer.

Keywords: magnetocaloric materials; caloric devices; cooling, heat pumping; refrigeration; thermocaloric energy conversion; caloric cascade parameterization; caloric material variation

Performance of an Electrocaloric Air-Conditioner

S. Ravi Annapragada (a), Aritra Sur (b), Bill Rioux (b), John Miano (b), Joseph Mantese (b)

(a) Carrier Corporation

13995 Pasteur Blvd., Palm Beach Gardens, FL 33418

(b) United Technologies Research Corporation

411 Silver Lane, East Hartford, CT 06074

EXTENDED ABSTRACT

It has been more than two decades since electrocaloric-based temperature lifts of 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. Conversely, theoretical models predict the potential for regenerative cooling with lifts in excess of 10 °C at COPs of ~6.

In this talk, we present our work on modeling electrocaloric systems and performance prediction of an electrocaloric based heat pump system under DOE-B conditions. Further, a summary of the experimental evaluation of the first direct-air electrocaloric heat pump module is presented. A multi-physics finite-element model was developed to provide pretest predictions. The experimental results compare well with the model predictions.

Keywords: electrocaloric materials; caloric devices; cooling, heat pumping; refrigeration;

Magnetic Pumping - Key Enabler For A Magnetocaloric Fluid Based Refrigerator With No Moving Parts

Keerthivasan RAJAMANI^{a*}, Jeroen BOERMA^b, H.J. Marcel TER BRAKE^b,

Theo VAN DER MEER^a, and Mina SHAHI^a

^aDepartment of Thermal and Fluid Engineering, Faculty of Engineering Technology, University of Twente, 7522NB, The Netherlands. *k.rajamani@utwente.nl

^bEnergy, Material, and Systems, Faculty of Science and Technology, University of Twente, 7522NB, The Netherlands.

Magnetic Pumping (MP) of Magneto-Caloric Fluids (MCF) - a mixture of micro-particles of magneto-caloric material in a heat transfer fluid, enables the operation of a magnetocaloric refrigerator with no moving parts (fig. 1). Galinstan is considered as the heat transfer fluid, owing to its high thermal conductivity (27 times that of water), and low specific heat (1/14th of water). The existing research on MP involves pumping of ferrofluids with magnetic field frequencies typically in the range of 100 Hz to 1000 Hz (the reference study [1] considered reports flow rate of 3 l/(s m²) at 10 mT and 1000 Hz). Such techniques while suitable for their intended application, cannot be used with MCF, as at these frequencies, the resulting heat generation from viscous dissipation and eddy current losses are significant. So the present study presents a MP design in which a ferrofluid flowrate of 10 l/(s m²) is achieved at 20 mT and at frequencies less than 1 Hz. This is made possible by using an upward and downward slope of the pipe carrying the MCF. The pumping performance is characterized for different magnetic field strengths (upto 40 mT), frequencies (upto 1 Hz), and pumping heights (0 to 10 mm). The experiments are complimented with a mathematical model which is used to perform a parametric study of critical design parameters to determine the optimal MP design. The starting point of the model is to determine the dynamics of a ferrofluid rise in a vertical pipe in the presence of a magnetic field (fig. 2), which is then used to simulate the pumping performance. The model is non-dimensionalized to make the study applicable to a broad range of operational conditions. For the MCF, MnFe(P,Si), and La(Fe,Mn,Si)H based compounds are chosen due to their high adiabatic temperature change (when compared to other magneto-caloric material families) at practical permanent magnet magnetic fields of 1 T. Furthermore, it is important to know the reactivity of galinstan on the magnetization of MnFe(P,Si), and La(Fe,Mn,Si)H based compounds to determine the long-term operational characteristics of the MCF. This is investigated by analysing and discussing the changes in the material structure and properties with magnetization, calorimetry, X-ray diffraction, energy dispersive X-ray, and X-ray photoelectron spectroscopy measurements.

Keywords: Magneto-caloric fluids; magnetic pumping; galinstan; magneto-caloric materials; no moving parts.

Barocaloric Effects in MnNiSi(1-x)Fe₂Ge(x) Alloys

V. Sharma^a, D. Clifford^a, K. Deepak^b, R.V.Ramanujan^b and R. Barua^a

¹ Dept. of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, VA 23284, USA

² School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

³ Dept. of Biomedical Engineering, Virginia Commonwealth University, Richmond, VA 23284, USA

Barocaloric materials exhibit reversible thermal changes that can be driven concurrently or in sequence by a magnetic field or hydrostatic pressure. The use of multiple driving forces can bring about larger thermal changes with smaller field magnitudes over wider operating temperature ranges while reducing hysteresis in one control parameter by shifting it to another. To this end, this study is focused on barocaloric effects in compositional variants of the intermetallic compound, Manganese Nickel Silicide (MnNiSi). Here, the ferromagnetic to paramagnetic transition temperature (T_c) of MnNiSi was reduced by adding Fe and Ge in the ratio of 2:1 (or Fe₂Ge), stabilizing the high-temperature hexagonal phase of MnNiSi down to near room temperature.

Samples of composition (MnNiSi)_(1-x)(Fe₂Ge)_(x) ($0.32 \leq x \leq 0.36$) were prepared by arc melting the constituent elements in stoichiometric proportion in a high purity Ar atmosphere. X-ray diffraction (XRD) characterization, performed to determine the samples' crystal structure and phase content, indicates that alloys with $x = 0.32$ and 0.33 showed an orthorhombic type structure; a hexagonal structure was observed for $x > 0.34$. Magnetization measurements in fields up to 5 T and in the temperature range $5 \text{ K} < T < 385 \text{ K}$ were carried out at ambient and hydrostatic pressures between the range of ($0 \text{ kbar} \leq P < 10 \text{ kbar}$) using a physical property measurement system (PPMS Dynacool, Quantum Design) with a VSM attachment. Isothermal entropy change due to the caloric effect was determined from the isothermal magnetization curves using the Maxwell relation, $\Delta S_{mag}(H, T) = \mu_0 \int (\partial M / \partial T)_H dH$ from H_{min} to H_{max} .

Experimental results indicate that the transition temperature (T_i) of (MnNiSi)_(1-x)(Fe₂Ge)_(x) compounds can be tuned from 365 K–200 K by varying x in the range of 0.33–0.36. Application of hydrostatic pressure decreases the magnetostructural temperature ($dT_i/dP \sim 7.5 \text{ K/bar}$) and thermal hysteresis (ΔT_i) significantly. Indeed, in the $x = 0.33$ sample, ΔT_i is reduced by a remarkable 83% from 30 J/kg·K at ambient pressure to 5 J/kg·K at $P = 7.9 \text{ kbar}$. A maximum magnetic entropy change, $\Delta S_{mag}(\mu H = 2T)$ corresponding to 30 J/kg·K, is noted at 270 K in (MnNiSi)_{0.67}(Fe₂Ge)_{0.33} at an applied pressure of 7.9 kbar. In the $x = 0.34, 0.35$, and 0.36 samples, application of pressures exceeding $\sim 7.5 \text{ kbar}$, results in decoupling of the magnetic (FM \rightarrow PM) and structural (orthorhombic \rightarrow hexagonal) transition. Consequently, a large drop in ΔS_{mag} and thermal hysteresis is noted. The coupling mechanism underlying the barocaloric response of the (MnNiSi)_(1-x)(Fe₂Ge)_(x) system will be explained in the context of temperature- and pressure-dependent structural changes in the crystal structure. Overall, these features emphasize strong coupling between the magnetic spins and the lattice and provide a guideline for tuning caloric effects in first-order materials wherein thermal hysteresis can be exploited to maximize its caloric cooling potential.

Barocaloric effects in metal-organic frameworks

Melony Dilshad(a), Enric Stern-Taulats(a), Juan Manuel Bermudez-Garcia(a,b), Guillaume Nataf(a), Xavier Moya(a)

(a) Department of Materials Science & Metallurgy, University of Cambridge, CB3 0FS, U.K.

xm212@cam.ac.uk

(b) Department of Chemistry, University of A Coruna, 15071 A Coruna, Spain

Abstract

Barocaloric materials display giant thermal changes but they require relatively large operating pressures, which can be challenging to implement in practical applications¹. Consequently, the search for new barocaloric materials with lower driving pressures is very active²⁻⁴. Here we report the barocaloric performance of metal-organic frameworks (MOFs), which present large values of barocaloric tunability, and large reversible barocaloric effects over a wide range of temperatures. The selection of porous frameworks allows for easy compressibility, thus lowering the required driving pressures.

Keywords: Barocaloric materials, metal-organic frameworks, porous materials

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Numerical modelling of hysteresis in caloric materials for solid-state cooling

M. Masche¹, L. Ianniciello¹, J. Tušek², K. Engelbrecht¹

¹Department of Energy Conversion and Storage

Technical University of Denmark - DTU

Anker Engelunds Vej B301,

2800 Kgs. Lyngby, Denmark

² Faculty of Mechanical Engineering University of Ljubljana Aškerčeva cesta 6, SI-1000 Ljubljana,

Slovenia Conventional refrigeration technologies based on the compression and expansion of greenhouse gases with high global warming potential (GWP) are a risk for environment and human health. Hence, the advent of alternative refrigeration technologies is a welcome development. Caloric cooling is a technology based on the caloric effect in solid-state materials driven by an externally applied field. Depending on the nature of the driving field, four main solid-state cooling technologies can be distinguished: magnetocaloric, elastocaloric, electrocaloric, and barocaloric. Caloric cooling that employs solid-state materials with zero GWP as refrigerants is an environmentally friendly cooling alternative and may solve problems associated with conventional refrigeration technologies. The most promising caloric refrigerants are first-order phase transition (FOPT) materials that yield large adiabatic temperature changes when an external field is applied, but also experience a hysteresis effect. One big concern manufacturers have about novel caloric cooling systems is the cyclability of the solid-state refrigerant through its FOPT, which can be impeded due to the existence of hysteresis. In this work¹, we quantify the hysteretic behaviour of six modeled caloric materials (with different isothermal entropy changes and specific heats) and its impact on their cooling performance. Understanding the hysteretic behavior can help to maximize the efficiency of solid-state cooling devices.

A 1D active regenerator model with hysteresis term (treated as an entropy generation) was used to quantify the impact of realistic hysteresis values (0%, 0.04%, 0.5%, 1%, 2%, 6% and 12%) on the cooling performance of caloric materials. The model shows that hysteresis has a larger impact on the coefficient of performance (COP) than on the caloric cooling power. Caloric materials with higher specific heat and lower isothermal entropy change (HiCLOs) show a greater reduction of the cooling performance, and

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performance reductions become more substantial at higher hysteresis levels and higher working frequencies. For instance, a hysteresis entropy generation value (q_{hys}) of 0.04% will lead to a large performance reduction for HiCLOs materials, while materials with low specific heat and low isothermal entropy change (LoCLOs) show positive COP and cooling powers up to a q_{hys} of 2% (see Figure 1). Modeling results are of great importance when designing a solid-state cooling system and selecting the most suitable caloric refrigerant.

Figure 1: Cooling performance maps (cooling COP vs. specific cooling power) for the model materials HiCLOs and LoCLOs with different hysteresis values at a cycle frequency of 1 Hz. Plots show only positive specific cooling loads and COPs, and thus negative values are not presented. The COP is plotted with solid lines, while the second-law efficiency is plotted with dashed line.

Keywords: Hysteresis; caloric materials; 1D model; solid-state cooling

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Performance Upgrade of a Magnetocaloric Heat Pump

M. Masche, J. Liang, K. Engelbrecht, C. R. H. Bahl

*1Department of Energy Conversion and Storage,
Technical University of Denmark – DTU, Denmark*

The magnetocaloric heat pump prototype, called the MagQueen, is a rotary active magnetic regenerator (AMR) system with a rotating permanent magnet ($B_{MAX}=1.46$ T) and 13 AMRs mounted on an iron ring. The MagQueen was initially developed in the Innovation Fund Denmark project ENOVHEAT (2013-2018).¹ The prototype has previously been tested, but performance was lower than expected due to eddy current braking losses and issues with the ten-layered magnetocaloric material (MCM) as an AMR material. In the new RES4BUILD project that aims to decarbonize the energy consumption in buildings, the MagQueen will be coupled to a lower-temperature vapor compression heat pump to provide heating to a building. Improvements have been made to optimize the MagQueen heat pump performance. These improvements include the use of new ten-layered MCM (Calorivac-HS produced by Vacuumschmelze GmbH) in the regenerators and the redesign of a new iron ring (see Figure 1) made of thin laminations to reduce the eddy current braking torque when rotating the magnet. The new MCM allows the packing of the regenerators without epoxy, leading to both a higher heat transfer performance and lower hydraulic resistance, which can decrease the pressure drop and power to pump the fluid through the regenerators.

