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14. ABSTRACT
This research aims to improve efficiency of thermal management systems for space platforms. Our efforts have focused on three areas, thermoelectric materials, magnetocaloric materials, and novel devices which use these mechanisms for space applications.

15. SUBJECT TERMS
thermoelectric materials, magnetocaloric materials, thermal devices.

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GENERAL ENGINEERING AND RESEARCH

Final Technical Report

Magnetocaloric Effect and Thermoelectric Cooling – A Synergistic Cooling Technology

NRL Grant N00173-14-1-G016
CODE 8200: Spacecraft Engineering Department
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Phase	**Funds Allocated**	**Funds Spent**	**Cumulative Over (Under) Budget**
Phase I (FY2015)	$372,613	$356,885	($15,728)
Phase II (FY2016)	$394,864	$412,007	$1,415
Phase III (FY2017)	$394,864	$393,406	($43)
Phase IV (FY2018)	$490,704	Project Ended	
Phase V (FY2019)	$484,112		
Phase VI (FY2020)	$484,112		

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Part 1. Introduction

This research is a collaborative effort between General Engineering & Research (GE&R) and the University of California, San Diego (UCSD) which aims to improve efficiency of thermal management systems for space platforms. Our efforts have focused on three areas:

1) Thermoelectric materials (TEC)
2) Magnetocaloric materials (MCE)
3) Novel TEC/MCE devices for Space Applications

Part 2. Identification and Significance of the Innovation

The Naval Research Laboratory (NRL) is continually looking for cutting-edge, innovative technologies to enable new space system capabilities. Currently, refrigeration and thermal management systems account for a large portion of the energy consumption on these platforms, and therefore, a more efficient cooling technology could have a dramatic impact on the cost and design of spacecraft systems. Cooling technologies run the gamut in size and heat removal requirements from those designed to cool microelectronics, to warehouse industrial sized refrigerators, with a plethora of applications and sizes in between. Recently, the DOD has become interested in development of revolutionary cooling technologies for microelectronics, as the current cooling systems for these devices have reached their thermal limit [1]. New technologies that have made progress in the last decade are thermoelectric cooling (TEC) modules and magnetic refrigeration. TEC uses the Peltier effect which creates a heat flux by applying an electric field [2]. Magnetic refrigeration utilizes the magnetocaloric effect (MCE), which is the temperature variation of a magnetic material after exposure to a magnetic field [3]. Our research is focused on developing a technology capable of utilizing both the TEC and MCE mechanisms simultaneously, to create a synergistic effect of which the efficiency is significantly higher than using either TEC or MCE alone.

TEC modules are at the forefront of new technology for many applications because they do not use liquids or pumps and have no moving parts, yielding an indefinite device lifetime. However, the drawback of current TEC technologies is their poor efficiency. MCE technologies have also drawn tremendous attention due to the possibility of good energy efficiency and environmental friendliness. However, MCE materials must operate in a predetermined temperature range and, therefore, development of magnetic coolers that can span a large temperature range has, to this point, been unsuccessful.

While much work has been performed on the TEC and MCE mechanisms separately, no known work has been documented on the potential combination of these two mechanisms. According to Yagasaki and Burkov, the thermoelectric efficiency of some materials can be considerably enhanced in a magnetic field [4]. Wolfe and Smith showed that the cooling efficiency of a single-crystal $Bi_{0.88}Sb_{0.12}$ alloy increases by ~2.8 times in the presence of a magnetic field [5]. The enhanced thermoelectric efficiency due to the magnetic field plus the added cooling from the magnetic refrigeration may create a synergistic effect that yields significantly higher cooling efficiency than using either TEC or MCE alone.

Part 3. Phase I Summary

3.1 Summary of Phase I

The goal of the Phase 1 research was to show that the TEC and MCE mechanisms have the ability to work together to produce additional (or synergistic) cooling effect. A summary of the Phase I research is described in Table 1. A detailed summary of the Phase I data was provided at the November 2015 quarterly review meeting.

