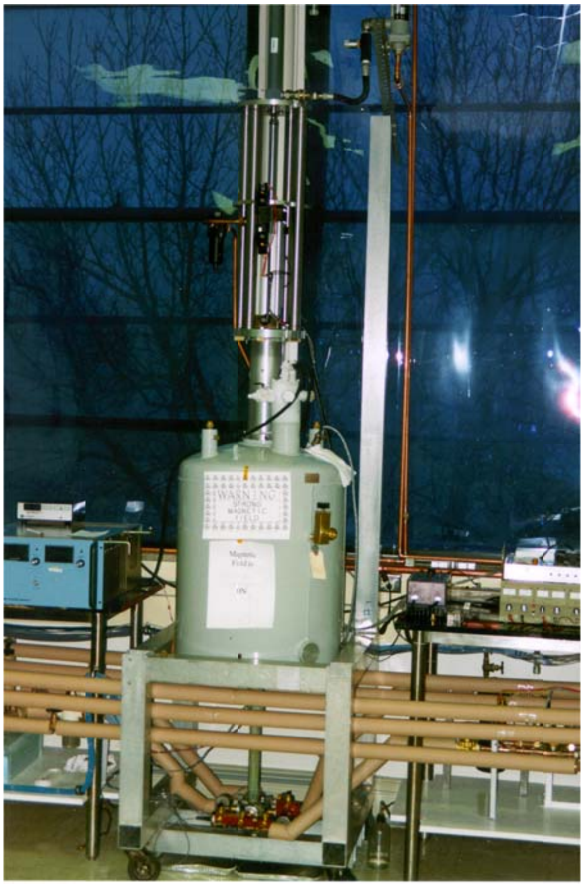
Advancing Caloric Materials for Efficient Cooling:

Key Scientific and Device-Related Materials Challenges for Impact



ON THE COVERS

FRONT

A photograph of the first magnetocaloric refrigerator prototype, built by Astronautics Corporation of America and Ames Laboratory in 1997, powered by a 5 Tesla superconducting magnet and operating near room temperature.

[From, Carl Zimm, et al., “Description and Performance of a Near-Room-Temperature Magnetic Refrigerator,” in *Advances in Cryogenic Engineering, Vol. 43,* Edited by P. Kittel, Plenum Press, New York, 1998.]

REAR

Shown is a photograph of the smaller, rotary magnetocaloric refrigerator prototype, built by Astronautics Corporation of America in 2002. Using 1.4 Telsa field, generated by a permanent magnet, cooling power exceeded 500 Watts and the device had a coefficient of performance, COP, greater than 6.

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Key Scientific and Device-Related Materials Challenges for Impact

A workshop engaging National Laboratories, Universities, and Industry

28-29 April 2015

Hosted by the University of Maryland, College of Engineering

Workshop report released December 2015

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Jun Cui	Pacific Northwest National Laboratory (now Ames Laboratory)
Duane Johnson	Ames Laboratory and Iowa State University
Vitalij Pecharsky	Ames Laboratory and Iowa State University
Ichiro Takeuchi	University of Maryland
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Workshop Participants on UMD campus (29 April 2015)

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Disclaimer: This report is informational briefing and update on context and key issues needed to advance caloric materials and refrigeration from this workshop. It is not intended to be a comprehensive review of caloric materials and refrigeration device efforts. So, examples are taken across the spectrum of research to present concepts and needs, without intention to support or neglect any specific work, researchers, or groups. Any errors remain the sole responsibility of the Chair, who collected and drafted this report on behalf of the participants.

executive summary

WORKSHOP GOAL

Assess current status of caloric materials and address key basic science challenges to advance reversible caloric materials exhibiting improved performance and long cycle life for transformational efficient caloric cooling technologies, and a systems approach for the use of the materials in device application. In addition, report on necessary paths forward for materials and systems design success for societal impact – a 20-30% drop in energy needs for cooling.

Vapor-compression refrigeration approaches its fundamental efficiency limit, yet cooling systems consume at least one out of every five kilo-Watt-hours (kWh) generated in the U.S. Compared to the vapor-compression cycle, solid-state, caloric-based cooling is universally predicted to have lower environmental impact and higher efficiency. The efficiency of caloric test-beds, which are in their infancy, exceeds that of available thermoelectric devices and rivals even the most refined vapor-compression units.

Yet, successful market penetration of the energy-efficient caloric cooling – a truly transformative refrigeration concept – is impeded by *missing basic knowledge on how to design the needed solid materials, and how to control the processes in solids that yield the caloric effect under the influence of external fields (magnetic, electric, and stress) at the needed temperature range*.

Such a materials design effort for reversible caloric behavior with long cycle life requires advances in control over *chemical and microstructure makeup, magnetic, and structural transformations* – particularly the associated entropy and interface physics. In addition, it is critical that the material(s) be amenable for integration into energy-conversion devices for applications, requiring ultimately a systems approach in the design process. Accelerating the pace of design to accomplish this has been further bolstered in the past decade by tremendous advances in theory and computational power, as well as in characterization, including thermodynamic measurements, imaging resolution, as well as coherent light sources and neutrons, such as increasingly available at national user facilities.

With the development of multi-million-cycle phase transformation materials, there are numerous potential uses, from actuation, sensing, switching, information storage, direct-energy conversion, and *solid-state refrigeration* – by far the biggest large-scale use. The societal impact of a solid-state refrigeration material and an operational device is a 20-30% drop in U.S. energy needs for cooling!

Chapter 1

Efficient Cooling with Caloric Materials:

Challenges and Opportunities for Basic Science

Caloric **– of or pertaining to heat.**
[1785–95; < French *calorique* < Latin *calor* heat + French *-ique* -ic]

Modern society is highly dependent on reliable cooling technologies. Without refrigeration, our food supply would be seasonal and limited to locally produced, non-perishable items, comfortable living conditions would be impossible everywhere, causing overpopulation in areas with modest climates, and certain medical advancements, such as organ and tissue cryostorage, and cryosurgery would be impossible. It is startling that most cooling applications are supported by *vapor-compression technology that remains essentially unchanged for over a century*.

All parts of a vapor-compression device have been refined over the years due, in part, to concerted R&D efforts made possible by a sustained dollar influx from federal and industrial sources. **Yet, still, U.S. residential and commercial cooling consumes at least 1 in 5 kWh of electricity generated!**

Future improvements may only be incremental because vapor-compression refrigeration is already near its fundamental limit of energy efficiency. Hence, new technologies with a potential to save as much as one-third of the estimated 20 to 25% of the generated electricity used today only to lower and hold temperature below the ambient *will make a tremendous impact on the energy future of the United State and worldwide*.

Caloric refrigeration relies on reversible caloric phenomena that emerge when a control field around a given solid is changed either isothermally or adiabatically. Does the caloric behavior arise from a scalar, vector, and tensor field – namely, *magnetic* (***H***)*, electric* (***E***)*, stress* (***σ***)*, pressure (P), and temperature (T)?* Magneto-caloric, electro-caloric, elasto-caloric, and baro-caloric effects all lead to a change of entropy (temperature) when the strength of the relevant control field is varied isothermally (adiabatically).

- The magneto-caloric effect (the most well studied) occurs as magnetic moments are aligned in an applied field (loss of spin disorder) that induces a *magnetization-demagnetization transition*. The thermodynamic cycles are textbook, but revisited for refrigeration [e.g., Gómez et al., 2013]. Many proof-of-principles devices (see cover) confirm the feasibility of magnetocaloric cooling at room temperature. The giant magnetocaloric effect discovered in $Gd_5(Si\text{-}Ge)_2$ alloy [Pecharsky & Gschneider, 1997] ignited great interest and devices.
- The electrocaloric effect is an electric-field-induced *polarization-depolarization transition* in ferroelectrics. See [e.g., Lu & Zhang, 2009; Valant, 2014; Ožbolt, et al., 2014].
- The baro-caloric and elasto-caloric (a.k.a. mechano-caloric or thermo-elastic) effects are related and triggered by hydrostatic pressure or uniaxial stress, respectively, that induces a crystallographic phase transformation – with absorption or release of latent heat.

Caloric materials generally have numerous features in common *despite vastly different chemical makeup:* the extended family includes metals, alloys, intermetallic and (in)organic compounds, polymers, and hybrid materials. Importantly, every caloric effect individually and collectively underpin forms of energy conversion (*e.g.,* spin–magnetic-field and dipole–electric-field coupling) that approach 100% efficiency! For example, in magnetocalorics, energy efficiency is 1/5 to 1/3 more overall, while (de)magnetization is 99+%.