Testing of the upgraded MagQueen heat pump system (see Figure 2) showed that the laminated ring reduces the eddy current braking power by up to 77 % compared to the previous solid ring. This has great potential to improve the overall heat pump efficiency. Initial tests running at 0.5 Hz and different flow rates showed that the upgraded heat pump can operate at a high efficiency. Heating power was measured as a function of the temperature span (i.e., the temperature difference between hot reservoir and cold reservoir) with varying the hot reservoir temperatures. Each temperature span provides a different maximum heating COP and heating power. Highest COPs and heating powers can be achieved at a hot reservoir temperature of 22°C. Calculated second-law efficiencies for the upgraded MagQueen heat pump design are higher than the previous record for magnetocaloric devices, which was 18 %.² To improve the performance of the MagQueen further, we plan to modify the hydraulic system in order to provide stable flows entering and exiting the regenerator beds. Future tests will also be run at higher cycle frequencies to improve the heat pump performance even further.

Keywords: Magnetocaloric materials; caloric devices; heat pumping

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Fatigue-resistant high-performance elastocaloric materials via additive manufacturing

Huilong Hou ^{1,9}, **Emrah Simsek** ², **Tao Ma** ², **Cheikh Cisse** ³, **Nathan S. Johnson** ³, **Suxin Qian** ⁴, **Drew Stasak** ¹, **Naila Al Hasan** ¹, **Lin Zhou** ², **Yunho Hwang** ⁵, **Reinhard Radermacher** ⁵, **Valery I. Levitas** ^{2,6,7}, **Matthew J. Kramer** ^{2,7}, **Mohsen Asle Zaeem** ³, **Aaron Stebner** ³, **Ryan T. Ott** ², **Jun Cui** ^{2,7}, **Ichiro Takeuchi** ^{1,8*}

¹ Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, United States of America

² Division of Materials Science and Engineering, Ames Laboratory, Ames, Iowa 50011, United States of America

³ Department of Mechanical Engineering, Colorado School of Mines, Golden, Colorado 80401, United States of America

⁴ Department of Refrigeration and Cryogenic Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, People's Republic of China

⁵ Center for Environmental Energy Engineering, Department of Mechanical Engineering, University of Maryland, College Park, Maryland 20742, United States of America

⁶ Departments of Aerospace Engineering and Mechanical Engineering, Iowa State University, Ames, Iowa 50011, United States of America

⁷ Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, United States of America

⁸ Maryland Quantum Materials Center, University of Maryland, College Park, Maryland 20742, United States of America

⁹ School of Aeronautic Science and Engineering, Beihang University, Beijing 100191, People's Republic of China

Huilong Hou: huilong_hou@buaa.edu.cn

Ichiro Takeuchi: takeuchi@umd.edu

Extended abstract

Elastocaloric cooling, which exploits superelastic transitions of shape memory alloys to pump heat, has recently emerged as a frontrunner in alternative cooling technologies. Despite its intrinsic high efficiency, elastocaloric materials exhibit hysteresis associated with input work, a common attribute of caloric cooling materials. Here, we employ additive manufacturing to design highly-reversible superelastic transition pathways at a microscopic level in elastocaloric Ni–Ti. Through rapid cooling and high-precision compositional tuning, we fabricate Ni–Ti-based nanocomposites with unique curved nano-interfaces, which give rise to quasi-linear stress-strain behaviors with unusually narrow hysteresis, resulting in enhancement in the materials coefficient of performance by a factor of four to seven. Our nanocomposite NiTi is stable over 1 million cycles of superelastic transitions, opening the door for their direct implementation in cooling devices where additive manufacturing now provides much-needed geometrical design flexibility in elastocaloric system components which serve as both refrigerants and heat exchangers.

Development of the Magnetocaloric Part of a Hybrid Multisource Heat Pump

Christian R.H. Bahl¹, Marvin Masche¹, Stefano Dall'Olio² and Kurt Engelbrecht¹

¹Department of Energy Conversion and Storage,

Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

²Faculty of Mechanical Engineering, University of Ljubljana, 1000 Ljubljana, Slovenia

The decarbonising of building energy consumption is key to reaching the ambitious energy and climate goals set out by the EU. Renewable energy heating and cooling solutions in buildings have not occurred at the same pace as the uptake of renewable electricity solutions. The RES4Build project will develop integrated renewable energy based solutions based around a multisource heat pump concept. The idea is a hybrid magnetocaloric and vapour compression heat pump, which is connected to solar collectors and borehole energy storage systems. In order to realise such a system, the performance and reliability of the magnetocaloric part must be improved.

The magnetocaloric part of the hybrid heat pump concept will be the MagQueen device at DTU Energy. This has a rotating two-pole permanent magnet, which generates an average of 1.46 T in 13 tapered AMR beds. The material in the beds is packed spheres of the type LaFeSiMnH, supplied by Vacuumschmelze. A number of computer controlled solenoid valves control the flow characteristics of the fluid circuit, allowing a high degree of automation. This automation is important for the integration of the magnetocaloric heat pump with the rest of the system.

The development towards this hybrid heat pump system will be discussed and initial results will be shown. These developments include the implementation of novel magnetocaloric materials with a higher degree of long-term stability. Also, control strategies for the efficient operation of the both the magnetocaloric heat pump and the overall system will be discussed.

Soft caloric materials for new heat-management technologies

Brigita Rožič(a), Gregor Skačej(b), Boštjan Zalar(a), Samo Kralj(a, c), Zdravko Kutnjak(b)

(a) Jožef Stefan Institute, 1000 Ljubljana, Slovenia, brigita.rozic@ijs.si

(b) Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia

(c) Faculty Natural Sciences and Mathematics, University of Maribor, 2000 Maribor, Slovenia

Abstract

Materials with large caloric effects, such as the electrocaloric (EC) and elastocaloric (eC) effects, have the promise of realizing new solid state refrigeration techniques (Kutnjak et al., 2015, Moya et al., 2014). First proof of such conceptual cooling devices was produced from relaxor ferroelectric ceramic and polymer thin films (Rožič et al., 2011), but with rather low power density, due to the relatively large EC inactive regenerator mass (Plaznik et al., 2015). The natural idea is to replace such regenerator with the EC active dielectric fluid, such as liquid crystals (LCs), which may improve the power density of EC cooling devices. Another soft material, called liquid crystal elastomers (LCEs), are good candidates with large elastocaloric effect with potentially better elastocaloric responsivity than shape memory alloys wires, in which the eC temperature change of 40 °C was observed at 0.8 GPa stress field.

In this contribution a review of recent direct measurements of the large EC effect in LCs and large eC effect in LCEs will be given. In smectic liquid crystalline materials and mixtures of LCs with functionalized nanoparticles the EC effect exceeding 8 K was found in the vicinity of the isotropic to smectic A phase transition. Direct EC measurements indicate that the EC response is significantly enhanced by the latent heat (Klemenčič et al., 2019). Further, the results of direct measurements of the eC in side-chain and main-chain (MC) LCEs will be presented. The eC change of temperature of about 1 K was observed in MCLCEs. However, both soft materials can play a significant role as active cooling elements and parts of thermal diodes or regeneration material in development of new cooling devices.

Keywords: Soft calorics, electrocaloric, elastocaloric, liquid crystal-based materials, cooling

Soft caloric materials for new heat-management technologies

Brigita Rožič(a), Gregor Skačej(b), Boštjan Zalar(a), Samo Kralj(a, c), Zdravko Kutnjak(b)

(a) Jožef Stefan Institute, 1000 Ljubljana, Slovenia, brigita.rozic@ijs.si

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Abstract

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Keywords: Soft calorics, electrocaloric, elastocaloric, liquid crystal-based materials, cooling

Experimental investigation of the influence of synchronization profiles between magnetic field and fluid flow on the performance of a magnetic refrigerator

Zhenxing Li (a)(b), Jun Shen (a)(b)*, Ke Li (a)(b)**, Xiaohui Guo (a)(b), Wei Dai(a)(b)

(a) Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

(b) University of Chinese Academy of Sciences, Beijing 100049, China

* e mail: jshen@mail.ipc.ac.cn, ** e mail: vlike87@163.com

Abstract: An active magnetic regenerator (AMR) with magnetic Brayton cycle has been adopted in a rotary type magnetic refrigerator. In the refrigerator, a double Halbach magnet group could provide an average magnetic field from 0.04 T to 1.50 T at a length of 100 mm when the inner Halbach magnet array was rotated. An AMR filled with 211.7 g gadolinium spheres was put in the center of the magnet group. A hydraulic piston displaced alkaline solution back and forth through the AMR to hot/cold heat exchangers.

In the experimental research, synchronization profiles of magnetic field and flow field were of great significance for improving the refrigeration performance. Based on the four processes (Magnetization Releasing heat Demagnetization Absorbing heat) in a cycle, a sequence ratio was defined for the relative time length of these four processes. The fluid flowed accordingly in releasing heat and absorbing heat processes. There were four time sequence ratios investigated in the experiments which are 1:1:1:1, 1:2:1:2, 1:3:1:3 and 1:4:1:4, respectively. With a better control of thermal losses, some performance parameters including temperature span, cooling power and coefficient of performances (COPs) were investigated at different utilization factors (0.26 to 1.52) and different operating frequencies (0.25 Hz to 1.00 Hz). A typical experimental result at 0.50 Hz revealed the better temperature span was obtained by the longer flow time. A no load temperature span of 19.9 K was achieved at time sequence ratio 1:4:1:4, which was 15.7 % higher than that at time sequence ratio 1:1:1:1. A largest temperature span of 20.5 K was obtained with a frequency of 0.65 Hz and a time sequence ratio of 1:3:1:3 (At relatively high frequencies investigated, range of time sequence was limited due to the difficulty in rotating the magnets in a short time). As for the COP, both electric power and cooling power were measured. Compared with a conventional continuous operating mode of magnet and fluid, the intermittent mode here could lead to a larger electrical power demand due to several stop--start processes in the moving of the magnet and the piston. The electrical power for the piston were far larger than that for pumping the fluid which was calculated from the pressure drop. Besides, when the flow time increased under the same utilization factors, the electric power of the piston had a slight downward trend. It could be mainly caused by slower acceleration and lower speed of the piston with the increase of the flow time. At a typical operating point, a temperature span of 12.3 K with a cooling power of 20 W was achieved and its specific cooling power was 94 W/kg in terms of refrigerant mass, when the time sequence ratio was 1:2:1:2 at 0.75 Hz. Based on the releasing heat in the hot end of regenerator, the corresponding COP was 1.02, and the COP in terms of the electric power was 0.31. So, it is necessary to reduce the start--stop processes for the synchronization profiles to obtain better COPs in the further study.

Keywords: Magnetocaloric effect; Active magnetic regenerators; Magnetic refrigeration device; Synchronization profiles; Experiments

Giant Barocaloric effect and Refrigeration capacity in $\text{CrI}_2(\text{depe})_2$

Paula O. RIBEIRO (a), Bruno P. ALHO(b), Rafael M. RIBAS(b), Vinicius S. R. DE SOUSA(b), Eduardo P. NOBREGA(b), Pedro J. VON RANKE(b)

(a) Instituto de Aplicação Fernando Rodrigues da Silveira, UERJ.

Rio de Janeiro, 20260-232, Brazil, e-mail: paula.ribeiro@gmail.com.