Table 1 Summary of Phase I Research

Phase	Goal
Phase I – Proof of Concept	**FY2015 Goal:** Show that a synergistic effect occurs when combining TEC and MCE. **FY2015 Tasks:** 1) Synthesize TEC nanomaterial *N-doped and B-Doped CNTs successfully synthesized. Also, high efficiency Bismuth Antimony Telluride nanomaterial synthesized via spark erosion.* 2) Build/Characterize TEC test circuit *TEC test circuits were built by packing nanomaterials into ceramic cylinders with copper plates adhered to each end. Delta T under vacuum was measured to confirm thermoelectric properties.* 3) Synthesize RT MCE material *Several RT MCE materials were investigated. Gadolinium was purchased in multiple forms and showed best MCE performance. A rare-earth free alloy of NiMnSn was obtained from a Korean University and successfully formed into a nano-material pellet.* 4) Characterize MCE response *MCE response of various materials was characterized using Vibrating Sample Magnetometer. Both the Gd and NiMnSn showed room temperature MCE response.* 5) Show Synergistic Effect *A Physical Property Measurement System (Versalab from Quantum Design) was modified and used to test TEC/MCE modules with two simple configurations. An induced cooling effect was observed with application and removal of 3T magnetic field. The cold side temperature of the device decreased by 0.6C and 1.3C depending on location of the MCE material.*

3.2 Phase I Challenges/Issues

Gadolinium based MCE materials have great room temperature MCE response, but this material is expensive and its form is limited due to rapid surface oxidation (nanograins not possible). NiMnSn bulk material shows good MCE properties (not as good as Gd, but much less expensive) and nanograins can be made via spark erosion process. However, the NiMnSn nanomaterial pellet from spark erosion has lower performance most likely due to oxidation. A procedure to prevent the oxidation of these nanomaterials to form practical structures for our devices is needed.

Our nanomaterial TEC circuits breakdown due to thermal stress, so we were unable to accurately characterize the effects of magnetic field on these materials (BiSbTe and CNTs). A more robust method of making TEC circuits with the nanomaterials is needed.

CNTs and BiSbTe alloys were initially chosen in Phase I because of their good (BiSbTe) or potentially good (CNTs) thermoelectric properties. The highest reported thermoelectric efficiency (ZT) values are of BiSbTe type materials, and in particular, nanomaterial forms of BiSbTe material [6]. However, the literature reports much higher magnetic enhancement in single crystal alloys versus polycrystalline alloys. It may be more beneficial to use a lower efficiency single crystal TE material if enhanced efficiency under magnetic field is significant.

The characterization of these materials and devices is a challenge. The MCE materials are characterized using a Vibrating Sample Magnetometer (VSM) which we have limited access to (up to 5hrs/week only). A Physical Property Measurement System (Versalab PPMS from Quantum Design) was modified and used to test TEC/MCE modules with two simple configurations. The PPMS allows total environmental control (temperature and vacuum) while also applying magnetic field of up to 3T. Unfortunately this is another Professors equipment and our ability to continue to use and modify this equipment is limited. We will need to purchase our own equipment or find another way of accurately characterizing our devices. Additionally, for the Phase II work we will also need to characterize ZT of our thermoelectric materials under magnetic field. The PPMS that we were using does not have this capability.

Part 4. Phase II and III Summary

The following summary of research for the Phase II and III effort describes the advancements we have made thus far in each of the three different areas of focus:

1) Thermoelectric materials (TEC)
2) Magnetocaloric materials (MCE)
3) Novel TEC/MCE devices for Space Applications

A significant milestone achieved for this research effort is shown in Table 2.

Table 2 Milestones

	Defined at start of FY2017	Status at end of FY2017
FY2017 Milestone	Low Temp. Device (180K): Space applications: TEC/MCE materials: T_{hot} ~ 180K, T_{cold} ~40K (In this temperature range, current state-of-art TEC materials that are utilized in commercial TEC modules achieve ZT ~0.05-0.2.	Our improvement in TE materials alone exceeds this milestone. We have reported highest ZT~0.4 for 180K applications with the Bi-Sb-Te composition. This is significant improvement over state-of-art. We also successfully demonstrated a solid state prototype utilizing MCE/TEC at 180K.