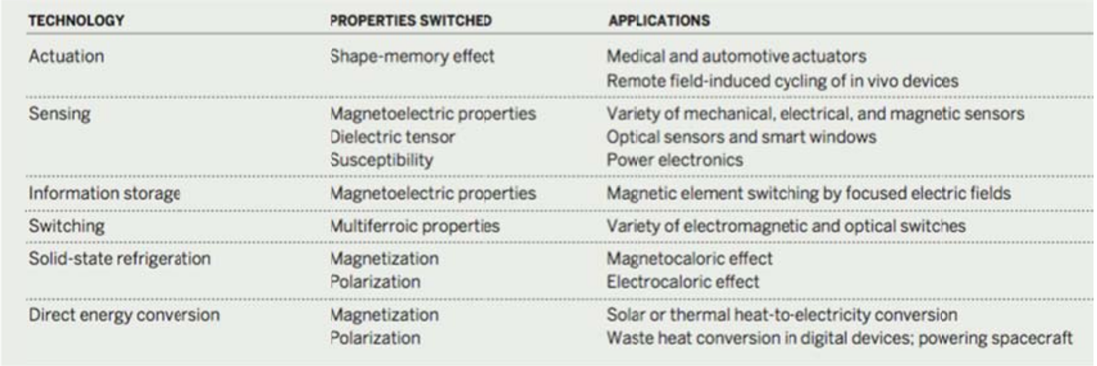
Basic Science Challenges and Transformative Opportunities in Caloric Materials

Better yet, can a material be developed that is controlled using multiple fields? Such materials require a new development paradigm where the response and its use are designed in concert. Necessarily, then, mapping and tuning a material's multi-field phase diagram is required, beyond the traditional temperature-composition (T-c) phase diagram, and for systems with several elements and complex interfaces (e.g., microstructure) which control the energy conversion for applications in a desired range of temperature and fields to achieve, for example, efficient room-temperature cooling in readily available fields without destroying the materials.

Caloric test beds, which are in their infancy, already exhibit efficiency exceeding that of available thermoelectric devices and rival refined vapor-compression units [Goetzler et al., 2014]. (Recent reviews show the lower efficiency and equally large materials challenges for thermoelectrics [e.g., Sootsman, et al., 2009].) Caloric cooling devices, however, require a systems approach in the design process because the material is an integral part of the system and fundamentally all systems rely on the size of the caloric effects and how they are controlled for efficiency.

The ***coefficient of performance*** (**COP**) – one metric of efficiency – is defined as the ratio of the cooling power and work input; or, for the material, it can be defined as the ratio of the released or absorbed heat to work required to induce the phase change. So, COP scales proportional to size of the caloric effect (e.g., change in entropy ΔS) and inversely proportional to the strength of the driving field (magnitude of applied field, assuming the minimum field is near zero). The effects are at their extremes when a material responds to a field change by transforming from one state into another (disordered to ordered, or from one polymorph to another), and the effect may be enhanced if the transition is discontinuous (i.e., first-order) for key thermodynamic variable. Regardless of the type of caloric event, altering the energy balance between relevant phases by small fields is key. Preferably a tuned material requires only small field changes (small work inputs) to control the transformations, thereby increasing COP (as a fraction of Carnot COP), and, if designed for reduced fatigue, a multitude of uses (**Table 1.1**).

Table 1.1. **Potential uses of multimillion-cycle phase transformation materials** [James, Science 2015].



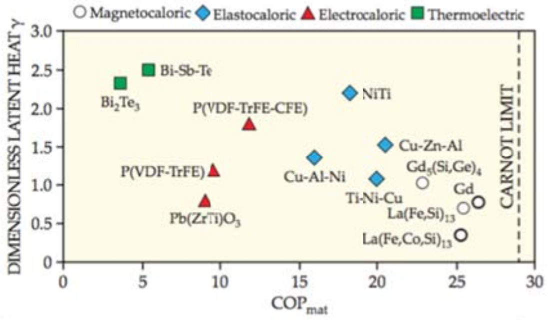
TECHNOLOGY	PROPERTIES SWITCHED	APPLICATIONS
Actuation	Shape-memory effect	Medical and automotive actuators Remote field-induced cycling of in vivo devices
Sensing	Magnetoelectric properties Dielectric tensor Susceptibility	Variety of mechanical, electrical, and magnetic sensors Optical sensors and smart windows Power electronics
Information storage	Magnetoelectric properties	Magnetic element switching by focused electric fields
Switching	Multiferroic properties	Variety of electromagnetic and optical switches
Solid-state refrigeration	Magnetization Polarization	Magnetocaloric effect Electrocaloric effect
Direct energy conversion	Magnetization Polarization	Solar or thermal heat-to-electricity conversion Waste heat conversion in digital devices; powering spacecraft

Whether the discovery of magnetocaloric effect was by E. Warburg [1881] or by P. Weiss and A. Piccard [1917], as argued recently [Smith, 2013], the first working magnetic refrigerators were constructed in 1933 [Giauque and MacDougall, 1933]. For cooling down to 10^{-1} Kelvin, magnetic refrigerators based on ^{3}He vapor are used today for research; whereas, for example, the nuclear adiabatic demagnetization in rare-earth-based $PrNi_5$ has permitted researchers to approach 10^{-3} Kelvin. Near-room-temperature prototype refrigerators for every-day use were constructed since 1997 (*see cover*). However, they are much more difficult to develop, both from materials, device, and operational temperature desired, unlike the adiabatic demagnetization refrigerators for low-temperature work.

So, why, even after two decades of a near-room-temperature working prototype, is a magneto-caloric refrigerator not here? *Basically, a small caloric effect (ΔT~ 5-10 K), price limitation in materials, and device engineering issues* (which depend on the material in use).

Numerous system-level studies predict lower environmental impact and higher efficiency for solid-state, caloric-based cooling compared to the vapor-compression cycle, see comparison of COP for various caloric and thermoelectric materials in **Figure 1.1**. Albeit in their infancy, the efficiency of caloric test beds exceeds that of thermoelectric devices and rivals even the most refined vapor-compression units. Yet, the banes of caloric refrigeration devices are parasitic losses at the system, device, and material levels, all of which reduce the COP of a physical system. Often good estimates of device and system level losses (e.g., I^2R, eddy current and mechanical losses, regenerator ineffectiveness, and system pressure drop) may by detailed by electrical, thermal, mechanical and fluidic modeling and, therefore, may be minimized.

Figure 1.1 **COP vs. dimensionless latent heat for caloric and thermoelectric materials.** Carnot limit is 28.8 for hot 298 K and cold 288 K (ΔT=10 K). From Fig. 3 in [Takeuchi & Sandeman, 2015].



Parasitic losses at the material level*, however, must be minimized in the caloric material itself as an intrinsic part of materials design.** The nature of the material's parasitic losses allows many of them to be addressed concurrently and synergistically, while maximizing caloric effects across the extended family of caloric materials. So, in fact, ***non-magnetocaloric properties must be also considered, especially concerning the assessment of performance metrics and COPs. Recent review articles [e.g., Smith et al., 2012] provide perspectives on thermodynamics, measurements, characterization, regenerator geometry, and device performance, as well as the need to consider non-magnetocaloric along with magnetocaloric properties. They also provide a massive list of relevant articles.

Challenges and Opportunities List

For societal impact, we need to develop and advance reversible caloric materials with long cycle life, within a systems approach, that will deliver transformational efficient cooling materials technologies. Thus, to achieve industry and market acceptance, several materials and technological challenges need to be overcome.

#1 Materials with Increased Caloric Effect for Reduction of Active Regeneration:

Regeneration – an engineering technique to increase the effective overall system temperature span (achieved by cascade from a series of caloric material beds, each with it unique ΔT range) – is a major source of system-related loss. Even with a good caloric effect, active regeneration (*which provides enhanced up to 5ΔT or more)* is required to achieve temperature spans needed for air conditioning (~60 F) and refrigeration (~30 F). Avoiding it altogether (*e.g.,* by increasing the caloric effect ~5 times what it is today) would be a major breakthrough that provides a simple integration of a caloric material within a caloric cooler, *potentially as simple as a thermoelectric (Peltier) cooler driven by an applied electric current,* but with significantly higher efficiency and performance*.*

Need: *Materials with **a factor of 3–10 increase** in the caloric effect in the same applied fields would lead to a rapid commercialization of caloric refrigeration technologies.*

This materials need is directly related to U.S. DOE **Grand Challenge #2** [GC Report, 2007]: *How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?* The field of caloric cooling would be greatly advanced by a new ability to create and manipulate caloric materials that operate at the theoretical limits and respond highly nonlinearly to their changing environments, much like living systems can do.

#2: Materials with Reduced Driving Fields for Efficiency:

Fields required to drive caloric effects are generally difficult to produce and sustain, and especially true for magnetic and electric fields. Even the stress field that is relatively easy to control may become unsustainable in an actual caloric device, considering that the strong stress field may be leading to material failure due to cyclic fatigue.

Need: *Highly efficient materials with reversible phase transitions at low driving fields* – capable of achieving useful caloric effects in fields that are 3 to 10 times lower than used today. Even though regeneration would still be unavoidable, the drastic reduction of cost to sustain the driving field would make commercialization of caloric cooling attractive.

This is directly related to U.S. DOE **Grand Challenge #1** [GC Report, 2007]: *How do we control materials processes at the level of electrons?* Here, one must manipulate the charge, spin, and dynamics of electrons to control behavior of material systems – shuttled between vastly different states using small driving fields, thereby producing strong cooperative caloric effects.

#3: Materials Near Instabilities for Strong Responses:

All progress in materials achieved to date is based on maximizing the difference between two or more equilibrium states of the material that are stable in high and low driving fields.

Need: Materials designed with access to non-equilibrium states due to nearly zero-energy barriers near invariant critical points*,* where *even a small change of field may lead to a drastically different concentration of phases that are in a metastable equilibrium,* and *to extremely strong caloric response*, holding substantial promise to exceed the current state-of-the-art by **a factor of 3 to 10**.