(b) Instituto de Física Armando Dias Tavares, UERJ

Rio de Janeiro, 20550-013, Brazil,

The search for new solid materials to be used as refrigerants in solid-state refrigerators has attracted great interest from the scientific community. Compared with widely used gas compression-expansion refrigeration technology, field induced refrigeration in solid materials reduces environmental damages and improves energy efficiency. Recently, spin-crossover materials were pointed out as strong candidates to working as refrigerant materials due to their huge barocaloric effect. In this work we report the giant isothermal entropy change (ΔS_T) and adiabatic change (ΔT_{ad}) upon moderated pressure variation in the spin-crossover complex $[\text{CrI}_2(\text{depe})_2]$, where depe =1,2-bis(diethylphosphino)ethane. This complex was investigated considering a model Hamiltonian [1] to describe the microscopic interactions in spin crossover compounds. The three main entropies contributions (configurational, magnetic and phonon) were simulated using proper microscopic parameters. The high values of $\Delta S_T = 40 \text{ J kg}^{-1} \text{ K}^{-1}$ and $\Delta T_{ad} = 10.6 \text{ K}$ for $\Delta P = 2 \text{ kbar}$, were obtained around low \leftrightarrow high spin phase transition temperature ($T_{1/2}$). Besides, due to the large barocaloric shift parameters ($\delta T_{1/2}/\delta P \sim 52 \text{ K/kbar}$), the giant refrigerant capacity ($RC = 3583 \text{ J kg}^{-1}$) was established for $[\text{CrI}_2(\text{depe})_2]$.

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Swirl generator design for tubular absorber of vapour absorption refrigeration system

Narasimha Reddy Sanikommu, Mani Annamalai, Shaligram Tiwari

Refrigeration and Air Conditioning Laboratory, Department of Mechanical Engineering, Indian Institute of Technology Madras, Tamil Nadu, 600036, India, mania@iitm.ac.in

Abstract

Generation of swirl flow of the fluid with a swirl generator is considered as a passive enhancement technique. Among all the passive enhancement techniques, wire coil inserts and twisted tape inserts were most widely used than other techniques (Wang and Sunden, 2002). Chang and Dhir (1995) carried out an experimental analysis on a tangential entry of air into tubes to study the mechanism of heat transfer enhancement. They recognized that the heat transfer was enhanced due to high maximum axial velocity near the wall and high turbulence level in the tube core region. Panda and Mani (2014) experimented with the tangential air entry in water with different flow directions. Later, the authors had extended their studies numerically to R134a refrigerant vapour and DMF liquid in a tubular absorber of vapour absorption refrigeration system (VARS). The results had shown that the mass and heat transfer coefficients were improved by 120-170% and 20-40% respectively (Panda and Mani, 2016). Banu and Mani (2019) showed that using the cavity type swirl generator in an ejector of vapour jet refrigeration system improved ejector performance by 5%. Amaris et al. (2014) studied the effect of internally micro finned surface in a tubular absorber of VARS working with $\text{NH}_3\text{-LiNO}_3$, and the absorption rate was increased up to 1.7 times due to fins. Experiments were carried out by Cerezo et al. (2018) to investigate the effect of helical static mixers of tube and annulus type in an absorber. The results showed a 31.61% increment in absorber load per unit area, and 20% more vapour had absorbed than a smooth pipe. A compound heat transfer enhancement technique, i.e. dimpled tube (pitch ratios of 0.7 and 1.0) with swirl generator (twisted tapes with twist ratios of 3, 5, and 7) was used by Thianpong et al. (2009) to examine the performance characteristics of the technique. It was observed that the heat transfer and friction factor increase with decrease in twist ratio and pitch ratio. A cavity-type swirl generator design is proposed in the present work, and numerical simulations will be carried out with commercial CFD software to study the swirl decaying characteristics in a pipe working with air. Moreover, effect of the camber angle and twist angle on the swirl number will be investigated. The profile used to generate the swirl generator is shown in Figure 1, and axial velocity variation along the radial direction is shown in Figure 2 for the proposed swirl generator. Since, the absorber in the vapour absorption refrigeration system suffers from poor heat and mass transfer coefficients (Castro et al., 2009), placing the proposed swirl generator at the inlet of tubular bubble absorber will enhance the absorption heat and mass transfer rates by increasing the refrigerant bubble residence time as well as turbulence.

Magnetocaloric Effect of Geometrical Frustrated Tb_{1-x}Y_xNiAl for Hydrogen Liquefaction

Hideaki Kitazawa (a), Kenta Kujirai (b), Kengo Morita (c), Akira Tamaki (and Hiroaki Mamiya (

(a) National Institute for Materials Science NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

(b) Graduate School of Engineering Tokyo Denki Univ., 5 Senju Asahi-cho, Adachi, Tokyo 120-8551, Japan

(c) School of Engineering Tokyo Denki Univ. 5 Senju Asahi-cho, Adachi, Tokyo 120-8551, Japan

Compared to gaseous hydrogen, liquid hydrogen has a volume of 1/800 that of gaseous hydrogen. It has features such as mass transportation, mass supply, mass storage, and space saving, and is indispensable for full scale spread of hydrogen energy. However, since the liquefaction temperature is 20 K, the energy for liquefaction should be reduced due to development of the cooling system with higher efficiency. Existing gas refrigeration technology has fundamental inefficiencies in compressors and liquefaction methods, and it is not easy to achieve liquefaction efficiency exceeding 50. Compared with gas refrigeration, the magnetic refrigeration hydrogen liquefaction efficiency can be expected to be 50% or more in principle. Our planned cooling system by magnetic refrigeration will be operated from 77 K to 15 K after hydrogen gas is precooled with liquid nitrogen. Since it is not possible to cover this wide temperature range with only one type of magnetic refrigeration material, we consider covering a wide temperature range with multiple magnetic refrigeration materials.

The ternary rare earth intermetallic compound TbNiAl with the hexagonal ZrNiAl type crystal structure has a specific structure in which Tb magnetic ions responsible for magnetism are connected in a kagome lattice form in the c plane. A successive magnetic phase transition ($T_{N1} = 48$ K, $T_{N2} = 25$ K) is exhibited, and a partially disordered state is realized in the intermediate temperature range ($T_{N2} \leq T \leq T_{N1}$) [1]. These unique magnetic properties are interpreted by geometric frustration effects, but there are still many unclear points such as details of the interaction. Previously, to investigate the stability of the frustration effect, a polycrystalline sample Tb_{1-x}Y_xNiAl in which the Tb site was replaced with Y nonmagnetic ions was prepared, and the magnetization and magnetic susceptibility were measured. Interestingly, we found that the antiferromagnetic order changed to the ferromagnetic order when $x > 0.08$ (see inset in Fig. 1) [2].

In this study, we investigated how the magnetocaloric effect (MCE) changes as a function of x by measuring the magnetization and specific heat of Tb_{1-x}Y_xNiAl (0 ≤ x ≤ 0.66) as the optimal magnetic refrigeration search for hydrogen liquefaction. Figure 1 shows the temperature dependence of magnetic entropy change ΔS_{mag} when the magnetic field is changed from 0 T to 5 T and the specific heat at 0 T for Tb_{1-x}Y_xNiAl ($x = 0$ and 0.1). It can also be seen that maximum magnetic entropy change ΔS_{mag}^{max} is 0.078 J/cm³K and 0.060 J/cm³K at 51 K and 49 K, respectively. These values are quite large for hydrogen liquefaction. Interestingly, the reduction rate of ΔS_{mag}^{max} is much larger than the reduction rate of 10% of the Tb

component.. It suggests that the geometrical frustration affects the enhancement of entropy change.

Keywords: hydrogen liquefaction, magnetocaloric effect, geometrical frustration, TbNiAl

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Colossal rotating magnetocaloric effect in highly textured HoNiSi polycrystal with strong magnetocrystalline anisotropy

Hu Zhang,^{a,*} ChengFen Xing,^a He Zhou,^a XinQi Zheng,^a WenTuo Han,^a and Yi Long,^a

^a School of Materials Science and Engineering, University of Science and Technology of Beijing, Beijing 100083, P R China.

Generally, magnetocaloric effect (MCE) is considered to be mainly contributed by the change of exchange energy during the magnetic transition, and many works have been made to explore and improve the contribution from exchange energy. Recent studies showed that the contribution from magnetic anisotropy energy could also be considerable during the rotation of spontaneous magnetization vector.^{1, 2} Based on that, a new concept named “rotating magnetocaloric effect (RMCE)” has been proposed and has been investigated in some single crystals.¹ Recently, we first reported a giant RMCE in textured polycrystalline DyNiSi compound.³ It opens up a more feasible way to realize the application of RMCE, that is, exploring RMCE in the oriented polycrystalline materials. In present work, we further report a colossal RMCE in highly textured HoNiSi polycrystal.

The inset of Fig. 1 shows the EBSD orientation map of the longitudinal cross section of HoNiSi compound. The alloy presents a strong texture structure with $\langle 010 \rangle$ crystal direction parallel to the solidification direction (SD). Fig. 1 shows the temperature dependence of zero-field-cooling (ZFC) and field-cooling (FC) magnetization under 0.05 T with the magnetic field parallel and perpendicular to the texture orientation, respectively. The magnetization along parallel direction is nearly one order higher than that along perpendicular direction, suggesting the strong magnetocrystalline anisotropy (MCA) and the easy magnetization axis is consistent with the preferred crystallographic orientation. energy under 0 H and zero field, respectively. Fig. 2 shows the temperature dependence of $-\Delta S_R$ by rotating HoNiSi from perpendicular to parallel direction. The $-\Delta S_R$ is as high as 26.7 J/kg K under 5 T, which is the largest rotating ΔS_R reported so far. Particularly, the $-\Delta S_R$ reaches 18.5 J/kg K under 2 T, which is even larger than those of most reported materials under 5 T. Consequently, the colossal RMCE as well as simple preparation make textured HoNiSi the promising material for rotating magnetic refrigeration. Fig. 1. The temperature dependence of ZFC and FC magnetization under 0.05 T with the magnetic field parallel and perpendicular to the texture orientation, respectively. The inset shows the EBSD orientation map of the longitudinal cross section of HoNiSi compound. Fig. 2. The temperature dependence of $-\Delta S_R$ by rotating HoNiSi from perpendicular to parallel direction. This work was supported by the National Key Research and Development Program of China (Grant No.: 2017YFB0702704); the National Natural Science Foundation of China (Grant Nos.: 51671022 and 51701130); the State Key Lab of Advanced Metals and Materials (Grant No. 2019-Z11); the Scientific and Technological Innovation Team Program of Foshan (Grant No.: 2015IT100044); and the Fundamental Research Funds for the Central Universities (Grant No.: FRF-TP-18-014B1).

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Magnetocaloric effect in GdNi₂ studied in magnetic fields up to 10 T

Sergey Taskaev(a,b,c), Vladimir Khovaylo(b,c), Maxim Ulyanov(a), Dmitriy

Bataev(a), Anastasiya Basharova(a), Marina Kononova(a,b), Daniil Plakhotskiy(a)

(a) Chelyabinsk State University, Chelyabinsk, 454001, Russia, khovaylo@mis.ru, (b) National University of Science and Technology “MISIS”, Moscow, 119049, Russia, (c) National Research South Ural State University, Chelyabinsk, 454080, Russia

Abstract

Natural gases have played significant role in different sectors of the global economy. Recent analysis has shown that the world's gas consumption doubled over the three decades; further growth of the gas consumption is predicted, rising to 23 – 28 % of the total primary energy demand by 2030. Therefore, liquefaction of natural gases rapidly gains global importance. In this context, magnetic refrigeration emerges as a modern energy-saving technique which is alternative to the traditional gas-compression refrigeration. This paper is devoted to the study of magnetocaloric effect in magnetic fields up to 10 T in a representative of Laves phase GdNi₂ which is considered as a perspective material for liquefaction of natural gases. For the magnetic field change 10 T, magnetic entropy change $\Delta S_m \approx -17 \text{ J/kg}\cdot\text{K}$ was attained around Curie temperature $T_C = 70 \text{ K}$. The adiabatic temperature change ΔT_{ad} estimated from the ΔS_m and specific heat data measured in magnetic fields up to 5 T, reached $\Delta T_{ad} \sim 4 \text{ K}$ in the vicinity of T_C .