4.1 Thermoelectric Materials

Thermoelectric cooling modules are attractive because they are solid state, have no moving parts, and can be designed to fit within small size constraints. Space application of thermoelectric (TE) modules typically require operation at sub 200K temperature ranges. Despite having been utilized on space platforms for decades, improvements in module efficiency for low temperature have been limited as the majority of research in this area is focused on room temperature applications. There are no known commercial suppliers of TE materials which have been optimized for high performance for sub 200K applications. One major reason is the difficulty of accurately characterizing TE materials at low temperature ranges. GE&R has invested in high end specialty equipment which can accurately characterize TE materials from 50-400K and also has the ability to apply up to 3T magnetic field. Figure 1 shows the thermoelectric material efficiency (ZT) versus temperature for the best reported materials from literature. Aside from the single crystals, our $Bi_{0.4}Sb_{1.6}Te_3$ (BST) bulk sample, as measured on our system, has the highest reported ZT at 180K. We believe additional significant improvements in low temperature TE materials are possible and our work has focused on two promising pathways to achieve this goal.

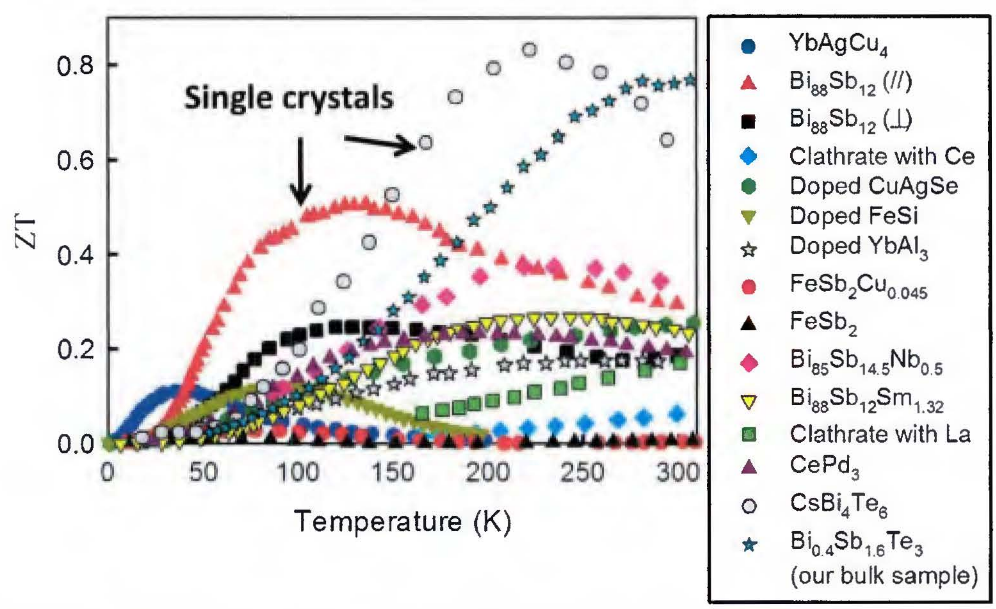
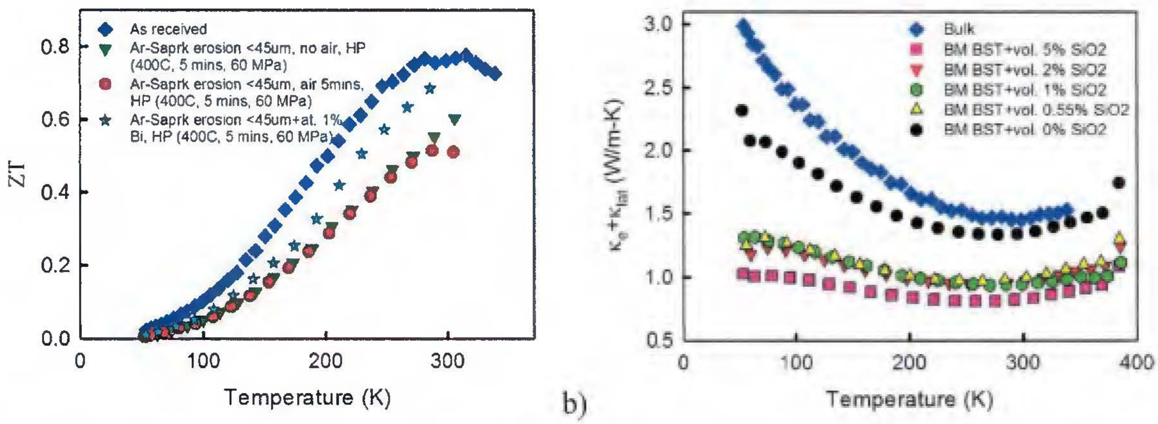


Figure 1 Thermoelectric material efficiency (ZT) versus temperature. (The $Bi_{0.4}Sb_{1.6}Te_3$ is GE&R measured data. All other data is from various literature sources, these materials are not commercially available).