This remarkably promising area is directly related to U.S. DOE **Grand Challenge #5** [GC Report, 2007]: *How do we characterize and control matter away - especially very far away - from equilibrium?* The advances in caloric materials will be strengthened by development of

computational and experimental tools to study and control phase separated states, enabling the realization of enhanced caloric effects in weaker fields, and potential multiple driving fields.

#4 Multi-Field Caloric or Novel Hybrid Materials for Better Control and Efficiency:

Even though commercial refrigeration utilizes several phenomena and, correspondingly, several driving fields to achieve cooling, for example, pressure in vapor-compression systems, or electrical current in Peltier systems, traditional cooling technologies cannot benefit from simultaneous use of more than one field. Vapor-compression refrigerators, for example, cannot be made more efficient by placing evaporator into an electric or magnetic field.

Need: *Calorics that uniquely exploit multi-field control, rather than the traditional single-field response* (e.g., H-field in magnetocalorics), see **Figure 1.2.**

Because advanced caloric materials exhibit phase volume changes, stress can be utilized as an additional control to either restore the initial state, or push a system further into the required state, thus maximizing the caloric effect and the range of operation, see **Figure 1.3**. Materials exhibiting multicaloric effects and, potentially, novel hybrid materials may surpass current state-of-the-art in calorics by **a factor of 2 to 10**.

This area addresses **DOE Grand Challenge #3** [GC Report, 2007]: *How do remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents and how can we control these properties?* By moving away from the restrictive 2-dimensional space, e.g., temperature–magnetic-field (T-H), or temperature–stress (T-P), to three- or four-dimensional space (e.g., T-P-H), it should become possible to orchestrate the behavior of electrons and atoms **to create new – *multicaloric* – phenomena**.

Figure 1.2 **(T,P,H) phase diagram for magneto- and baro-caloric effect in $Gd_5(Si_2Ge_2)$.** (T,P,H)-surfaces for transition from ferromagnetic (FM) to paramagnetic (PM) states. Hysteresis lies between FM-to-PM (red) and PM-to-FM (blue) surfaces. Data taken from [Magen, et al., 2005]. Graphic provided by V.K. Pecharsky, Ames Lab (2015).

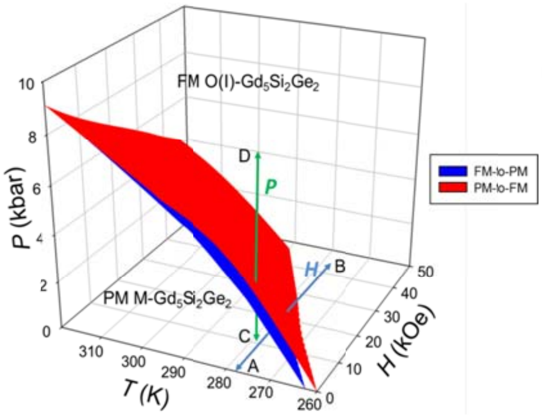
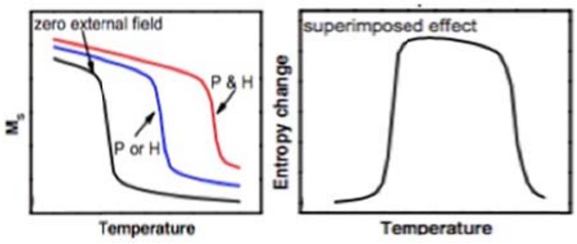


Figure 1.3 **Schematic of magnetization (right) and entropy change (left) versus temperature for P and/or H applied.** Superimposed caloric effects spans a larger range of operational temperatures, as shown in **Fig. 1.1**, for practical uses.



Obvious Commonality of Needs

Even with a material in-hand, how do we move forward? There are three desperately needed wants to advance the field, namely:

Needs Beyond the Material

- **Consistency for measurement protocols and data reporting for caloric-related phenomena** (like entropy change ΔS and hysteresis), which requires a necessary coordination across the R&D and industrial communities.
- **Availability of infrastructure to get prototypes and new materials tested.** Essentially, a modular test bed is required to assess rapidly materials properties, caloric cooling COP (as a fraction of Carnot limit), device performance, and design concepts – in effect a one-stop testing facility that is available to researchers, R&D groups, agencies, and industry.
- **Advancing modeling with coordination needed for guiding development** – design and characterization of new multi-field materials (Materials Genome type approaches) and devices/systems (heat transfer, performance, losses, and efficiencies).

Numerous materials have been synthesized and characterized by magnetization or electric polarization measurements. However, if such materials are to be assessed for performance, there is a need for more detailed protocols and characterization, including field-dependent specific heat and direct measurements of the adiabatic temperature change. For device use, one must explore the interrelationship between microstructure, shaping process, and performance for candidate materials. Additionally, concepts, such as enhancements of caloric effect in nano-materials or composites, thin-films, and heterostructures, may hold promise. The effect of hysteresis on actual device performance has been largely unexplored, which also depending on the active magnetic regenerator model used. Indeed, temperature hysteresis, for example, in a giant magnetocaloric material remains a drawback and reducing/eliminating such first-order hysteresis without sacrificing the magnitude of the caloric effects remains a significant materials challenge for applications. Over the past two decades a few studies have deliberately addressed hysteresis reduction by materials design [*e.g.,* Pecharsky & Gschneidner, 1997; Magen, et al., 2005; Smith, et al., 2012; Guillou, et al. 2014], especially in elastocaloric systems (Chapter 2). Beyond serendipitous discoveries, a dedicated and deliberate systematic approach is needed to advance caloric materials, as noted above. In addition, it remains outstanding that few materials have been tested in a device. Indeed, no systematic studies of different materials have been performed using the same device (it is difficult to compare data between different device for different materials). Such studies would be invaluable for improving regenerators, devices, and materials development by direct feedback.

In Closing

Exemplified briefly above are opportunities in caloric materials design, modeling and characterization that is currently lacking but necessary to achieve basic science understanding and control, device design, and, ultimately, a technology with societal impact and acceptance. In the following chapters, we provide similar examples and needs beyond magnetocalorics – such as the very promising elastocaloric materials – as well as what is needed for industry to extend concepts to create a product for the marketplace. The goal is a solid-state caloric material and operational caloric cooling devices that, ultimately, realizes a potential for 20-30% drop in U.S. energy needs for cooling – a true societal and energy-security impact!

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Chapter 2

Stress-Induced Caloric Cooling:

Elastocalorics Exemplifying Technical Challenges

Just a Squeeze to Remove the Heat **– Elastocaloric effect offers the potential for materials designed with long fatigue cycles and large ΔT** – *a step toward efficient, 'green' cooling.*

A subject of a recent AIP News Item: March 2015 Journal of Applied Physics

Stress-driven calorics are of special importance because changing stress can greatly enhance the magnetocaloric (electrocaloric) effects when coupled with a change of magnetic (electric) field. Furthermore, elastocaloric cooling, also known as thermoelastic cooling, is a stand-alone solid-state cooling technology undergoing early-stage research and development. Elastocaloric cooling relies on the reversibility of structural phase transformations, which generally have profound technological implications in numerous applications; especially relevant are fatigue life and hysteresis width, as exemplified in shape-memory alloys. The elastocaloric cycle is demonstrated in **Figure 2.1**. In 2014, the U.S. DOE Building Technology Office issued a report [Goetzler, et al., 2014] compared alternative technologies, and identified (besides magnetocalorics) thermoelastic cooling as the most promising non-vapor-compression cooling technology. Despite the great progress made since 2010, recent results show that technical barriers – such as *materials performance, fatigue life, effective heat exchange, and system cost* – must be thoroughly addressed to compete with popular vapor-compression technology, which is already cost effective and efficient. This chapter, therefore, presents the elastocaloric effect, technology development, potential applications, and key science and engineering challenges.

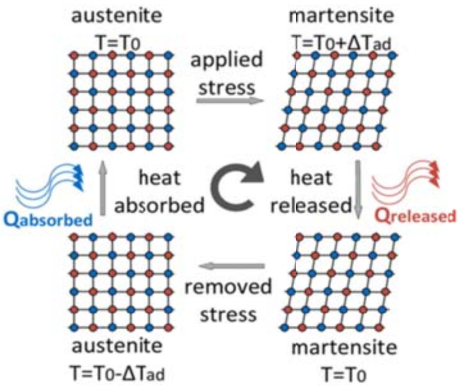
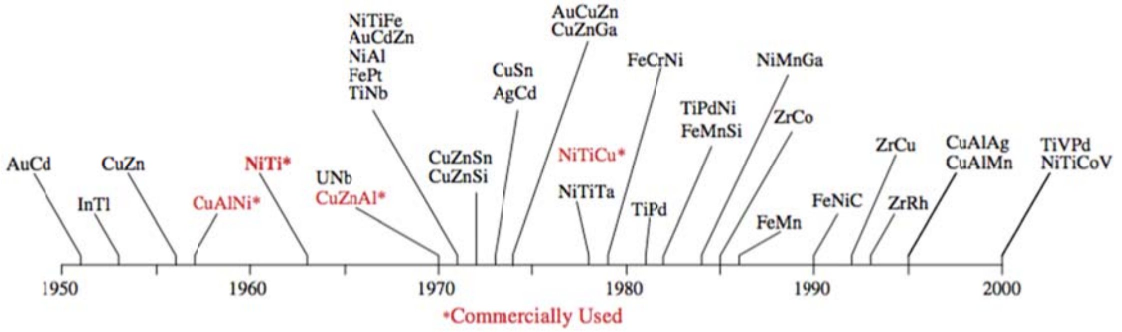


Figure 2.1 Schematic for the elastocaloric cooling cycle [from Tušek, et al. 2015].