Keywords: Magnetocaloric, Laves phase, gas liquefaction

Heat switch for the magnetic refrigerator operating at cryogenic temperatures of 20-77K

Konstantin A. KOLESOV(a), Olga V. BELOVA(a), Alexey V. MASHIROV(b), Victor V. KOLEDV(b), Alexander P. KAMANTSEV(b), Dmitriy A. Kalinkin(a), Sergey V. Gorynov(a), Vladimir G. SHAVEROV(b)

(a) Bauman Moscow State Technical University

Moscow, 105005, Russia, kolesovkka@mail.ru

(b) Kotelnikov Institute of Radioengineering and Electronics of RAS

Moscow, 125009, Russia, a.v.mashirov@mail.ru

Mechanical heat switches have become widely used in low-temperature calorimetry. They come into use at the beginning of the last century [1, 2] and now are used in tasks where it is impossible or inefficient to use heat exchange gas [3]

The aim of this work is to study the heat transfer coefficient of two disks with a diameter of 15 mm and a thickness of 5 mm, which came into contact with different forces and represented a prototype of a heat switch for the magnetocaloric refrigeration. Moreover, it was necessary to study which effect different coating of the discs and the disc material produce on the thermal resistance. These heat switches are planned to be used for magnetic cooling in the temperature range 20-77K, so the experiment was also carried out in a magnetic field up to 10 T. The discs were made of annealed copper or magnetocaloric materials such as DyNi₂. Heat transfer surfaces were polished or the structure was applied on them by epitaxial method or using intermetallic nanowires [4].

The prototype of the heat switch was placed in a tube, which was located in the cryostat. In order to create a magnetic field of 10 T a superconducting coil, which is cooled with a cryocooler, was placed around the tube in its lower part. The heat switch consists of a fixed holder, in which the discs are fixed with a thermal insulation material, and a movable part, in which the disc is also fixed. In order to obtain a temperature difference, heaters were installed in the fixed part of the heat switch. The moving part of the heat switch was transferred by a linear motor.

As a result of the study, data on the amount of heat, which was transferred from one studied sample to another and the coefficient of thermal resistance had been obtained. The time of complete heat transfer between disks had been obtained. The influence of the surface on the contact heat exchange had been investigated.

The reported study was funded by RFBR and JSC Russian Railways according to the research project № 17-20-04236.

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refrigeration, DyNi₂, thermal switch, heat transfer

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Keywords: Cryogenic magnetic refrigeration, DyNi₂, thermal switch, heat transfer

The prototype of a cryogenic magnetic refrigerator based on a cryomagnetic system with a 10 T superconducting coil

Alexey Mashirov(a), Victor Koledov(a), Konstantin Kolesov(b), Alexandra Demyanenko(c), Akhmed Aliev(d), Mikhail Alekseev(c), Evgeniy Kostrov(c), Olga Belova(b), Maxim Klenov(c), Alexander Kamantsev(a),

Sergey Taskaev(e), Vladimir Shavrov(a)

(a) Kotelnikov Institute of Radioengineering and Electronics of RAS, Moscow, 125009, Russia, a.v.mashirov@mail.ru (b) Bauman Moscow State Technical University, Moscow, 105005, Russia (c) Cryotrade Engineering, Moscow, 125367, Russia (d) Amirkhanov Institute of Physics of Daghestan Scientific Center of RAS, Makhachkala, 367003, Russia (e) Chelyabinsk State University, Chelyabinsk, 454001, Russia

Abstract

The concept of a magnetic refrigerator at cryogenic temperatures below the temperature of liquid nitrogen based on a reciprocating mechanism was considered (Mashirov et al., 2018). This type of design implies that a mechanical heat switch will be used, in contrast to the well-known cryogenic magnetic refrigerator, in which gaseous helium is used as heat keys (Park et al., 2017). Theoretically, it was estimated that the amount of heat obtained as a result of the magnetocaloric effect will be transferred due to thermal conductivity to the hot and cold heat exchanger in a time of about 1 s. Ponderomotive forces will be equal to values of about 70 N. The aim of this work was to create a prototype of a single magnetic cooling cycle based on a cryomagnetic system with a superconducting coil with a magnetic field induction of 10 T and with the possibility of maintaining the temperature of the working body of a magnetic refrigerator from 2 K to 300 K. The superconducting magnet was made based on the superconducting Nb₃Sn coil. Using a Hall sensor measurements of the magnetic field were carried out the maximum value of the induction was 10+/-1% T. The prototype of the magnetic refrigerator is located in the mine of the superconducting magnet, the diameter of the mine is 29 mm. A sample of a polycrystalline DyNi₂ alloy with a Curie ferromagnetic point $T_c = 23$ K was used as a magnetocaloric working body. In this design of the magnetic refrigerator mechanical heat switches were used. The dependence of the thermal resistance of mechanical heat keys on the heat transfer surface was separately investigated. This paper presents the results of modeling and preliminary experiments to determine the thermodynamic characteristics of a prototype of a single cycle magnetic refrigerator of the reciprocating type based on the DyNi₂ alloy, the aforementioned superconducting magnet up to 10 T and a cryostat of 2-300 K. The reported study was funded by RFBR to the research project No. 18-07-01321 and partially was carried out within the framework of the state task.

Keywords: cryogenic magnetic refrigeration, heat switch, DyNi₂.

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High-throughput computational search of MM'X alloys for magnetocaloric applications

N. M. Fortunato, I. Opahle, O. Gutfleisch and H. Zhang

Hexagonal MM'X compounds are a promising class of compounds for magnetic cooling, where the magnetocaloric effect (MCE) is greatly enhanced by magneto-structural coupling. In these compounds, such as MnNiGe, a transition occurs between the low temperature Pnma and high temperature P63/mmc phase [1]. By compositional substitution it is possible to couple the structural and magnetic transitions in a first-order magneto-structural transition, leading to the desired large and discontinuous magnetization change. Likewise, the magneto-structural transition can be tuned to near room temperature. For instance, by alloying between MnNiGe where there is a high temperature transition and FeNiGe where only the Pnma phase is found, it is possible to adjust the transition temperature [2].

An underlying design principle for the MCE in this type of systems is to perform isostructural alloying, by interpolating between two stable pure compounds [3]. In this spirit, we performed a high-throughput density functional theory (DFT) screening of novel parent compounds, to accelerate the search for new magnetocaloric phases. We compute the thermodynamic (formation energy and convex Hull), mechanical and dynamical stability of the martensite and austenite phases, finding 138 magnetic compounds where the Pnma martensite phase is the stable structure, with P63/mmc austenite being metastable. To serve as guidance for later experimental optimization of the MCE we estimate the magneto-volume coupling (dT_c/dP) [4], structural and magnetic transition temperatures. For selected novel compounds we explicitly evaluated the magnetic and vibrational from DFT calculations, to verify the presence of a structural transition, and discussed potential paths of isostructural tuning. Further, in order to elucidate the underlying physics of the MCE effect in the known MM'X, we study the effects of substitutional disorder on the electronic, magnetic and vibrational properties in the Mn-Fe-Ni-Ge system.

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A lead-free and antiferroelectric materials as electrocaloric coolants

Brigita Rožič(a), Bouchra Asbani(b), Mimoun El Marssi(b), Hana Uršič(a), Jurij Koruza(c), Barbara Malič(a), R. Pirc(a), Daoud Mezzane(d), Zdravko Kutnjak(a)

(a) Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia, Zdravko.kutnjak@ijs.si

(b) LPMC, University of Picardie Jules Verne, 33 rue Saint-Leu, 80000 Amiens, France

(c) Technical University Darmstadt, Alarich-Weiss-Str. 2, 64287 Darmstadt, Germany

(d) LMCN, University Cadi Ayyad, BP 549, Marrakech, Morocco

Abstract

The request for greener heat-management technologies has recently developed significant interest in new electrocaloric (EC) effect-based cooling devices that have the potential to replace the existing cooling technics (Kutnjak et al., 2015, Mischenko et al., 2006).

In this contribution the direct measurements of the large EC effect in antiferroelectric, lead-based and lead-free ferroelectric materials (Pirc et al., 2015, Asbani et al., 2015) will be presented. Specifically, the large positive EC response observed by direct experiments in lead-free BCTZ-based ferroelectric materials will be reviewed. In addition, the negative EC effect in antiferroelectric PZSTN, n/95/5 PLZT and PBZ ceramics will be investigated by direct experiments. Here, it is demonstrated that both negative and positive EC response can be arbitrarily invoked in antiferroelectric materials by properly controlling the electric field and temperature, which enables enhancement of the electrocaloric cooling power for up to 100%.

Keywords: Antiferroelectric, ferroelectric, electrocaloric, cooling, lead-free

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Study of a self oscillating Thermo-Magnetic Generator; towards a fully autonomous system

S. Ahmim¹, M. Almanza¹, A. Pasko¹, V. Loyau¹, F. Parrain², F. Mazaleyrat¹, M. LoBue¹

1SATIE, ENS Paris-Saclay, CNRS, 94235 Cachan, France

2C2N, Université Paris-Sud, CNRS, 91405 Orsay, France

smail.ahmim@satie.ens-cachan.fr

Development of new technologies to convert waste heat into electricity is today considered a major goal in order to scavenge the huge and low cost energy source represented by low-grade heat from industrial processes and residential buildings. Caloric materials (CM) are classified according to the field triggering the effect. This field defines the main technological challenges and opportunities of different CM classes. Magnetocaloric materials (MCM) have been the focus of researches aiming cooling applications since a couple of decades so that an abundant, and reliable amount of data are available on their characterization. Besides field generation using magnets, at the macroscopic and at the micro-device scales, offers some unique opportunities in term of autonomy and of energy efficiency. Thermomagnetic generators (TMG) harness the pyromagnetic effect, namely the variation of magnetization as a function of the temperature, to perform thermodynamic cycles under varying field converting the magnetic energy into electrical one. Several thermo-generation prototypes using MCM have been proposed relying on different conversion chains. Here we have developed a new prototype based on a three steps conversion: thermal to magnetic, magnetic to mechanical and finally mechanical to electrical energy. The geometry is similar to the one studied in [1] with three main differences: the magnetic field lines are spatially confined by the use of a Halbach array improving the magnetic force and the field inside the magnetocaloric material [2]; the active substance is a first-order La(Fe,Si)_{13} from Vacuumschmelze; the mechanical displacement of the MCM is eventually converted to electrical energy using piezoelectric material. Our prototype has been designed to serve as a test bench where most of the main physical quantities characterizing the thermodynamic working cycle are directly measured: the displacement, the temperature of the MCM and the piezoelectric voltage.

Here we focus our discussion on the goal of full autonomy through a self oscillating working cycle where the magnetic field is triggering the caloric effect, acting on the oscillating moving part (viz. activating the thermal switch) at once. The generation and maintenance of a periodic motion [3] and its achievement in a TMG are a matter of smart balance between thermal, mechanical, and magnetic state variables. Numerical and semi-analytic modeling of the dynamic of our device will be discussed and compared with measurements directly performed on the working prototype.

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

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A thermoacoustically driven thermomagnetic electrical generator system without mechanical moving parts

Chao JIANG(a,b), Kaiqi LUO(a,b), Guoyao YU(b), Shunming ZHU(a,b),
Ercang LUO(a,b)

(a) CAS Key Laboratory of Cryogenics, Chinese Academy of Sciences, Beijing, 100190, China,

(b) University of Chinese Academy of Sciences, Beijing, 100049, China

jiangchao18@mails.ucas.edu.cn, Ecluo@mail.ipc.ac.cn

Abstract

In this paper, a thermoacoustically driven thermomagnetic electrical generator (TAD-TMEG) system is presented, in which consists of a thermoacoustically driven self-excited oscillation subsystem and a thermal-magnetic-electrical conversion subsystem. In the two subsystems, there are no any moving mechanical parts, leading to a novel thermal-to-electrical energy conversion system with high reliability and simplicity.

In the thermoacoustic subsystem, it operates between a heat source and a heat sink. When the temperature difference between the heat source and heat sink reaches a threshold value, the subsystem starts oscillating itself. The unique characteristic of the subsystem is that it has no any moving mechanical parts, leading to a simple and reliable method for supplying oscillating heat transfer to drive the thermomagnetic electrical generator (TMEG). In the TMEG, a heat transfer liquid driven by the thermoacoustic oscillating gas is used as the heat exchange medium in the subsystem. The liquid flow channel with symmetrical configuration is a U tube with a square cross-section. There are 4 water coolers and 2 high-temperature heat exchangers in the U tube, and on each side the high-temperature heat exchanger is arranged in the middle of 2 water coolers.