Nanograined structuring with doping. Improvements in ZT near room temperature have been reported with nano-grained structuring and doping of these materials [6]. Synthesizing nano-materials with consistent batch-to-batch properties and no oxidation is not easy. We have successfully developed these methods and have shown consistent and repeatable performance for nano-grained TE materials. Now that we have this capability developed, a systematic investigation of doping effects on ZT performance for low temperature applications can be performed (to date this has only been done for near room temperature). This will provide a fundamental understanding of doping effects on ZT, and allow us to optimize our BST material composition for various low temperature applications. Figure 2a shows oxidation and composition doping effects on ZT for our BST material where doping with Bi acted to shift the peak ZT to lower temperatures. Figure 2b shows effects of metal oxide doping with as much as 45% reduction in thermal conductivity. Future work is needed to improve dispersion techniques so that carrier mobility is not degraded with doping and ZT can be enhanced. We believe a 30% improvement in ZT at 180K over current standard is achievable with additional effort.



a) b)

Figure 2 a) shows oxidation and composition (Bi) doping effects on ZT versus temperature and b) shows effects on thermal conductivity with metal oxide doping.

Single crystal BiSb material. The highest reported ZT for low temperature applications is BiSb single crystal with applied magnetic field. This data was reported several decades ago, but has not yet found utility due to the challenges associated with synthesizing single crystals, as well as accurately characterizing TE properties under magnetic field [5]. We have investigated multiple methods of forming this material. Using a Bridgeman furnace, which is what was used in the literature, we were able to successfully synthesize this material but determined this method was not practical as only very small quantities can be made (~a few grams). In FY2017 we successfully modified our in-house furnace to synthesize useful quantities (10+ grams on first pass, with room for >100g) of this single crystal, see Figure 3. With in-house economical synthesis capability, we can now develop processing and optimize performance of this material for low temperature. Figure 1 shows the reported ZT for this material is actually quite good even for sub 100K applications. TE cooling modules currently have almost no utility for sub 100K applications as the efficiency is too low. Successful development of BiSb single crystal could open the door for the use of these modules in sub 100K applications.

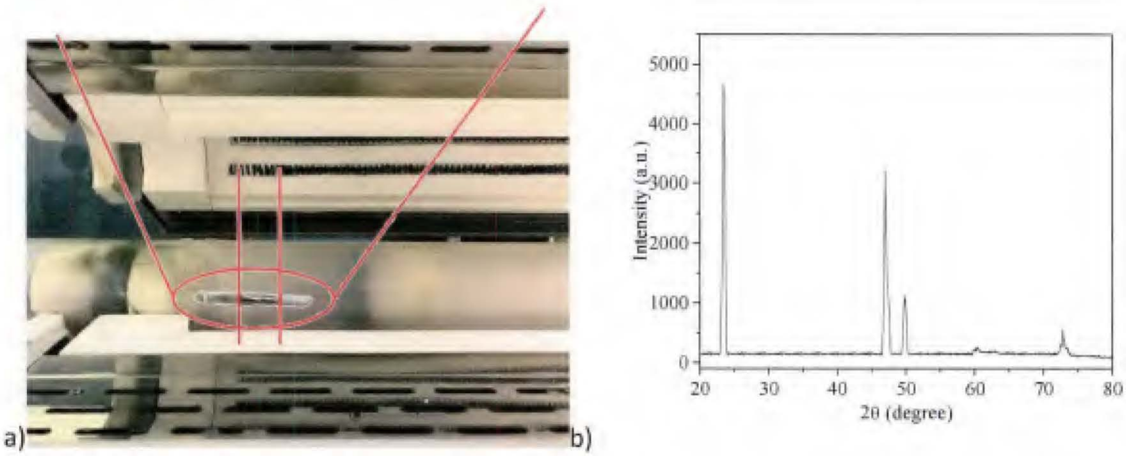


Figure 3 a) GE&R modified furnace for single crystal growth of BiSb and b) XRD showing crystallinity for GE&R BiSb with 4X passes in furnace.