Most of the elastocaloric materials exhibit shape-memory effects, which are closely related to reversible martensitic phase transformation in **Figure 2.1**. A shape-memory alloy (SMA) can recover its original shape after deformation when conditions (e.g., temperature, stress, magnetic and electrical fields) are suitably changed. As caloric harvesting from SMAs is relatively recent, a review of elastocaloric materials is essentially a review of SMAs. Prior to 1998 no thermal performance was reported in SMA reviews [Miyazaki and Otsuka, 1989]; later Otsuka and Wayman [1998] made a more comprehensive review of SMAs. Nevertheless, thermal properties were seldom reported for the early SMAs, like $Au_{52.5}Cd_{47.5}$ [Chang and Read, 1951] and [Lieberman et al., 1955], In-Tl [Basinski & Christian, 1954], Ag-Cd [Krishna & Brown, 1973],

Ag-Zn [Cornelis & Wayman, 1974], and, of course, the now infamous Ni-Ti [Beuhler et al., 1963]. In their review, with some early thermal properties, Otsuka and Wayman [1998] also suggested that Cu could be used to reduce the stress-hysteresis in the stress-strain curve for Ni-Ti. After this, the literature started to explode on the effects of alloying, as well as thermal properties. For example, from early on, copper-based SMAs were popular due to lower cost than Ni-Ti, e.g., Cu-Zn-Au [Miura et al., 1974]; most focus has been on ternaries, led by the University of Barcelona, Spain, to improve mechanical and thermal performance, e.g., Al-Cu-Be [Manosa et al., 1993], Al-Cu-Ni [Picornell et al., 2004], and Al-Cu-Zn [Bonnot et al., 2008]. The relatively slow progress in developing relevant thermoelastic materials (SMAs) is shown in **Figure 2.2**, which partly reflects the lack of thermal property measurement early on to grasp their potential.

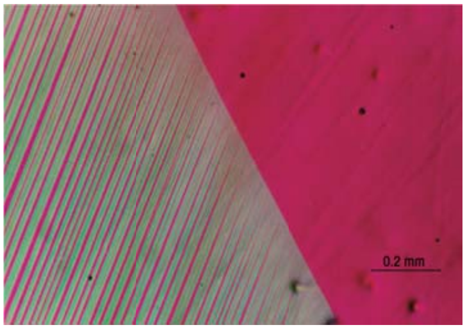
Figure 2.2. **Shown is the timeline for the discovery of various shape-memory alloys.** [Shaw et al., 2008]



Recent Advances in Materials Performance

Combinatorial, high-throughput methods are well suited, for example, to search for materials with specific properties or performance, like long fatigue life desired for cooling devices, and have been used to find reduced hysteresis and longer fatigue life in ternary Ni-Ti-X shape-memory alloys, and verify an underlying theory of martensitic transformations [Cui, et al. 2006; Zhang et al. 2009]. This work had potentially far-reaching applicability for functional materials with structural transitions, which also affect hydrogen solubility, thermal and electrical resistivity, optical transparency, luminescence and thermoelectricity.

Figure 2.3 **Microstructure of twinned martensite meeting a region of austenite (red) in a Cu-Al-Ni** [James & Zhang, 2005 similarly in other shape-memory alloys.



A proof that fatigue life can be extended via materials design was recently demonstrated. Chluba et al. [2015], extending earlier work in Ni-Ti-X (X=Cu, Pt, Pd, Au) [Cui, et al., 2006; Zhang et al. 2009], significantly reduced interfacial strain on (110) austenite planes in $Ti_{54}Ni_{46}$ between martensite and austenite regions, see **Figure 2.3**, by simple, but exact alloying of Cu for Ni, which, for $Ti_{54}Ni_{34}Cu_{12}$, the temperature hysteresis between the two phases was reduced, and **fatigue life reached 10^7 cycles!** An exhaustive search developed a near-zero hysteresis alloy ($Ti_{50.2}Ni_{34.4}Cu_{12.3}Pd_{3.1}$) [Zarnetta, et al., 2010].

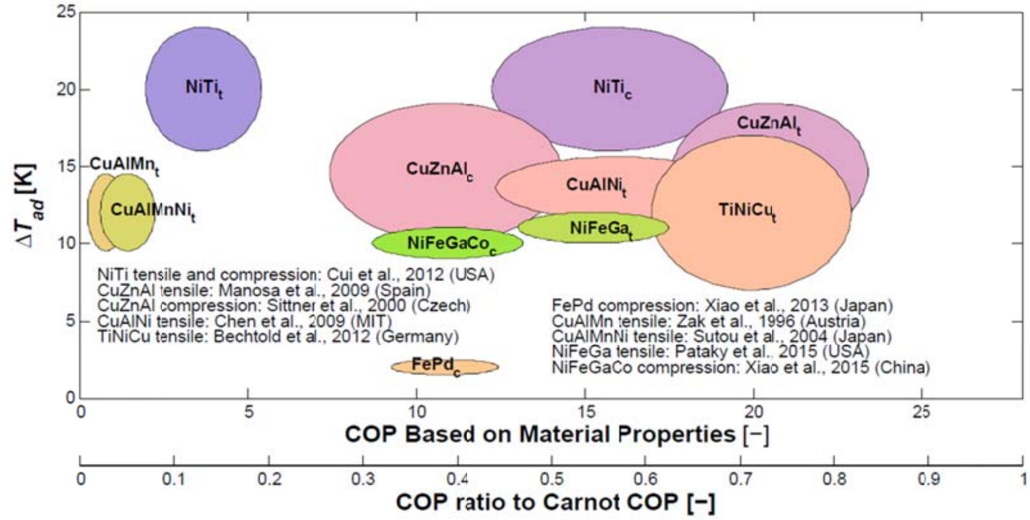
Beyond 10^7 cycles nears that needed for practical caloric refrigerators. If developed in concert with a system (device) and cost is addressed, industry and the market place will have reason to *embrace* this non-vapor-compression, efficient, and 'green' technology.

A thermoelastic-cooling project started in 2010 by J. Cui (PNNL), I. Takeuchi and M. Wuttig (U. of Maryland), and F. Johnson (GE Global Research), supported by a seed grant from the U.S. Department of Energy (ARPA-E), demonstrated elastocaloric cooling in NiTi wires based on the latent heat (energy required to complete a phase change of a unit mass) of the reversible shape-memory transformations, which is directly measured using differential scanning calorimetry. The NiTi wires exhibited a COP~11 with a ΔT of 17°C [Cui, et al., 2012]. In 2013, the project passed to a Tech-Readiness Level 4 (TRL-4) to develop a residential grade prototype, supported by an ARPA-E grant. Recently, to continue the advance towards a device, similar concepts were extended in Denmark for "training" wires to achieve ΔT of 25°C (21 °C) during (un)loading [Tušek, et al. 2015]. Stressing a NiTi wire by hand can induce the phase transformation, and the elastocaloric latent heat for some alloys can be as high as 31 J/g [Shaw et al., 2008], enough to cause a burn on the skin; or an icy-cold sensation when the stress is released and the wire transforms back to its parent phase.

A comparison of performance for some studied binary, ternary, and pseudo-ternary shape-memory systems are shown in **Figure 2.4** (upper right is the target areas for best materials performance). In shape-memory alloys, axial tension or compression respond differently, as then does performance. The stress-strain curves of the same 3-mm *NiTi wire* clearly shows compression uses less energy than tension [Cui, et al., 2012]. When system energy consumption (e.g., motor efficiency, friction, heat leaks, and auxiliary power) is considered as energy input, the system COP can be accounted (consistent measurement protocols are still needed). As always, for a given temperature lift (ΔT), the higher the system COP the higher the efficiency of the cooling technology.

By way of comparison, for the same weight, liquid-to-vapor phase change involves more degrees of freedom than a solid-to-solid phase change, and, therefore, the liquid-vapor latent heat is typically more than 10 times that of an elastocaloric material. However, a solid is denser than a liquid, so, for a given volume, the energy density difference between elastocaloric materials and a traditional liquid refrigerant in a vapor-compression system becomes less. For example, the latent heat for Ni-Ti and a conventional refrigerant like R134a are 12 J/g and 182 J/g, respectively; while the corresponding volume specific latent heat are 82 MJ/m^3 and 770 MJ/m^3, respectively.

Figure 2.4. Graph of performance (ΔT vs. COP) of elastocaloric materials, with subscript "t" ("c") for tension (compression). Provided by J. Cui, Ames Laboratory (2015).