The thermal-magnetic-electrical conversion subsystem consists of two up-down symmetrically arranged units, while each unit has 2 permanent magnets, 2 TM regenerator modules, 2 stacks of silicon steel sheet and induction coils wound around them. To fully utilize the high-temperature heat source, the TM module is designed as a cascade of ferronickel plates with variable Curie temperatures. In addition, the unique configuration of two separated magnetic loops is helpful to efficient utilization of magnetization change for producing electricity.

The operating principle will be described in the paper. In particular, a demonstrating prototype will be designed and built, and the preliminary experimental results will be reported on the 9th Thermag conference.

Keywords: Thermomagnetic electrical generator; Symmetrical magnetic loop;
Thermoacoustically driven self-oscillation; No mechanical moving parts.

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A Generalized Locally Analytical Model for Energy Conversion of Active Caloric Regenerator

Ercang LUO(a,b), Kaiqi LUO(a,b), Shunmin ZHU(a,b), Jingyuan XU(a,b),
Chao JIANG(a,b)

(a) Key Laboratory of Cryogenics, Chinese Academy of Sciences, Beijing, 100190, China

(b) University of Chinese Academy of Sciences, Beijing, 100049, China

Ecluo@mail.ipc.ac.cn

Abstract

There are four kinds of caloric-effect-based energy conversion systems mainly including magnetocaloric, electrocaloric, elastocaloric and barocaloric heat engines and refrigerators/heat pumps[1-2]. Generally, a cyclic exertion of externally applied field and oscillating-flow heat transfer are necessary for their cyclic thermodynamic operation. In the systems, a so-called active caloric regenerator is one of key components.

Indeed, there are several previous papers about the numerical simulations and analysis on their active regenerators[3-5]. However, there are not so much research on analytical models for concise and quick understanding and design of the cyclic solid-state caloric regenerator.

In this paper, a generalized locally analytical model is developed for the four solid-state caloric regenerators. Firstly, a group of mathematical equations for describing the energy conservation of porous regenerator's solid and fluid are given. For the porous regenerator, there is an implied assumption of ideal heat transfer inside both fluid and solid in the paper's model, so thermal penetration depths inside solid and fluid are large enough. However, the limited skin heat transfer coefficient in between the solid and fluid is necessary for practical situation. Then, taking account of the cyclic characteristics of externally applied field and oscillating-flow heat transfer, a perturbation method is used to transform the originally time-domain dependent conservation equations into only domain-dependent equations. As a result, a group of locally analytical equations can be developed, and the solutions for the solid and fluid temperatures can be obtained analytically. Furthermore, the energy conversion characteristics can be analyzed and discussed. In particular, some important factors and relationships about the phase relation between the external cyclic applied field and cyclic heat transfer flow, the heat capacity ratio between the solid and fluid, and the skin heat transfer coefficient and operating frequency can be discussed and better understood. The results of the paper will be described and reported in more detail on the 9th Thermag conference.

Keywords: Caloric regenerator, Cyclic applied field and flow, Locally analytical model.

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Unconventional magnetocaloric wine cooler initial performance

Stefano Dall'Olio, Urban Tomc, Katja Klinar, Simon Nosan, Andrej Kitanovski
University of Ljubljana, Faculty of Mechanical Engineering, Ljubljana, 1000, Slovenia,
stefano.dallolio@fs.uni-lj.si

Abstract

To exploit the potential of magnetic refrigeration, a prototype of wine chiller based on an active magnetic regenerator (AMR) was designed and built in our lab. The device consists of two regenerators working in parallel, containing around 100 g of gadolinium (Gd) in total. In our system the magnetic flux is provided by an electromagnet and the applied flux can reach a magnitude of 1 T in the high field mode, while being close to zero when the coil is not activated. The magnet can work at a frequency up to 20 Hz. To increase the cooling power and the coefficient of performance (COP) of our magnetic prototype we focused on the optimization of the core component of the technology, i.e. the active regenerator. In our prototype the fluid passes through a porous media consisting of a packed bed of Gd spheres having an average diameter between 100 and 300 μm . The regenerator has a cross section of 167 mm², length of 55 mm, and is 3D printed with the technique of stereolithography (SLA). The optimization of the regenerator has been achieved by focusing on three main areas: structural characteristics of the housing, flow distribution and heat losses of the regenerator to the environment. For each of the previous points, there was an iterative process based on numerical simulations carried out in ANSYS to decrease the amount of dissipations. For the mechanical design of the regenerator, we considered 8 bar as the highest flow working pressure, and we consequently optimized the geometry to have a maximum deformation of the housing lower than 150 μm , threshold which corresponds to the average sphere diameter.

The flow maldistribution inside the regenerator is another important source of dissipation, together with the amount of the dead volume. Therefore, a flow distribution chamber has been added at the regenerator inlet and outlet, and the geometry of this space has been adjusted to have the most uniform flow along the regenerator. The effect of the different chamber shapes on the flow distribution has been verified in FLUENT and is shown in the Figure below. Because the distribution chamber acts as dead volume for the regenerator, we tried to keep it as small as possible. Moreover, we also focused on how to decrease the parasitic losses to the environment. This process has been done by insulating the regenerator from the environment and by installing some passive heat sink on the iron core of the electromagnet. After initial validation tests and debugging of the system, we were able to obtain the first experimental results that will be presented in this paper.

Comparison of magnetocaloric properties and hydrogen stability in $\text{La}_{1-z}\text{R}_z(\text{Fe},\text{Si},\text{Mn})_{13}\text{H}$ ($\text{R} = \text{Ce}$ and Pr) compounds

Asaya Fujita(a)

(a) National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, 463-8560, Japan
Abstract

To utilize excellent magnetocaloric properties of LaZn_{13} -type $\text{La}(\text{FeSi})_{13}\text{H}$ for the room-temperature magnetic refrigeration, it is necessary to manage a hydrogen re-distribution phenomenon, which splits a magnetically single phase into two kinds of portion with different values of the Curie temperature T_C . One of workarounds for this “splitting” phenomenon is a collaboration of the full-charge hydrogenation and the elemental modification; i.e., the former suppresses hydrogen mobility, while the latter regulates T_C at desired working ranges. Especially, a dual substitution of 3d and rare-earth elements for Fe and La is profitable for modification of thermal profile of the entropy change DSM, in addition to tuning of T_C . From viewpoint of the physical mechanism, substitution for Fe causes modification of 3d electronic structures, and among substitutable elements, Mn has a significant impact on lowering of T_C .

Meanwhile, substitution for La mainly brings about change of magnetic state owing to the magnetovolume effect (MVE). Because of the lanthanide contraction, substitution of other rare earth for La is followed by the lattice contraction. In addition, the appearance of 4+ valence state results in a distinct shrinkage of atomic radius in Ce. Comparing to application of the hydrostatic pressures, the substitution of Ce reveals a change larger than the MVE caused by the chemical pressure, and this fact means that the hybridization of Ce 5d / 4f with Fe 3d electrons would enhance the MVE. Meanwhile, the substitution of Pr gives a change well explained from the chemical pressure and the MVE.

An increase of T_C by hydrogenation is also explained from the MVE, and therefore, an enhancement of the MVE by the Ce substitution results in a rise in a sensitivity of T_C against hydrogen amount. For example, an increasing rate of T_C for $\text{La}_{0.7}\text{Ce}_{0.3}(\text{Fe}_{0.89}\text{Si}_{0.11})_{13}\text{H}_y$ against y is about 8-10% larger than that for $\text{La}_{0.5}\text{Pr}_{0.5}(\text{Fe}_{0.89}\text{Si}_{0.11})_{13}\text{H}_y$. In the case of the first-order phase transition, the Curie temperature T_C is a point where the free energy of the low- T phase becomes equivalent to that of the high- T phase, and the change in T_C corresponds to the change in the free-energy difference between two phases. Accordingly, the increasing rate of T_C against y is approximately regarded as a measure of “chemical potential” per hydrogen. This concept becomes very important to reveal the driving force of the splitting phenomenon, because it involves the up-hill diffusion (from dilute to condensed state), which is not explained from the entropy term but from the chemical potential term. Actually, when a “ready-to-saturate” hydrogenated specimens is prepared by tuning the absorption condition, the splitting phenomenon still clearly appears in $\text{La}_{0.8}\text{Ce}_{0.2}(\text{Fe}_{0.875}\text{Mn}_{0.015}\text{Si}_{0.11})_{13}\text{H}_y$, while it is fairly suppressed in $\text{La}_{0.7}\text{Pr}_{0.3}(\text{Fe}_{0.885}\text{Mn}_{0.005}\text{Si}_{0.11})_{13}\text{H}_{1.5}$. In

addition to the superiority of hydrogen stability, it is also noticed that the hysteretic loss is relatively smaller in the Pr-substituted specimens than that in the Ce-substituted ones, while the value of DSM exceeds 20 J/kg

K at 1 T in both the specimens.

Keywords: Magnetocaloric effect, $\text{La}(\text{Fe},\text{Si})_{13}$, Phase transition

Study on Electrocaloric Cooling Performance of Multilayer Ceramic Components

C. Molin,^{1,*} P. Neumeister,¹ H. Neubert,¹ and S. E. Gebhardt¹

¹Department of Smart Materials and Systems, Fraunhofer IKTS, Fraunhofer Institute for Ceramic Technologies and Systems, Winterbergstr. 28, 01277 Dresden, Germany *Corresponding Author: christian.molin@ikts.fraunhofer.de

Exploitation of the electrocaloric (EC) effect enables the development of novel and efficient concepts for solid state cooling. The EC components used for this purpose require materials, which show high EC temperature change, high cooling capacity, low dielectric loss and a phase transition temperature close to the working range. The relaxor ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ turned out to be a very promising candidate due to its broad, frequency dependent peak in the permittivity vs. temperature, indicating a diffuse phase transition that can easily be shifted by changing the material composition. This allows for system-specific adjustment of operating temperature.

In order to improve cooling performance, an optimized design of the EC component for the specific cooling system is required. While thin film structures withstand high electric fields and hence show high EC temperature changes, they are limited in volume and therefore total heat per operation cycle. The most promising results are achieved with EC components based on multilayer ceramic (MLC) structures. They are characterized by their robustness and their high refrigerant volume. Furthermore, MLCs show an increased dielectric strength accompanied with low operation voltages by the reduced thickness of single ceramic layers. In our work, 0.92 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – 0.08 PbTiO_3 (PMN-8PT) MLCs were prepared using doctor blade process, followed by screen printing of AgPd inner electrodes, stacking and isostatic lamination. By reducing layer thickness dielectric strength could be improved up to $ED=29 \text{ V } \mu\text{m}^{-1}$ and an EC temperature change of $\Delta T_{EC}=2,7 \text{ K}$ ($\Delta E=16 \text{ V } \mu\text{m}^{-1}$) was measured directly. Based on the so manufactured MLCs and their characteristics we modeled the feasible cooling performance using finite element analysis (FEM). Variations of geometry parameters and electrical driving conditions allow for the identification of optimum device design and operation conditions to achieve maximum cooling power for given thermal boundary conditions. The simulation takes into account two different modes of heat transfer (i.e. perpendicular or parallel to internal electrodes) and two component geometries (i.e. oblate or prolate) (see figure 1).

The presentation will give an overview on our studies on MLC structures based on relaxor ferroelectric PMN-8PT. The cooling performance of the fabricated MLC layout is discussed in detail and an optimum layout derived by variation of design parameters.

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Regulation of phase transition and multicaloric effect in magnetocaloric materials

Feng-xia HU^{a,b,c}, Jing WANG^{a,b}, Ji-rong SUN^{a,b,c}, Bao-gen SHEN^{a,b,c}

^a Beijing National Laboratory for Condensed Matter Physics and State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China.

^b School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

^c Songshan Lake Materials Laboratory, Dongguan, Guangdong, 523808, P. R. China.