Accomplishments up through FY2017	- Self-financed specialty equipment to rapidly and accurately characterize TE efficiency at low temperature and with application of up to 3T magnetic field. - Developed robust material processing methods to synthesize nanograined materials without oxidation. - Demonstrated composition doping and metal oxide doping into nanograined mixtures have potential to both shift and increase peak ZT performance temperature. - Successfully built and demonstrated single crystal growth furnace to synthesize useful quantities of one of the highest reported low temperature TE materials, BiSb.

4.2 Magnetocaloric Materials

Magnetic refrigeration has long been touted as a promising high efficiency technology to replace vapor compression systems. However, there are several major issues that need to be solved to move this technology forward. One of these issues is the lack of commercially available low cost magnetocaloric materials that will actually function, for a long period of time, in a magnetic refrigeration environment. Synthesizing MCE materials is not easy, and the known materials are expensive rare-earth based and/or poor performance. Another major issue inhibiting magnetic refrigeration is the lack of experience designing and engineering these systems. Millions of research dollars have been spent on magnetic refrigeration leading to exponential growth mainly in material science discoveries (much of which are useless in an actual refrigeration environment because of poor stability, performance, and/or cost), while the engineering activities for these systems have remained low.

Our research efforts have focused on building solid state cooling devices for low temperature applications utilizing the magnetocaloric mechanism. We successfully synthesized many of the best-known compositions of MCE materials for 180K applications (Heusler alloys, GdSiGe alloys, La based alloys, etc.). These materials were evaluated in high frequency magnetization environments, and the fundamental knowledge our team gained from this research directly led to the discovery of the highest performing economical MCE alloys for sub 50K applications. We were able to obtain significant additional funding from the DOE to develop and manufacture high performance MCE materials for all temperature ranges. All MCE materials development is now done solely under the DOE award. Figure 4 shows the relevant MCE materials discoveries and expected performance exceeding that of Gd (one of the best known MCE materials) following optimization under our DOE award.

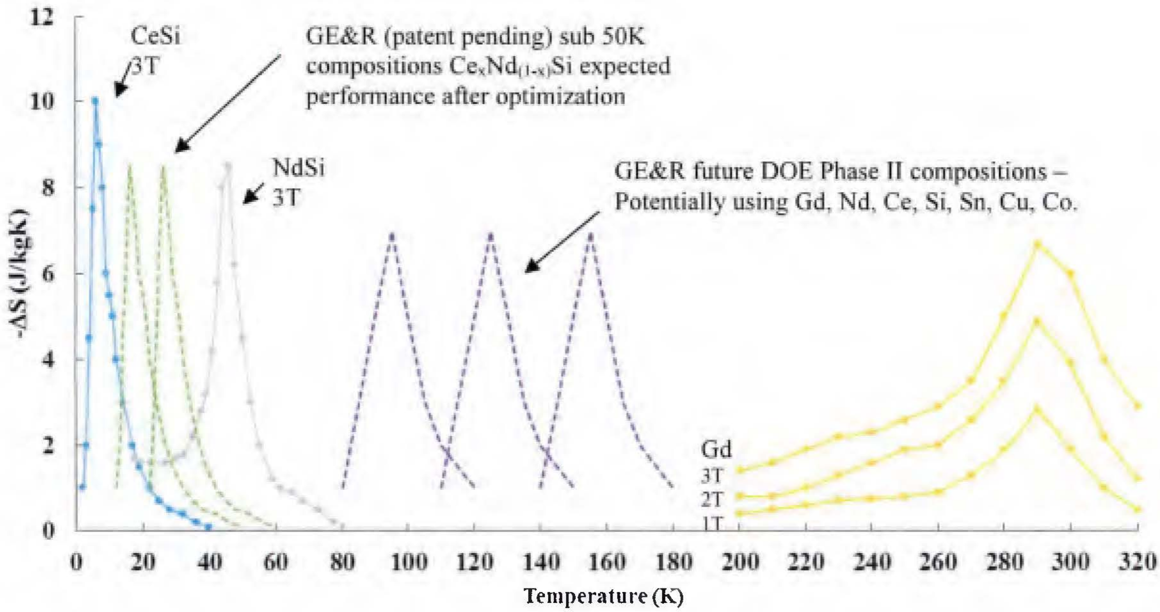


Figure 4 ΔS versus temperature for various MCE materials. Peaks with solid lines are from actual data (either literature or measured by GE&R) and dashed lines are expected performance of GE&R materials which will be developed under DOE grant.