A recent comprehensive review on fracture mechanisms in SMAs [Baxevanis & Lagoudas, 2015] indicates that crack-propagation mechanism of elastocaloric materials differs significantly from traditional metallic alloys, such as steel, due to suppression of crack-tip growth during the reversible martensitic phase transformation. More systematic fracture studies are needed to understand and eventually control the fracture failure for a successful implementation of elastocaloric materials into the cooling industry.

Advances of so-called ***multicaloric materials***, for which multiple driving fields induced entropy changes (Chapter 1), are only just beginning. For example, coupled magnetocaloric and barocaloric materials have been investigated, including $Gd_5(Si_2Ge_2)$ [Magen, et al., 2005], Ni-Mn-In [Manosa et al., 2010], Ni-Mn-Ga [Cui, et al., 2008; Manosa et al., 2013] and Ni-Mn-In-Co [Lu et al., 2015]. Studies in coupled multicaloric materials are currently in their infancy, and often only cursory. Given the discovery timeline (**Figure 2.2**) and the performance characteristics of these materials (**Figure 2.4**), it is clear that more focused, deliberate studies on both materials and their performance in a system, particular in possible hybrid material systems, will expand the scope of possible applications and performance for entry into the marketplace.

Elastocaloric Device & System Considerations

Many participants at the workshop, as noted by Tušek et al. [2015], re-iterated requirements for an efficient and useful device: (1) Reduce as best as possible sources of irreversibility: hysteresis on cooling and residual strain on unloading; (2) Design materials with suitable transformation temperatures; and (3) Extend fatigue (and fracture) life and functional stability, which removes two main limitations for elastocaloric technology. Missing is a third critical limitation – *cost* – which must also be included. The issues remain part to the challenges articulated in Chapter 1. Example prototypes are discussed in the next Chapter.

In Closing

Elastocaloric cooling joins magnetocaloric and electrocaloric cooling as highly promising non-vapor-compression cooling technology. The **Challenges and Opportunities identified in Chapter 1** remain unchanged, regardless of the caloric material explored. Given the above discussion, to develop a highly-efficient and cost-effective cooling technology, any elastocaloric material must be optimized for *large latent heat* (high power density), *small heat capacity*, *large ΔT, high thermal conductivity, low critical stress and strain, long cycle life, shape in the regenerator, and lowest material/system cost*. These optimizations require materials designed for both thermodynamic and mechanical responses, as well as device performance (more examples are in Reviews, e.g., [Smith et al., 2012], for which phase transformations, thermal properties, and interface phenomena play dominant roles in advancing caloric materials for efficient cooling.

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Chapter

3

Caloric-based Systems:

Scientific and Engineering Challenges

> *"Few things are harder to put up with than the annoyance of a good example."*
>
> **– Mark Twain**

Figure taken from Camfridge.com

A few developed magnetocaloric and elastocaloric cooling prototypes have been produced around the world, and these developments still continue in an effort to make them more viable for the marketplace. On the covers are the early (1997-2003) magnetocaloric (*proof-in-principle*) prototypes from *Astronautics Corporation of America* in collaboration with Ames Laboratory (a U.S. Department of Energy National Laboratory). The magnetocaloric material utilized for the devices was a non-research-grade of *Gadolinium*, key for future cost considerations. While devices continue to improve, *e.g.,* better regeneration configurations and higher COP, issues described in Chapters 1 & 2 continue to haunt advancement of devices, particularly efficiency and range of temperature, see **Physics Today** [Takeuchi & Sandeman, 2015]. Nonetheless, after almost 15 years, a marketplace device remains elusive.

The magnetic refrigeration market is expected to reach $315.7M by 2022, at a CAGR* of 98.7% between 2017 and 2022.

Summary of the first published market report on magnetic refrigeration based on interviews with major industry stakeholders.

http://www.marketsandmarkets.com/Market-

As noted in Chapter 1 (box highlight), concerted R&D efforts to refine vapor-compression devices were made possible, in part, by a sustained funding from U.S. federal and industrial sources. So, beyond the possible serendipitous discovery, a dedicated and deliberate systematic approach is needed to advance caloric materials. With the relatively high COP of caloric cooling cycle and no environmental impact, solid-state cooling will be a highly disruptive and commercially successful if **the system's COP is 4 or higher at temperature spans comparable** to those in practical vapor-compression systems. Innovations required are in materials development (maximizing the caloric effects) and system design (e.g., heat-exchange properties), as noted in earlier Chapters. Like other cooling technologies, magnetic refrigeration can be used 'in reverse' as a heat pump. The key for these cooling applications is a large ΔT and a small applied field for efficiency (best for first-order transition materials); in magnetocaloric materials ΔS~10-15 J/K-kg in a 1 Tesla field, giving a latent heat extraction of about 30 MJ/m^3, but the range of operation can be limited and the field required is really too large for broad application and efficiency, and fatigue (hysteresis) must be minimized, see needs Chapter 1.

Magnetocalorics: The U.S. DOE's Buildings Technology Office (BTO) has an initiative planned in Fiscal Year 2016 in advanced building materials R&D, which includes potential applications in magnetocaloric refrigeration, but it is only a small part of their technologies focus, such as visibly transparent insulating films for window, new insulations, and controlled gas-flow materials, no large-scale support for caloric materials or devices for refrigeration. Larger scale efforts, especially reduction in use of rare-earth elements are funded in Japan (e.g., by *New Energy and Industrial Technology Development Organization*, NEDO) and in Europe (e.g., by the European Union Seventh Framework Programme (FP7), with €50.5B in 7 years (2008-2014)). This project-based funding falls across many areas (not just materials and solid-state cooling) and was renewed under HORIZON 2020 (2014-2020) – *The Framework Programme for Research and Technological Development* from European Commission, with €70B in 7 years [Horizon, 2020], also called FP8 – the 8th continuation of this large-scale funding block.

Figure 3.1 Camfridge [2015] device shown is *21 x 14 x 18 cm*.

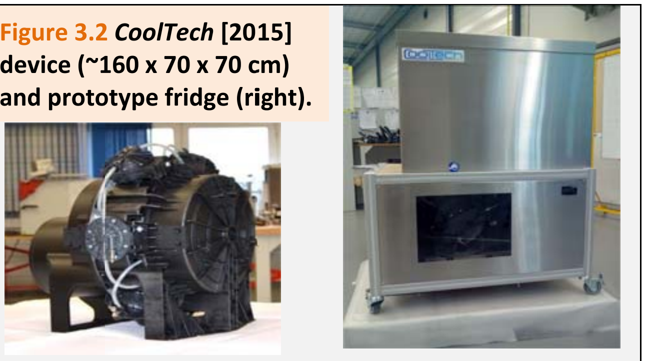

Figure 3.2 *CoolTech* [2015] device (~160 x 70 x 70 cm) and prototype fridge (right).

These projects range over many areas. For example, the DRREAM Project [DRREAM, 2013] collaborative is focused on materials with reduced use of rare earths in magnetocalorics. Whereas, the *Camfridge* Project (2007-2014) was focused on developing a magnetocaloric device and system [Camfridge, 2007]; currently, the focus is on optimization for a marketplace system, see **Figure 3.1** (*25 W cooling with mW/cm^3 (kW/m^3) of 4.7*, with claimed 5-10 smaller device size for same cooling power as those below), as presented at ICR2015 with comparisons to other efforts [Camfridge, 2015]. *CoolTech* in Holtzheim, France, mostly privately funded, claims the first "industrialized" refrigeration system (2013), see **Figure 3.2** (estimated by [Camfridge, 2015] at *300 W cooling with mW/cm^3 of 0.38*), which is not yet commercialized but planned by 2017. A strong R&D effort for over a decade in Denmark was funded mostly by the Danish Council for Strategic Research, e.g., *MagCool Denmark* (2007-2010) lead by Nini Pryds and Christian Bahl (12 of 230 researchers at TU Denmark) working on materials development, modeling, and prototype development (2 generations created), with industrial partners Danfoss and Sintex. A follow-on, 5-year (2013-2017) project (www.enovheat.dk) was established to build technical foundations for residential high-efficiency heat pump passed on caloric effect; with four industrial partner, Technoflex and Alpcon from Denmark together with Vacuumschmelze and BSH Bosch und Siemens Hausgeräte from Germany, ensures a close focus on the project's industrial relevance. And, a related effort at the Institut Polytechnique de Grenoble, France under Afef Kedous-Lebouc [MagCool France, 2010], funded by the French National Research Agency (ANR), however, no working device was developed. The University of Victoria in Canada has device efforts under Andrew Rowe, with government and natural gas industry funding. Spain and Germany (see its Ferroic Cooling priority programs) have no known device work.

In the U.S. in early 2014, General Electric Appliances (Louisville, KY) announced by press release [GE Report, 2014] a "portable" magnetocaloric-based refrigeration prototype (no system), see **Figure 3.3**, funded in part by $1.4M, 3-year DOE-BTO's CRADA between GE Appliance and Oak Ridge National Laboratories. It has not yet neared a practical stage for a system to pursue marketing. In early 2015, Haier announced a *wine-cooler fridge* based on system designed by Astronautics with materials from BASF (**Figure 3.4**), where the cooling unit is in the base of the fridge with a 75 W cooling power and mW/cm^3 of 0.87 (estimated). Astronautics Corporation of America has had varying funding from internal to DOE/ARPA-E, with which they have improved devices, especially regeneration and heat-exchange. The concerted R&D efforts made possible by a sustained funding and community efforts is ~10-50 times smaller in the U.S. versus the E.U.