*email: fxhu@iphy.ac.cn

EXTENDED ABSTRACT

Solid state refrigeration based on caloric effect has been regarded as an attractive alternative to conventional gas compression technique. Increasing the caloric effect as much as possible is a long-term pursuit. Proper regulation of phase transition by external physical field is an effective means to enhance the caloric effect. Here we report our recent research progress[1-5]. Large enhancements of magnetocaloric effect (MCE) and barocaloric effect (BCE) by hydrostatic pressure have been demonstrated in $\text{La}(\text{Fe}_{0.92}\text{Co}_{0.08})_{11.9}\text{Si}_{1.1}$ with second-order transition. First-principles calculations are performed, which offers a theoretical support for the enlarged caloric effect relative to the evolution of phase transition nature[1]. Moreover, enhanced lattice entropy change was calculated by Debye approximation, and a reliable way to evaluate BCE is demonstrated under a high pressure. Hysteresis loss is a longstanding problem seriously harming refrigeration efficiency. By utilizing nonvolatile strain triggered by a pulse electric field to engineer phase transition process of FeRh film grown on PMN-PT substrate, a nonvolatile reduction of hysteresis loss was observed. The application of electric field is avoided during heat absorb/release (magnetization/demagnetization) process, which is helpful to the technical design of electric-magnetic dual field refrigeration cycle [2].

Moreover, multicaloric and coupled caloric effect driven by hydrostatic pressure and magnetic field has been systematically investigated in Ni-Mn-In [Ref.3] and $\text{La}(\text{Fe,Si})_{13}$ -based compounds. Thermodynamic analysis indicates that the MCE at a certain pressure is equivalent to the MCE at ambient pressure adjusted by the coupled caloric effect. This theoretical result is verified by magnetic measurements under various pressures for the both Ni-Mn-In and $\text{La}(\text{Fe,Si})_{13}$ -based compounds. Detailed analysis indicates that the coupled caloric effect involving the strengthened magnetostructural coupling under pressure is responsible for the enhanced MCE. The quantitative analysis of cross coupling term driven by dual fields can help to reveal the essence of regulated phase transition and caloric effect by pressure. This work was supported by the National Key Research and Development Program of China, and the National Natural Sciences Foundation of China.

Keywords: Phase transition, multicaloric effect, magnetocaloric materials

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Barocaloric effects in fluorinated polymers

Jiyeob KIM(a), Pol LLOVERAS(b), María del BARRIO(b), Josep Lluís TAMARIT(b),
Xavier MOYA(a)

(a) University of Cambridge
Cambridge, CB3 0FS, United Kingdom

Jiyeob Kim jyk32@cam.ac.uk

Xavier Moya xm212@cam.ac.uk

(b) Universitat Politècnica de Catalunya
Barcelona, 08019, Spain

Pol Lloveras pol.lloveras@upc.edu

María del Barrio maria.del.barrio@upc.edu

José Lluís Tamarit josep.lluis.tamarit@upc.edu

We present barocaloric studies of ferroelectric polymers of poly(vinylidene fluoride-trifluoroethylene) [PVDF-TrFE]. These copolymers are well known because of their giant electrocaloric response, but here we study pressure-driven thermal changes. PVDF-TrFE polymers undergo first-order phase transition with very large latent heats and volume changes, near room temperature. These three properties make them ideal materials for barocalorics.

Keywords: barocaloric effect; ferroelectric materials; polymer; differential thermal analysis; volume change

Magnetocaloric properties of HoB₂

Kensei Terashima(a), Pedro Baptista de Castro(a,b), Takafumi D Yamamoto(a), Zhufeng Hou(c), Suguru Iwasaki(d), Noriki Terada(a), Claire V. Colin(e), Hideaki Kitazawa(a), Hiroyuki Takeya(a) and Yoshihiko Takano(a,b)

(a) National Institute for Materials Science, Tsukuba, 305-0047, Japan, TERASHIMA.Kensei@nims.go.jp

(b) University of Tsukuba, Tsukuba, 305-8577, Japan (c)

State Key Laboratory of Structural Chemistry,

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002,

China, (d) Research Institute for Electronic Science, Hokkaido University, Sapporo, 001-0020, Japan,

(e) Université Grenoble Alpes, CNRS, Institut Néel, 38042 Grenoble, France

Abstract

The entropy associated with spins in solids can be manipulated by application/removal of external magnetic

field, whose change (DSM) appears as a magnetocaloric effect (MCE). Such MCE is expected to be applicable to form a thermal cycle for cryogenic use with an efficiency possibly higher than conventional gas cycles especially in low temperature region, with suitable materials that show significant MCE in the working temperature range.

Guided by a prediction from machine-learned model developed for DSM in magnetic materials, we have examined MCE of HoB₂ (AlB₂-type structure, P6/mmm), which has been known only as a ferromagnet below TC = 15 K (Buschow, 1977). As a result, we have found that this material exhibits |DSM| as large as 40.1 (J kg⁻¹ K⁻¹), 0.35 (J cm⁻³ K⁻¹) peaked around 15 K, under field change of 5 T (Castro et al., 2020). In addition, it is clarified that HoB₂ shows another magnetic transition around 11 K that seems to be associated with orientation of spins (Terada et al., 2020), manifesting as a shoulder structure in the temperature dependence of |DSM|. In the presentation, we will introduce obtained physical properties of HoB₂.

Keywords: Magnetocaloric material

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Machine-learning assisted search for magnetocaloric materials:

Discovery of gigantic magnetocaloric effect in HoB₂

Pedro Baptista de Castro(a,b), Kensei Terashima(a), Takafumi D Yamamoto(a), Zhufeng Hou(c), Hiroyuki Takeya(a) and Yoshihiko Takano(a,b)

(a) National Institute for Materials Science, Tsukuba, 305-0047, Japan, CASTRO.Pedro@nims.go.jp (b) University of Tsukuba, Tsukuba, 305-8577, Japan (c) State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002, China

Abstract

The magnetocaloric effect (MCE), often characterized by the magnetic entropy change (ΔS_M) for a given applied field change (ΔH), is one of the most promising alternative paths for the development of greenhouse-gas free refrigeration devices (Franco et al., 2018). The magnitude of ΔS_M tends to peak at a material's magnetic ordering temperature (T_{mag}), such as Curie (T_C) or Néel (T_N) temperature, and its maximum value for a ΔH strongly depends on the material. Since the discovery of gigantic MCE in materials such as Gd₅Si₂Ge₂ (Pecharsky and Gschneidner, 1997) and La(Fe,Si)₁₃ (Shen et al., 2009) an explosive increase in the search for materials which could exhibit such effect lead to the accumulation of magnetocaloric properties of a vast number of magnetic materials. However, it remains a challenge to design materials that can exhibit such a remarkable effect. To tackle this challenge, we constructed a machine learning model for predicting ΔS_{MMAX} purely based on chemical composition descriptors. For this, we gathered the accumulated data of magnetocaloric materials, and trained a model for the prediction of ΔS_{MMAX} for a given material composition and an applied ΔH . Then, by exploring a text-mined database called MagneticMaterials (Court and Cole, 2018) the obtained model was used in conjunction with domain expertise to filter possible candidates for experimental verification. Through this approach, we found HoB₂ ($T_C = 15$ K), exhibits that highest volumetric ΔS_M of 0.35 J cm⁻³ K⁻¹ for $\Delta H = 5$ T (Castro et al., 2020), to the best of our knowledge, of all known characterized second-order magnetic phase transition materials in the temperature range between 4.2 and 77 K, as shown in the figure below.

In this talk, we will discuss the process of model building, the choice of compositional based features, the current challenges and will briefly introduce and compare the experimental results with other materials in the same temperature range

Keywords: Magnetocaloric effect, machine learning

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Magnetocaloric spherical particles for hydrogen liquefaction fabricated by a gas atomization process

Takafumi D. Yamamoto(a), Hiroyuki Takeya(a), Akiko T. Saito(a), Kensei Terashima(a), Pedro Baptista de Castro (a, b), Takenori Numazawa(a), and Yoshihiko Takano(a, b),

(a) National Institute for Materials Science, Tsukuba, 305-0047, Japan, YAMAMOTO.Takafumi@nims.go.jp (b) University of Tsukuba, Tsukuba, 305-8577, Japan

Abstract

Hydrogen liquefaction by magnetic refrigeration is expected to play a significant role in realizing the so-called hydrogen society that utilized hydrogen as a clean energy source (Numazawa et al., 2014). For establishing refrigeration technologies to liquefy hydrogen, many efforts have been devoted to the survey for giant magnetocaloric compounds that work at lower temperatures below 100 K (Zhang et al., 2019) and the development of highly efficient magnetic refrigeration systems using an active magnetic regenerator (AMR) cycle (Kim et al., 2013). On the other hand, for use in AMR systems, the candidate materials must be processed into submillimeter-sized spherical particles. The candidate materials for hydrogen liquefaction are often found in rare-earth intermetallic compounds, e.g., the Laves phase RT₂ (R = rare earth element, T = Al, Co, Ni). However, they have poor mechanical properties and a high melting point, which makes it difficult to fabricate spherical particles by using conventional atomization methods. Up to date, the way to make spheres has not been fully established for such magnetocaloric materials.

In this study, we have succeeded in developing the route to stably produce magnetocaloric particles for hydrogen liquefaction by using a unique crucible-free gas atomization method. The figure below shows the photograph of gas-atomized particles of HoAl₂, which is one of the candidate materials. As can be seen in this figure, we obtained almost spherical particles with a suitable size for AMR systems. In this talk, we will present the particle yield, morphology, magnetic and magnetocaloric properties of the fabricated particles for several candidate materials.

Keywords: Magnetocaloric effect, Gas atomization, hydrogen liquefaction

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Digital microfluidics in magnetocaloric cooling

Urban Tomc(a), Matej Šadl(b), Katja Klinar(a), Hana Uršič(b), Andrej Kitanovski(a),

(a) Faculty of mechanical engineering, University of Ljubljana, Ljubljana, 1000, Slovenia, urban.tomc@fs.uni-lj.si (b) Electronic Ceramics Department, Jožef Stefan Institute, Ljubljana, 1000, Slovenia

Abstract

Today's state-of-the-art magnetocaloric technology is based on the so called Active Magnetic Regeneration (AMR) principle. The AMR is based on the reciprocating movement of the fluid through a porous magnetocaloric (MC) structure. Such a system usually comprises a large amount of caloric material and a fairly complex hydraulic system, which is more suitable to be implemented in large cooling, refrigeration or heat pump devices. On the other hand, miniaturized electronics also produce vast amounts of heat that need to be efficiently managed. In this manner, an alternative research approach is emerging in the fields of MC technology. It involves new concepts of devices, which would apply so called thermal switches. The application of thermal switches could lead to drastic improvements in the heat transport from/to the MC material and consequently to the miniaturization of MC devices. An interesting domain, to look for thermal switch mechanisms, is microfluidics, which has enabled the development of integrated lab-on-chip devices. Although most microfluidic devices are based on a continuous flow of liquids in microchannels, there has been an increasing interest for the past couple of years in devices that rely on manipulation of discrete droplets using surface tension effects. One such technique is ElectroWetting On Dielectric (EWOD), which is based on wettability of liquids on a dielectric solid surface by varying the electrical potential. In this contribution we will present a new concept of a magnetocaloric device which couples MC effect and EWOD droplet actuation as a thermal switch mechanism. We will show different potential designs of such devices and their operation. For example, Figure 1 presents CFD simulations (Ansys Fluent) of the operation of such a potential device. Furthermore, the materials and its properties which constitutes the whole device will be discussed.

Keywords: magnetocaloric, digital microfluidics, electrowetting, thermal switch

Active Elastocaloric Regenerator with Staggered Tube Bank Configuration: An Experimental Investigation

Nehemiah Emaikwu(a), Yunho Hwang(a), Ichiro Takeuchi(a), Reinhard Radermacher(a)

(a) University of Maryland, College Park, 20740, USA, yhhwang@umd.edu

Abstract

Elastocaloric cooling devices have shown growing trends towards designs that use tubular NiTi shape memory alloys (SMA) [1]. Most tube geometry designs flow a heat transfer fluid through the internal areas of the tubes [2]. One novel concept configures the tubes in a staggered bank arrangement, using the external surface area instead, which theoretically leads to larger fluid-side temperature gradients ΔT , and higher heat transfer coefficients between the refrigerant and the heat transfer fluid [3]. These have not been validated, however, so this contribution presents an experimental set-up for analyzing these parameters quantitatively. A single staggered tube bank test-piece comprising of 17 mm NiTi tubes secured in a 3D-printed flow insert is used (Figure 1a). Both components are in a 3D-printed housing which has two flow channel ports, a free plate on the top end for axial compression of the tubes, and a fixed plate on the bottom end. The extended sections on each plate interface the test-piece with the grips of the MTS 810 hydraulic universal testing machine. The MTS records load and displacement data associated with compression of the NiTi tubes. A separate data acquisition system is used to measure the fluid and material-side temperature changes. Figure 1b shows characteristics of the fluid loop, and Figure 1c shows the proposed operation scheme based on the active regeneration method. The combination of an MTS machine which offers high displacement rate, the short NiTi tubes, and an appropriate pumping system allows the cycle time to be kept low, which yields high ΔT performance when the system is operated using the full 4-step Active Elastocaloric Regeneration (AER) method [4,5]. Details on the cycle time, load and displacement data, and fluid and material-side temperatures during operation of the system can be analyzed to determine the total ΔT generated in the system, and the heat transfer coefficient associated with the staggered tube configuration. Various tube arrangements can be investigated by modifying the flow insert. This set-up also applies to a range of cylindrical SMAs materials that exhibit the elastocaloric effect and can be utilized simultaneously with various elastocaloric materials as suggested by [1]. Additionally, tests conducted on a single bank can be used to inform the design concept in [2].