Figure 3.3 **GE magnetocaloric device [GE Report, 2014].** Photograph from [GEEK.COM, 2014].

Figure 3.4 ***Haier* Wine Fridge [2015] with *BASF & Astronautics*)**, using BASF's Fe-Mn-based magnetocaloric, sold as Quice® brand.

Electrocalorics: Several electrocalorics devices have been built, where a good material has a ΔS from 1-10 J/K-kg, permitting heat extraction in the range of 10 MJ/m^3. For cooling, electrocaloric materialss require an electric field of 100-1000 kV/cm, comparable to a ferroelectric coercive field – for a 1 μm thick film, the field is 10-100 Volts, but for some polymer and bulk ceramics the voltage for cooling can be a kV or more. So, the target applications currently are for cooling of electronic devices and local climate control. For example, a 6-cm diameter device operating at 20 W/cm^3 based on polyvinylidene-fluoride polymer and ferroelectric ceramics multilayers was developed at Pennsylvania State University under DOE funding [Gu, 2014], see picture [Takeuchi & Sandeman, 2015]. UTRC has had some efforts, but it is unclear if any actual device has been tested and compared. The main challenge is scale up to thicker materials (huge electric fields and dielectric breakdown), which limits large-scale refrigeration applications.

Figure 3.5 **Compression device using Ni-Ti tube (top) and schematic [Qian, et al., 2015].** Takeuchi lab, U, of Maryland.

Elastocalorics: A few elastocaloric cooling prototype devices have been built worldwide, where a good material near room temperature has a ΔS from 10-80 J/K-kg, offering significant latent heat for first-order materials (like NiTi) in the range of 50-90 MJ/m^3. Under DOE/ARPA-E supported, Ichiro Takeuchi (U. of Maryland) has developed multiple prototypes. First, a Ni-Ti wire-based rotary device, using a steady heat-transfer fluid and moving SMA with unload recovery (no heat recover) at 0.5 Hz. Second, the first compression-driven elastocaloric cooling prototype was recently reported [Qian, et al., 2015], see **Figure 3.5**. Two beds consisted of multiple Ni-Ti tubes and steel supports were compressed by a motor-driven screw jack. The symmetric system layout allowed the linear actuator to recover the unloading energy, if Ni-Ti tubes were 50% pre-compressed. Eliminating motion of elastocaloric beds reduces the friction.

A more symmetric re-design is being developed (**Figure 3.6**) having four beds with 37 Ni-Ti tubes in each. Hydraulic cylinders were sized accordingly to drive the system, potentially saving 74% volume and 54% weight compared to that in **Figure 3.5**, while cooling capacity increases ~4 times. This Ni-Ti-tube compression device driven by screw jacks operating at 0.5 Hz, which uses a cyclic heat-transfer fluid and stationary SMA, with unloading recovery and heat recovery.

Plate-based designs are also being tested. Schmidt, et al. [2014] at Saarland University is testing tension on Ni-Ti plates induced by linear motors, which uses a stationary SMA, mobile solid heat sink/source, no unloading or heat recovery, operating at 0.4 Hz. Similarly, from Karlsruhe Institute of Technology, Germany, a tension induced by a spindle motor, using a mobile SMA, steady solid-state heat sink/source, with unloading recovery but no heat recovery, operating at 0.66 Hz operating. The double-bridge design consists of coupled stacked bridges of Ni-Ti plate, such that when one plate is stressed, the other one is fully released.

For useful devices, the major challenge is to develop efficient and inexpensive means to impart the cyclic mechanical stress – tensile or compressive (typically 400-600 MPa) – so the SMA refrigerant can repeatedly and continuously induce the transition. In addition, although ductile, the SMA undergoes large strains (up to 10%), which must be accommodated and which is not always reversible! Hence, while a proof-in-principle design is easily achieved in a lab setting, clever mechanical designs and new elastocaloric materials (high COP) requiring much lower stresses to induce the transition are really needed for practical applications.

Figure 3.6 **Redesigned, compression device driven by hydraulic cylinders [Qian, et al., 2015].** Takeuchi lab, U. of Maryland.

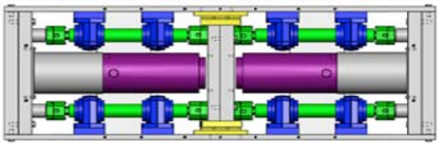

Table 3.1 Summary of key challenges for elastocaloric technology.

Working materials	o	Low hysteresis; High latent heat; Long fatigue life
	o	Small transformation stress; High heat conductivity
	o	Low cost
Drive	o	Compactness; Moderate precision
	o	Large force and small displacement
	o	Low cost
Regenerator configuration	o	Minimum friction; Uniform phase change
	o	Large heat transfer (surface-to-volume ratio)
System Structure	o	Compact design capable to handle a large force
	o	Light weight; High heat transfer (S-to-V) ratio
Heat transfer design	o	Compactness; Small heat transfer time constant
	o	High efficient heat recovery/regeneration
	o	Minimum pressure drop; and parasitic parts and loss
	o	Optimum fluid thermal mass

Challenges and Opportunities List

Notably, the workshop participants resoundingly supported four areas to make magneto-caloric cooling transformative (similar for other effects, too) – *with at least 2 of the 4 required for commercial viability*. Namely, **(1) Greater power in driving field** (e.g., magnet); **(2) Better caloric properties** (higher COP relative to Carnot limit at useful temperature span, limited hysteresis, better fatigue cycle) – compared to chemical systems. **(3) Greater system knowledge and efficiency on heat transfer/exchange/regeneration**; and **(4) Better system integration/design**. For #4, tailoring a material and the system will require materials theory and characterization, and device simulation. In the end, besides performance – cost is king.

Material and System: These have been emphasized earlier from a materials and system design perspective. On the materials front, the temperature span and latent heat may not display large enough effect, but optimism for marketable device would be dramatically extended with materials examples that overcome these limitations. With the “miracle material” it may require 5-10 years from material to commercialization, examples include: aerospace 25+ years versus GMR-effect materials 2-10 years – 2 Gb iPod to 100 Gb thumb-drive. A good example is shape-memory Ni-Ti that is reaching maturity after 60 years – bench-top experiments in 1990’s showed good biocompatibility and stress properties, but failed as an actuator. Today it is a few $B medical-device industry, with projection to be $20B by 2020. Often industry is limited to invest in materials development from profit versus development costs considerations. In waves of development, patience is a virtue, e.g., “high-temperature superconductors”. So, for industry using well-established technology, this is solving “machine issues” (engineering) versus “materials issues” (research) – exemplified by the history of the vapor compressor. On the system front, better regeneration performance in a long run needed. In actuality, for real-life production, both materials and systems issues need to move forward hand-in-hand. Caloric system performance is short of 50% found in today’s vapor compression units; that is, currently, device performance has a COP of ~2.6, whereas the Carnot entitlement is 5.3 – given by the Carnot efficiency is $T_{cold}/(T_{hot}-T_{cold})$ – giving $COP/COP_{Carnot} = 0.49$ (49% Carnot).

Energy Security, Sustainability, and Environment: Importantly, because COP determines sustainability and efficiency, *a system COP > 4 at useful temperature spans* will provide a *transformational opportunity for commercial viability*. However, compared with other technologies, advantages are clear: reduced energy consumption; no reliance on greenhouse gases (no possible releases); no compressors so reduced operational noise (quiet) and heat; no compressor failures (reduced warranty costs). As such, these systems should have long-lived interest from a variety of government agencies, DOE (BES and EERE for mission), Department of Defense (large DOD cost savings), and the Environmental Protection Agency (EPA) on policy and energy savings. With a good caloric refrigerator, a 20-30% reduction in energy use and a drop in foreign energy sources.

Measurement Protocols and Standardizations (Metrics): Currently, no protocols or standard performance metrics have been accepted for measuring and reporting data, for materials or system. Measurement protocols for sharing samples to get critical information from experiments not available in all laboratories do not exist.

Example Opportunities

Protocols and Reporting

- ✓ **Develop metrics** – for what needs to be measured and reported.
- ✓ **Establish measurement protocols** – for sharing samples for testing between groups.
- ✓ **Standardization via broad community agreement** (maybe a standards organization, such as NIST, can be recruited for this purpose).
- ✓ **Create a round-robin format for measurements for the community.**
- ✓ **Establish an open, modular test facility** – dedicated to rapid assessment, device certification, and standardization of prospective materials, as for solar-cell technology.
- ✓ **Establish community design metrics for theory or experimental assessments.**

  Metrics, e.g., $\Delta S \bullet \Delta T$ for optimization [Sandeman, 2012], and community milestones are useful, e.g., +25% in $\Delta S \bullet \Delta T$, +50% in COP/COP_{Carnot}, and increased range (–23° to 55° F) for refrigeration.
- ✓ **Assess system performance:** compare machine versus modeling, and test accuracy.

Materials Development

- ✓ **Accelerate materials discovery.** Use a dedicated and deliberate systematic approach with a coordinated experimental efforts and theory and computational advances (at least 20-30%).
- ✓ **Develop novel, multi-field controlled caloric materials with increased fatigue life.**
- ✓ **Highly efficient materials with reversible phase transitions at low driving fields** – 3 to 10 times lower than used today.
- ✓ **Define limits to materials performance** – from impurities and other effects.
- ✓ **Provide enough material for testing.** Supply and demand must be overcome.
- ✓ **Provide scale-up to material production** – needed from grams to kilograms.
- ✓ **Develop supply chains of material** – for prototype development, like Dupont/Dow.
- ✓ **Possible benefits in developing a materials consortium** – outside manufacturing factors.

Device Development

- ✓ **Accelerate device design and materials integration.** Use a dedicated and deliberate systematic approach within team(s) that incorporates academia, national laboratories, and industrial partners, and include IP people for reality check.
- ✓ **Establish national lab/industry exchange program** (e.g., utilize the nascent industry-based EERE program to fund cross-fertilization of personnel and ideas).

Additional Opportunities

- ✓ **Training the next generation (students)** across multiple disciplines.
- ✓ **Create a 'working group'* to coordinate the material solutions.**

*Notably, workshop participants have already established an informal working group to coordinate information and opportunities. Chapter 4 shows examples of this for international meetings.

In Closing

After less than two decades of uncoordinated research and development, caloric-based cooling systems have convincingly demonstrated their potential for high-energy efficiency. Caloric cooling technologies based on magneto-, electro-, and elasto-caloric effects are, therefore, ripe for market penetration and future widespread adoption by consumers. Yet, considering far from straightforward caloric material-device integration, anticipated market penetration is likely to be unacceptably slow, starting from small market niches and high-end products not available to the general public. Potential energy savings will, therefore, not be realized for a long time. Clearly, technical challenges remain to be overcome before refrigeration and air-conditioning *original equipment manufacturers* (OEMs) embrace the technology as mainstream and begin investing heavily in internal R&D to improve their systems and reduce manufacturing costs – making efficient commercial caloric-cooling devices more and more attractive to consumers. The rate of market penetration and adoption of caloric cooling, however, can be drastically accelerated by establishing an open, modular test facility dedicated to rapid assessment, device-certification, and standardization of prospective caloric materials. Such a facility will be greatly appreciated by academia and across the refrigeration-HVAC industry, and it will make a tremendous impact on the fundamental and applied science to advance caloric materials and devices by significantly shortening the typical 10-15 year time span for a material developed in a research laboratory to make it into the marketplace. The new caloric materials and devices to realize a marketplace refrigerator will make it possible to approach the expected 20-30% reduction in U.S. energy use for cooling.

References Chapter 3

[Camfridge, 2007] Funded by European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement 603885 (see http://www.camfridge.com).

[Camfridge, 2015] The project has received additional funding, for example, partly under the ELICiT-Project.EU (***Environmentally Low-Impact Cooling Technology*, elicit.project.eu)**, and some venture capital. A cooling device appears to have been constructed (see *http://www.camfridge.com)*, with an estimated performance to GE and Haier devices, which was presented at The 24th International Congress on Refrigeration (ICR2015), link in Chapter 4. **Online:** see ELICiT-Project.EU (ICR2015 slides)

[CoolTech, 2015] see, **online**: www.cooltech-applications.com. See presentation September 2015

[DRREAM, 2013] DRREAM Project: *Drastically Reduced Use of Rare Earths in Applications of Magnetocalorics* (see website). A €3.7M-project funded by European Union Seventh Framework Programme (2013 – 2016). The goal was to reduce the use of rare earth elements in the life cycle of technologies that use magnetic phase change materials for solid-state magnetic cooling. The prime focus in DRREAM is to facilitate the most efficient use of critical raw materials in the application of magnetic cooling in the domestic refrigeration market.

[GE Report, 2014] (February 2014) **Online:** GEReports.com news item*

*Engineers arranged magnets in a series of 50 cooling stages, and claim they are capable of reducing temperature by 80 degrees. They believe they are the first group to shrink the system enough so that it could be transported and shown; and also the first to go below freezing with the stages. Funded in part by a DOE BTO CRADA between GE and Oak Ridge National Laboratories.

[GEEK.COM, 2014] (13 March 2014) news item, **Online:** Geek.com

[Gu, 2014] Haiming Gu, "Chip-scale cooling devices based on electrocaloric effect," PhD thesis, Pennsylvania State University (2014). Advisor Prof. Qiming Zhang.

[Haier Wine Fridge, 2015] Presented at the International Consumer Electronics Show (ICES), Las Vegas, NV (January 2015) by Manufacturing: Haier (Hong Kong, China), Design: Astronautics Corporation of America (Milwaukee, WI, USA), and Material: BASF SE (Ludwigshafen, Germany). No traditional compressors, and runs more quietly and more efficiently than current fridges.

Online: (9 January 2015) Refrigerators.reviewed.com (13 January 2015) Chemistryviews.org

Screenshot from video (YOUTUBE.COM) that notes that there is no refrigerator being manufactured.

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[MagCool Denmark, 2007] (2007-2010) lead by Nini Pryds (TU Denmark) with two prototype developed in 2010 with industrial partners Danfoss and Sintex.

Online: (project description) http://www.staff.dtu.dk/nipr/Research/magnetoCaloric

Online: (details) http://www.energy.dtu.dk/Forskning/Magnetisk-koeling

[MagCool France, 2010] Research at the Institut Polytechnique de Grenoble, France under Afef Kedous-Lebouc, funded by the French National Research Agency (ANR).

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[Qian, et al., 2015] S. Qian, Y. Wu, J. Ling, J. Muehlbauer, Y. Hwang, I. Takeuchi, and R. Radermacher, "Design, development and testing of a compressive thermoelastic cooling prototype." International Congress of Refrigeration (ICR) 2015, Japan. Paper 0092.

[Schmidt, et al., 2014] M. Schmidt, A. Schutze, S. Seelecke, "Experimental investigation on the efficiency of a control dependent NiTi-based cooling process." Proc. of ASME SMASIS 2014, Newport, RI.

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[Takeuchi & Sandeman, 2015] Ichiro Takeuchi and Karl Sandeman, "Solid-state cooling with caloric materials," Physics Today **68** (12), 48 (2015). DOI: http://dx.doi.org/10.1063/PT.3.3022

Chapter 4

Recent & Upcoming Caloric Events:

International Conferences & Workshops

> *You have got to show me!*
>
> The U.S. state of Missouri is nicknamed "The Show Me State" as widely credited to U.S. Congressman Willard Duncan Vandiver during a speech in Philadelphia (1899): *"I come from a state that raises corn and cotton and cockleburs and Democrats, and frothy eloquence neither convinces nor satisfies me. I am from Missouri.* ***You have got to show me!****"*

Meetings involving **Caloric Materials for Solid-State Refrigeration, Energy-Efficient Cooling, or Renewable-Energy Applications** continue to grow and gather significant interest and impetus. Below is a list of international meetings from 2013 to 2017 (currently announced). Information for these meetings is provided, including known websites and proceedings, if available, as for the 2014 *International Conference on Martensitic Transformations* [ICOMAT-2014, 2015]. The importance of the caloric material and device R&D continues to grow due to the increasing energy unnecessarily and wastefully spent on cooling worldwide. Hence, the scientific and engineering advances needed remain the center of world efforts. However, the cumulative progress and device performance needs to be vetted, not just publically released – *You've got to show us* – the real data, how it was established, how the devices were tested, and how they compare to established data.

Below is an up-to-date listing of the recent and upcoming workshops and symposia where researchers have or can show everyone.

Recent Meetings on Caloric Materials, Refrigeration, and Devices

2013 MRS Spring: Symposium I – **Materials for Solid State Refrigeration**
Date/Location: 1-5 April 2013; San Francisco, Ca.
Organizers: Profs. Scott Beckman (Iowa State University/Ames Laboratory); Alex Greaney (Oregon State U.); Takeshi Nishimatsu (Tohoku U., Japan)
Website: http://www.mrs.org/s13-cfp-i/
Invited Speakers Included: Fons de Waele (Eindhoven Univ. of Technology, Netherlands), Asaya Fujita (Tohoku Univ., Japan), Heiner Linke (Oregon Univ.), Arun Majumdar (USDOE), Vitalij Pecharsky (Ames Laboratory/ Iowa State U.), Jukka Pekola (Aalto Univ., Finland), Simon Phillpot (U. of Florida), Steven Russek (Astronautics Corp.), Akiko Takahashi Saito (Toshiba Corp., Japan), Brian Sales (Oak Ridge National Laboratory), James Scott (U. of Cambridge, England), David Singh (Oak Ridge National Lab), Jeffrey Snyder (Cal. Tech.), Rama Venkatasubramanian (RTI International), Junqiao Wu (U. of California, Berkeley).