Keywords: Elastocaloric Cooling, NiTi SMA, Staggered Tube Bank, Active Elastocaloric Regenerator

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Durable elastocaloric effect in thin walled Ni-Ti tubes

Luka PORENTA (a), Parham KABIRIFAR (a), Andrej ŽEROVNIK (a), Matjaž ČEBRON (a), Borut ŽUŽEK (b), Miha BROJAN (a), Jaka TUŠEK* (a)

EXTENDED ABSTRACT

Elastocaloric cooling technology is being considered as one of the most promising alternatives to vapor-compression cooling in the recent years. This technology is based on elastocaloric effect (eCE), which is closely related to the superelasticity of shape memory alloys. When a superelastic shape memory alloy (elastocaloric material) is mechanically loaded, an exothermal martensitic transformation occurs and consequently a latent heat is released, which heat up the material under adiabatic conditions. Upon unloading, the reverse transformation occurs and the latent heat is absorbed, which cool down the material under adiabatic conditions.

Elastocaloric cooling or heat-pumping devices need to work continuously and require long-term cyclic loading/unloading of elastocaloric materials, therefore, the fatigue life of the elastocaloric material is their crucial limiting factor. In tensile loading, lower transformation stresses and the possibility of utilizing geometries with good heat transfer properties (thin wires or sheets) are advantageous. Nevertheless, an acceptable fatigue life in tension can be achieved only through the application of small strains (and therefore small eCE) [1]. On the other hand, compressive loading prevents crack growth and consequently increases the fatigue life of the elastocaloric material [2, 3], but, thin elastocaloric elements that have good heat transfer properties are prone to buckle under compression forces (strains) that are required for a complete phase transformation. Currently, thin-walled tubes seem to present the best compromise between buckling stability and the required heat transfer properties. Therefore, this study aims to evaluate the buckling stability, eCE (manifested through adiabatic temperature changes) and structural and functional fatigue behavior of thin-walled Ni-Ti tubes (with outer diameter of 3 mm and wall thickness of 0.25 mm) with austenitic finish temperature (A_f) around 0 °C. Initially, buckling stability of the tubes with different gauge lengths (between 10 mm and 20 mm) were tested under compressive stresses of up to 1600 MPa at a strain rate of $1.3 \times 10^{-3} \text{ s}^{-1}$. Six tubes of 10 mm gauge length, which showed a stable response through the entire transformation plateau, were used in subsequent fatigue life and eCE studies. All six tubes were first subjected to 100 training (stabilization) cycles at a strain rate of $2.3 \times 10^{-3} \text{ s}^{-1}$ between 10 MPa and 1150 MPa. Four tubes were further subjected to fatigue cycling between 185 MPa and 1015 MPa (full transformation plateau) at a frequency of 5 Hz. All four tubes survived 106 cycles (runout) without enduring any noticeable structural damage. The eCE (i.e., adiabatic temperature changes) of all six tubes (four fatigued and two only trained tubes) were measured at a strain rate of $6.8 \times 10^{-2} \text{ s}^{-1}$ (adiabatic conditions) up to the strains that corresponded to the end of the transformation plateau. All six tubes generated adiabatic temperature changes of 27 K and 20 K upon being loaded and unloaded, respectively. The results demonstrate that eCE of thin-walled tubes does not degrade during compressive fatigue cycling and thus durable and stable adiabatic temperature changes, which are prerequisites for practical applications of eCE, can be achieved.

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Keywords: shape memory alloys, elastocaloric effect, fatigue life, compressive loading, structural stability

Study on durability of Mn-based magneto-caloric material for Magnetic Heat Pump

Naoki HIRANO(a), Tetuji OKAMURA(b) , Sangchul BAE(c)

Koichiro WAKI(d), Tsuyoshi KAWANAMI(e)

(a) National Institute for Fusion Science Toki, 509-5292, Japan, Hirano Naoki@chuden.co.jp (b) Tokyo Institute of Technology Yokohama, 226-8502, Japan, tokamura@es.titech.ac.jp

(c) Sanden Advanced Technology Corporation Isesaki, 372-8502, Japan, sangchul.bae.ul@g-sanden.com

(d) Railway Technical Research Institute Kokubunji, 185-8540, Japan, waki.koichiro.08@rtri.or.jp

(e) Meiji University Kakasaki, 214-8571, Japan, kawanami@meiji.ac.jp

ABSTRACT

In order to put the magnetic heat pump into practical use, it is essential to confirm the reliability of the heat pump. Recently, an iron-based magnetocaloric material (MCM) has been developed, but the MCM and liquid come into contact for heat exchange, so it is important to evaluate the durability of the MCM against contact with the liquid under changing magnetic fields. In the previous research, in order to evaluate the durability of MnFe-type MCM, an experiment was conducted to investigate the occurrence of corrosion by adding some rust inhibitor to water. As a result, it was observed that rust occurred after a few days when no rust inhibitor was added, but rust formation was prevented when rust inhibitor was added. It has been confirmed that the MCM characteristics do not change by selecting an appropriate rust inhibitor. In addition, a durability evaluation test was conducted to confirm whether the mechanical strength and magnetization characteristics of MnFe-type MCM change with repeated magnetic field changes. There was no noticeable change in mechanical properties. Therefore, in this study, we conducted an accelerated material durability evaluation test under the same conditions as those actually used as a magnetic heat pump, that is, repeated changes in the magnetic field and contact with the liquid for heat exchange. Magnetization measurements were performed with a magnetometer equipped with a superconducting quantum interference device. Mechanical strength was measured with a micro Vickers hardness tester. We will report on material property changes due to magnetic field changes of about 30 million times when exposed to heat exchange liquids.

Keywords: MnFe-type Magneto Caloric Materials, magnetic heat pump, Durability, Magnetic Properties, Mechanical Strength

Thermal switches in solid state magnetic refrigeration: conductivity change requirements and effects

D. J. SILVA(a), J. C. R. E. OLIVEIRA(b), A. M. PEREIRA(a), J. O. VENTURA(a), J. P. ARAÚJO(a)

(a) IFIMUP, Department of Physics and Astronomy, Faculty of Sciences, University of Porto, Porto, 4169-007, Portugal

(b) CFP, Department of Physics Engineering, FEUP, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Porto, 4200-465, Portugal

The efficient use of energy has become a mainstay in the current world economic growth. The fact that approximately 30% of all energy consumed in the world is used in cooling and heating engines places refrigeration on the top of the priority lists of any modern economy [1]. In that respect, vapour compression is still the most used refrigeration technology, but requires bulky and noisy compressors. Alternative thermoelectric refrigerators are more compact and environmentally friendly, but at the cost of a much lower efficiency and cooling capacity [2].

In a different rank, mainly due to its higher efficiency, is magnetic refrigeration (MR). With the discovery of the giant magnetocaloric effect by Perchasky and Gschneider, it is now possible to induce large temperature variations and develop MR applications near room temperature [3]. MR is hence an excellent candidate to replace the vapor-compression technology. However, there are still obstacles to overcome, such as the use of moving parts and fluids that can easily reduce the working lifetime of the refrigerators. To solve these issues, the use of solid state thermal switches was proposed [4, 5]. Instead of using fluids to transfer heat from one reservoir to the other, this task can be achieved by externally controlling the thermal conductivity (k) of solid materials that establish contact between the magnetocaloric material (MCM) and each of the reservoirs. Such thermal switches (TSs) are already used in space applications and cryogenics, although involving fluids or mechanical mechanisms. Even though some experimental results have been reported for Peltier based TSs, the performance of a fully solid state magnetic refrigerator making use of TSs has been addressed mostly by means of numerical simulations [4-6]. However, until now, the numerical studies always considered ideal TSs which behave as perfect insulators ($k = 0$) in the OFF state.

In this work, we numerically searched for the most favourable thermal properties of non-ideal solid TSs. We based the TS properties on real materials, commonly used as thermal conductors, and simulated a percentage change of their conductivity (Δk ; from 0% to 100%) for different operating frequencies (f) and working temperatures (T_0). For each parameters combination, the temperature span between the hot and cold reservoirs (ΔT) was registered and mapped. Our results show that for high performance both thermal switches with near ideal behavior are required. However, for an intermediate performance, only one thermal switch with acceptable behavior is needed. We discuss all the possibilities and related performance.

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Modeling of a High Frequency Thermal Switching Active Regenerator

J. Slaughter¹, L. Griffith¹, A. Czernuszewicz¹, and V. Pecharsky^{1,2}

¹Ames Laboratory of the US Department of Energy, Iowa State University Ames, IA 50011,

julies1@ameslab.gov ²Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011

Abstract

High frequency operation of caloric devices has been identified as a promising method to improve power density and decrease cost (Kitanovski and Egolf 2010). Solid-state regenerators using thermal switching have been proposed to achieve operation in the range of 100 Hz compared to the <10 Hz of current caloric devices (Kitanovski et al. 2015) and have received increased attention in recent years (Jia and Ju 2012). We have developed simple models that account for constant fluid flow, contact with hot and cold heat exchangers, and heat transfer into and out of a caloric material. These initial models are independent of the source of the caloric effect and are intended to quickly evaluate different design variables.

A combination of finite element and numerical models is used to estimate performance of solid-state regenerators. In these first-pass models, the caloric effect is simulated by increasing and decreasing temperature of the caloric material periodically at a defined frequency, typically a sine wave. Thermal switches are modeled by changing thermal conductivity at the interface between caloric material and heat exchangers periodically, and coordinated with the temperatures. While the temperature changes have a sine wave form, a square wave for thermal switching better represents contact thermal switches (Wehmeyer et al. 2017). We assume the switch mechanism changes thermal conductivity by two orders of magnitude (Tso and Chao 2016). Thermal switching and temperature changes occur on a small time scale (100 Hz, 10 msec) and require small time steps; heat transfer to a constant velocity fluid stream occurs on a time scale measured by 10's of seconds to reach steady state. A fully coupled finite element model with heat transfer and fluid flow requires many hours to solve because of the combination of short time steps and long time scales; modified models reduce solution times to minutes, which enables optimization and design evaluation.

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Keywords: Active regenerator, thermal switching, simulation.