2014 ICOMAT (International Conference on Martensitic Transformations):
Symposium 10.03 – Applications & Design: Materials for Solid State Refrigeration
Date/Location: 3-5 July 2014; Bilbao, Spain
Organizers: Prof. Antoni Plane (U. of Barcelona, Spain)

Website: http://www.icomat2014.com
Proceedings: see, *International Conference on Martensitic Transformations* 2014; in Materials Today: Proceedings **2**, Supplement 3, Pages S475-S998 (2015). Edited by Jose San Juan, Angel López-Echarri, María L. Nó and Gabriel A. López
Online: http://www.sciencedirect.com/science/journal/22147853/2/supp/S3
Speakers Included: Plenary: Chris Schuh (MIT); Antoni Planes (U. of Barcelona, Spain); Ryosuke Lainuma (Tohoku U., Japan); Yinong Liu (U. of Western Australia); Alfred Ludwig (Ruhr-University of Bochum, Germany); and **Invited:** Valry Levitas (Iowa State U.); Xiaobing Ren; Sergey Kustov; Georiy Firstov; Oliver Kastner; Tadashi Furuhara; Federic Nanoix; David Duand; Yuri Chumlyakov; Fan Sun; Shuichi Miyazaki; Yoko Yamabe-Mitarai; Ibrahim Karaman; Wojciech Maziarz; Volodymyr Chernenko; Akira Ishida; Vladimir Brailovski.

2014 Thermag VI (International conference on magnetic refrigeration).
Date/Location: September 2014; University of Victoria, Canada.
Organizer: Prof. Andrew Rowe.
Website: now defunct, but mention is made here:
http://www.uvic.ca/research/centres/iesvic/home/news/archive/thermag_vi.php

2015 American Physical Society (APS), March Meeting: Symposium G19: Caloric Materials and Advances in Solid-State Cooling Technologies
Date/Location: 2-6 March 2015; San Antonio, Texas, USA.
Organizers: Jun Cui (PNNL – now Iowa State U./Ames Laboratory)
Website: https://meetings.aps.org/Meeting/MAR15/Session/G19.1
Invited Speaker: Vitalij Pecharsky (Ames Laboratory/Iowa State U.), Ichiro Takeuchi (U. of Maryland); Kurt Engelbrecht (TU Denmark), Jeffrey Snyder (Northwestern U.)

2015 Advancing Caloric Materials for Efficient Cooling: Key Scientific and Device-Related Materials Challenges for Impact
Dates/Location: 28-29 April 2015; University of Maryland, College Park, MD, USA.
Organizers: Jun Cui (PNNL – now Iowa State U./Ames Lab), Duane Johnson (Ames Laboratory/ISU), Vitalij Pecharsky (Ames Laboratory/ISU), Ichiro Takeuchi (U. of Maryland), Qiming Zhang (Penn State U.)
Website: https://www.nanocenter.umd.edu/events/amec/
Invited Speaker: Christian Bahl (TU Denmark); Karl Sandeman (CUNY – Brooklyn), Zdravko Kutnjak (Jozef Stefan Institute, Poland)); Shane Stadler (LSU); S. Pamir Alpay (U. of Connecticut); Richard James (U. of Minnesota); Radhika Barua (Northeastern U.), Frank Johnson (GE Research), Thomas Radcliff (UTRC), Steve Russek (Astronautics Corp.); Vitalij Pecharsky (Ames Lab); Jun Cui (PNNL); Manfred Wuttig and Ichiro Takeuchi (U Md); Qiming Zhang (Penn State U.). **Discussion Lead:** Duane Johnson (Ames Laboratory/ISU)

2015 The 24th International Congress on Refrigeration (ICR2015)
Dates/Location: 16-22 August 2015; Yokohama, Japan
Sponsor: (IIR) International Institute of Refrigeration (http://www.iifiir.org/)
Website: http://www.icr2015.org
Keynote Speakers: Yoichiro Ikeya (Sumitomo Heavy Industries, Japan); Motohiko Nishimura (Kawasaki Heavy Industries, Japan); Mark McLinden (NIST, USA); Yong Tae Kang (Korea University, S. Korea); Jacques Guilpart (IIR President, France); Kuniako Kawamura (Mayekawa Mfg., Co., Ltd., Japan); Gerald Valaier (Cemafroid, France); Pega Hrnjak (U. of Illinois Urbana-Champaign, USA); Chen-Yuh Yang (National Central U., Taiwan); Per Lundqvist (KTH, Sweden); Yi Jiang (Tsinghua U., China); Shin-Ichi Tanabe (Waseda U., Japan); Hsien-Te Lin (National Cheng-Kung U., Taiwan).

2015 DDMC: Delft Days on Magnetocalorics
Dates/Location: 2-3 November 2015; Science Centre, TU Delft, The Netherlands
Organizers: Prof. Ekkes Bruck and N.H. van Dijk (TNW, TU Delft), and Dr. F. Doetz (BASF).
Website: http://rst.tudelft.nl/DDMC
Invited Speakers: Mehmet Acet (U. Duisburg-Essen), Franka Albertini (Institute of Materials – NRC, Italy), Levente Vitos (Royal Institute of Technology KTH, Stockholm, Sweden), Kurt Engelbrecht (TU Denmark), Oliver Gutfleisch (TU Darmstadt, Germany), Enke Liu (Inst. Of Physics, Chinese Academy of Sciences, Beijing, China), Lluis Manosa (U. of Barcelona, Spain), Xue-Fei Miao (TU Delft), Karl Sandeman (City University New York – Brooklyn), Hargen Yibole (TU Delft), Coray Patrick (U. of Applied Sciences Northwestern Switzerland)

Upcoming Meetings on Caloric Materials, Refrigeration, and Devices

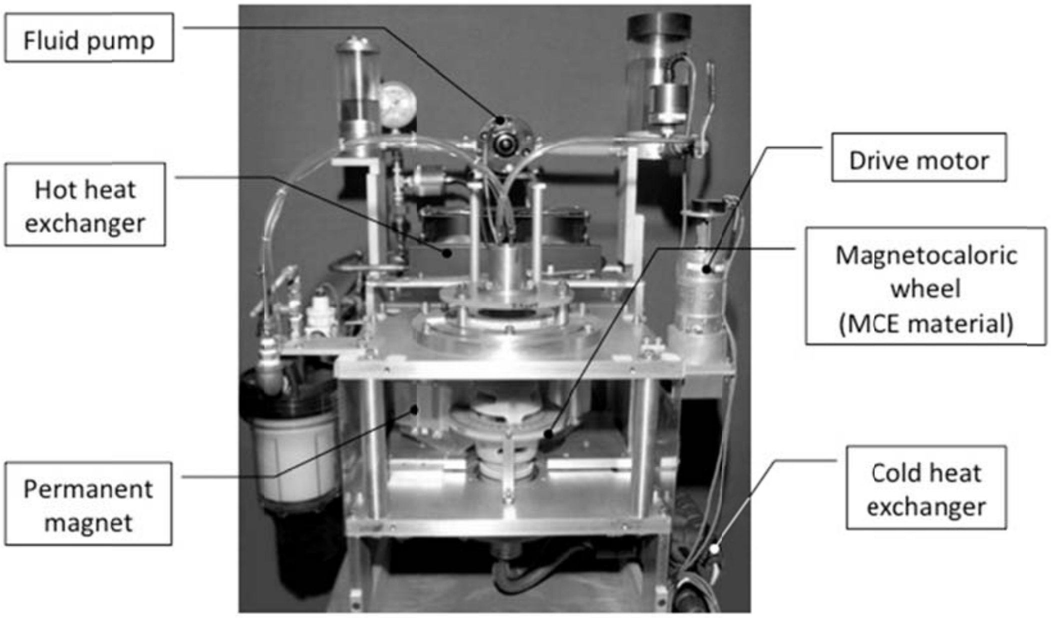
2016 Royal Society Discussion: Taking the temperature of phase transitions in cool materials
Date/Location: 8-9 February 2016; London, England.
Oganizer: Prof. Neil Mathur.
Web site: https://royalsociety.org/events/2016/02/phase-transitions/

2016 Winton meeting on caloric materials (Auspices of the Winton Program in Cambridge for the Physics of Sustainability)
Date/Location: 10-11 February 2016, University of Cambridge, England.
Organizer: Dr. Xavier Moya.
Website: http://people.ds.cam.ac.uk/xm212/campl_site/winton.shtml

2016 MRS Spring: Symposium Energy & Environment (EE11)—Caloric Materials for Renewable Energy Applications
Date/Location: 28 March - 1 April 2016; Phoenix, AZ, USA.
Organizers: Asaya Fujita (National Institute of Advanced Industrial); Nini Pryds (TU Denmark); Neil Mathur (U. of Cambridge); Ichiro Takeuchi (U. of Maryland)
Website: http://www.mrs.org/spring2016/
Speakers: Jun Cui (Ames Laboratory); Vitalij Pecharsky (Ames Laboratory)

2016 Thermag VII (International conference on magnetic refrigeration)
Date/Location: September 2016, Torino, Italy.
Organizer: Dr. Vittorio Basso.
Website: http://www.thermag2016.com/
Advisory Board includes: V.K. Pecharsky (Ames Laboratory/Iowa State. U.)

2017 MRS Spring: Symposium on Caloric Materials for Energy-Efficient Cooling (TBA)
Date/Location: 17-21 April 2017; Phoenix, AZ, USA.
Organizers: Emmanuel Defay (Luxembourg Institute of Science and Technology – LIST); Christian Bahl (TU Denmark); Jun Cui (Ames Laboratory); Xavier Moya (U. of Cambridge, England)
Website: http://www.mrs.org/spring2017/



For details, see inside front cover.