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Tuning of magnetic anisotropy during additive manufacturing of magnetocaloric Gd₅Si₄

Karam Al Milaji,¹ S. Gupta,² V. K. Pecharsky,^{2,3} Radhika Barua¹, H. Zhao,¹ and R. L. Hadimani^{1, 4, 5}

¹Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, VA 23284, USA

²Ames Laboratory, U.S. Department of Energy, Ames, IA 50011, USA

³Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011 USA

⁴Department of Electrical and Computer Engineering, Iowa State University, Ames, IA 50011, USA

⁵Department of Biomedical Engineering, Virginia Commonwealth University, Richmond, VA 23284, USA

Significant progress has been made in the development of high-performance magnetocaloric materials for potential applications in refrigeration and air-conditioning. However, the progress in the device development and their performance has been hindered by manufacturing of device components such as regenerator beds/tables which need to exhibit optimal magnetic and thermal properties that have gradient variation across the geometry. Additive manufacturing of multiple phases/compositions and magnetically aligning of magnetocaloric materials will enhance the performance of the refrigerators [1]. In this work, thin films of ball-milled Gd₅Si₄ particles [2] were deposited using inkjet printing process in the

presence of an external magnetic field. During printing, NdFeB permanent magnet arrays were used to align the particles along the axis of the printing plane, normal to the printing plane and without the magnets. The external magnetic field aligns the magnetic particles along their magnetic easy axis. The combined effect of all the particles enhances the magnetization of the film by aligning the particle's magnetocrystalline easy axis with the direction of the magnetic field of the permanent magnet. Angle dependent magnetization measurements were used to investigate the effect of the aligning field on the film. We demonstrate the ability to print thin magnetic films with a defined anisotropy in any chosen direction which could lead to the enhancement of magnetic properties approaching those of single crystal

materials. Fig.1 (a) shows hysteresis graphs at 300K measured along long axis of films printed with no applied field (random), field applied in parallel orientation to the plane and along long axis (parallel), field applied in parallel orientation to the plane and along short axis (random 90 deg.), field applied normal to

the plane (normal) and photo paper without the Gd₅Si₄ particles. It can be seen that the when films are printed with a field applied parallel to long axis the magnetization is highest and the lowest magnetization

is seen for particles printed with field applied normal to the paper. Fig. 1 (b) shows SEM images of random and parallel films. Fig.2 shows magnetization measurement at 280K for the random, parallel and normal films and they exhibit the same behavior. Entropy change was calculated from Maxwell's equations for random, parallel and normal films. The entropy change for an applied field of 3T at 310K showed an increase of 440% for parallel films compared to normal films (2.3 J/kgK, 3.4 J/kgK and 10.2 J/kgK for normal, random and parallel films respectively).

Study of electrostatic actuation for electrocaloric cooling devices

Lucas Depreux(a,b), Morgan Almanza(b), Martino Lo Bue(b), Fabien Parrain(a)

(a) C2N, Université Paris-Saclay, CNRS

Palaiseau, 91120, France, @u-psud.fr

(b) SATIE, ENS Paris-Saclay, CNRS, 94235 Cachan, France

Cachan, 94235, France, @ens-paris-saclay.fr

EXTENDED ABSTRACT

Solid-state refrigeration offers potential advantages over traditional cooling systems, but few devices offer high specific cooling power with a high coefficient of performance (COP); they fall short of the well-established performances of gas-based refrigerant devices. Electrocaloric (EC) polymers present various specificities : they have a high adiabatic temperature change ($\sim 10\text{K}$) and a low mass density (1g/cm^3). Thus, using these materials could lead to refrigeration with high specific power (W/g), and high COP. Even more importantly, polymers are softer than other caloric materials; therefore they are surface-conformable ($E \sim 1\text{GPa}$), which allows one to increase the effective contact surface between the polymer film and the heat reservoir. Additionally, films can be very thin and therefore show a remarkable surface/volume ratio. Because of their properties (softness and thinness), these films are well-suited to enhance the heat transfer and achieve the power density that is required in cooling devices.

However, the handling of such films is not easy—precisely because they are soft. Ma et al. present an EC cooling device based on a polymer film, showing a COP up to 13, a specific cooling power of 2.8W/g , and working at a frequency of 0.8 Hz . In their device, the EC film is electrostatically moved from the hot reservoir to the cold one and vice-versa, thus allowing one to control the heat transfer. Using this method, they outperform most of the existing magnetocaloric and elastocaloric cooling devices.

Using a similar setup, we [Almanza et al. (2018)] have recently shown that the heat transfer can be significantly enhanced, which enables a significant increase in the working frequency—up to 100Hz for a $20\mu\text{m}$ thick film. The resulting output power, which is estimated at around 200W/g , would be of the same order of magnitude as in conventional cooling devices. The key to achieve such working frequencies is a wise balance between film displacement (mechanical switching) and heat transfer characteristic times. Here, we focus on how to reduce the switching time down to a few milliseconds.

This issue has been studied in the MEMS field, particularly in RF switches, and micro-pumps. It combines several branches of physics, such as electrostatics, thin film mechanics and hydrodynamics. Here, the main challenge is to understand and harness the airflow and squeeze film damping which limit the film's dynamic.

In this work, we investigate different approaches in order to increase the frequency of our previously-presented electrostatic thermal switch, using an EC film as active material.

The measurements will be discussed with regard to a simple model, taking into account the way air affects the dynamic of the moving part.

Our results will provide insight on the potential of EC polymers as caloric substance for high cooling power devices.

Keywords: electrocaloric polymer; caloric devices; cooling; electrostatic actuation; thin film

Impact of epoxy blockage on the AMR performance of La(Fe,Mn,Si)13Hz regenerators

Bernardo P. VIEIRA(a), Henrique NEVES BEZ(a), Higor TEZA(a), Deise SCHAFER(b), Marcelo A. ROSA(b), Jaime A. LOZANO(a), Cristiano da S. TEIXEIRA(b), Paulo A. P. WENDHAUSEN(b), Jader R. BARBOSA Jr.(a)

**(a) POLO – Federal University of Santa Catarina
Florianópolis, 88040-900, Brazil, jrb@polo.ufsc.br**

**(b) MAGMA – Federal University of Santa Catarina
Florianópolis, 88040-900, Brazil**

EXTENDED ABSTRACT

The challenge of fabricating reliable active magnetic regenerators still remains within our community after a couple of decades of research and development of magnetic cooling systems. With a few exceptions, most first-order magnetocaloric materials are brittle and undergo volume changes during phase transition. Therefore, to avoid fatigue related issues and guarantee the mechanical integrity of the regenerator, the magnetocaloric material granules are usually glued with a binder, while still providing tortuous paths for the fluid flow. In this context, we evaluate two regenerators consisting of spherical granules of La(Fe,Mn,Si)13Hz alloys and an epoxy binder. The first regenerator was composed of three layers of alloys with different compositions (hence Curie temperatures), while the second regenerator was assembled with eight layers. We have characterized the materials through magnetization, scanning electron microscopy, dynamic light scattering, x-ray diffraction and calorimetric measurements. Moreover, we have evaluated the porous media based on geometric measurements, micro-tomography, helium pycnometry and pressure drop tests. Finally, the active magnetic regeneration performance was evaluated using a custom-built test facility. The magnetocaloric measurements have shown an adiabatic temperature change and entropy change of approximately 3.5 K and 9 J kg⁻¹ K⁻¹, respectively, for a field change of 1.5 T. Moreover, the microscopy analyses have shown that the granules are porous with about 15 vol.% of α -Fe, which has been confirmed by the x-ray diffraction results. The helium pycnometer tests have shown that the granules present about 13% of pores. From the geometric measurements and considering the density of the materials, we have expected an open porosity of ~47%, value corroborated by the tomography analyses. Nonetheless, from the pressure drop measurements as a function of mass flow rate, we have calculated an open porosity of approximately 28.5% and 20%. This discrepancy between the tomography and pressure drop measurements can only be related to epoxy blockage of open pores, which leads to higher pressure drops, poor heat transfer between the magnetocaloric granules and the fluid, and a smaller surface area density. All that combined drastically reduces the performance of active magnetic regenerators, so further analyses using advanced computational techniques are required to identify solutions to improve the thermal performance of the composite porous media.

Keywords: La-Fe-Si alloys; AMR; regenerator; magnetocaloric.

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

Hugo A. VIEYRA, Konrad LÖWE, Alexander BARCZA, Matthias KATTER
Vacuumschmelze GmbH & Co. KG

Hanau, 63450, Germany, hugo.vieyra@vacuumschmelze.com

EXTENDED ABSTRACT

The good magnetocaloric properties of the LaFeSi-based alloy family CALORIVAC® make it very attractive for magnetic cooling applications on a large scale.

Furthermore, the currently used powder metallurgical fabrication route for LaFeSi alloys is suitable for production upscaling. Nevertheless, typical shaping techniques

based on compaction and sintering of fine powder with subsequent secondary machining are not cost effective. In addition, the available machining technologies are unable to yield the intricate regenerator geometries required for cooling machines having high coefficient of performance.

In this work alternative near net-shape production methods for LaFeSi-based regenerators are presented. The use of compatible organic additives during shaping opens up new possibilities for the production of more complex geometries.

Furthermore such methods have the benefit of high production yield and minimal requirements for secondary machining. Methods like extrusion and tape casting combined with a suitable debinding process prove successful for the production of fully dense organic-free parts with hydraulic diameters less than 0.3 mm and good magnetocaloric properties.

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

Keywords: magnetocaloric materials; LaFeSi, shaping.

A multicaloric approach to cool magnetocaloric wires

Alexander Funka , Susanne-Marie Kirschb , Felix Welschb , Jens Freudenbergerc , Tino Gottschalld , Maria Krautzc , Stefan Seelecke b , Anja Waskea,*

(a) Federal Institute for Materials Research and Testing (BAM), 12205 Berlin, Germany,
anja.waske@bam.de

(b) Intelligent Material Systems Lab, Saarland University, 66123 Saarbrücken, Germany

(c) Leibniz Institute for Solid State and materials Research (IFW) Dresden, 01169 Dresden, Germany

(d) Helmholtz Center Dresden, 01328 Dresden, Germany

*presenting author

Keywords: magnetocaloric materials; elastocaloric materials; barocaloric materials; multicalorics, shaping, powder-in-tube

Caloric materials can be stimulated by external forces, like e.g. pressure, tension, electric or magnetic fields to induce a materials phase transition near its transition temperature, resulting in an adiabatic temperature change ΔT_{ad} [1]. Such caloric effects of bulk materials can be utilized in heat pump cycles and are promised to be highly efficient, making these materials and heat pump approaches suitable for future air-conditioning and refrigeration applications. The strong lattice coupling of (magneto-)caloric materials enables the possibility to combine different external forces, e.g. magnetic and mechanical forces, simultaneously or sequentially, that may lower the magnitude of the single forces without losing the high adiabatic temperature change ΔT_{ad} . Especially materials with a 1st order transition benefit from different / multiple forces, as the application of one force usually results in a hysteresis whereas two forces can be combined to overcome the hysteresis smoothly[2].

One general drawback of multicalorics is that most caloric materials do not have mechanical properties that allow for repeated application of large pressure or even strain without premature failure of the material. Furthermore, most caloric alloys need corrosion protection that shields the material from influences of the heat exchange fluid. These two aspects represent considerable hurdles to implement a second external stimulus. Recently, we presented a novel approach to shape magnetocaloric materials with the powder-in-tube technology, leading to magnetocaloric cores with a thin steel shell [3]. We are now using this geometry to induce mechanical forces upon the core in order to adiabatically induce a change in temperature or shift the magnetocaloric transition.

In this proof-of-concept study we apply axial tension stress followed by relaxation to La(Fe,Co,Si)₁₃ – steel core-shell wires in the vicinity of its phase transition temperature to observe the adiabatic temperature change ΔT_{ad} of the wire by thermographic imaging. The La(Fe,Co,Si)₁₃ core cools down under tension, indicating a conversion from tension to pressure forces via the wires' shell stabilizing the paramagnetic phase, and heat up by relaxing the force stabilizing the ferromagnetic phase. This unconventional behavior of core-shell wires, experiencing radial pressure via axial tension, is explained by the brittleness of the material leading to a string of separated core sections. Numerical simulations carried out in this study confirm this hypothesis.

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Evaluation of the TEWI in the Electrocaloric Materials

Xiaoshi Qian*(a), Donglin Han(a), Qiang Li(a), Feihong Du(a), Jiangping Chen(a)

(a) Shanghai Jiao Tong University, Shanghai, 200240, China, *xsqian@sjtu.edu.cn

Abstract

The EC solid-state cooling represents a zero-global-warming-potential, high efficient refrigeration alternative. Due to the fact that the electrocaloric materials are mostly wide band-gap, insulating dielectrics, which operate as an electricity-driven capacitor, the electrocaloric working bodies inherent the advantages in the cyclic energy efficiency and the device integration. However, how to evaluate the energy efficiency and the environment impact is still not clear in the research field of the EC cooling technology. Here we report an evaluation method of the environmental impact and the cyclic efficiency of the EC refrigeration technology by calculating the total effective warming impact (TEWI) and the material coefficient of performance (COP), respectively. The assessment provides a clear insight of why the EC solid-state cooling has advantages in certain applications even in near future. The results would also facilitate researchers in the related fields to access detailed information when they are design new materials and/or devices for advanced heat pump.

Keywords: Electrocaloric Effect, Material COP, TEWI.

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