Accomplishments up through FY2017	- Successfully synthesized and evaluated best known MCE materials. This work will be presented at the 2017 MMM conference in Pittsburg on Nov 8. - Our evaluation of Huesler alloys led to the discovery of high performance low cost MCE alloys for sub 50K applications. - The fundamental understanding gained from developing AND testing MCE materials in ACTUAL devices under the NRL grant has provided our team with a unique expertise in this area. - Additional DOE funding has been obtained to develop and manufacture high performance MCE materials.

4.3 Novel devices for Space Applications

Magnetic refrigeration devices for sub 4K applications have been around for decades, however devices utilizing this mechanism for higher temperature applications have yet to be commercialized. Depending on the application, many technical challenges exist for implementation of MCE mechanism into real world systems, including: thermal conductivity issues, space constraints due to required magnetic field, how to safely oscillate MCE material and/or magnetic field, and identifying where potential efficiency losses occur in these systems.

Under the NRL grant award, prototypes for solid state cooling utilizing both TEC and MCE mechanisms were successfully demonstrated for both room temperature and low temperature (180K), see Figure 5. We have three patents pending for our novel structures. Previous efforts to develop devices utilizing MCE have had issues with low thermal conductivity. We designed a layered structure which solves these issues and allows rapid thermal transport for high frequency magnetization cycles (patent pending).

Additionally, a major effort was needed to custom build a platform to characterize the performance of these devices. To date, nearly all reported performance metrics for MCE devices at low temperatures have been only theoretical. With our system we can build different MCE configurations and study thermal transport properties under varying conditions, down to 20K. We will use this knowledge to aid in designing an optimal system (size constraints, required magnetic field force, cycle time, MCE thermal capacity, etc.)

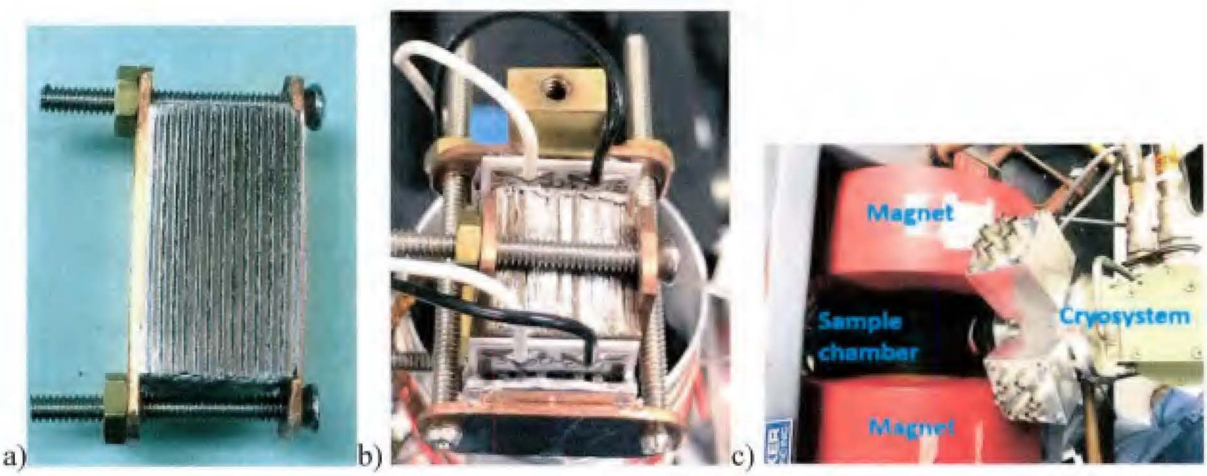


Figure 5 a) MCE high thermal conductivity structure used in b) MCE/TEC solid state cooling device tested at 180K in c) our custom built device testing system.

As previously stated, an enormous amount of work has been performed to develop MCE materials, but very little work has been done designing and engineering actual systems which utilize the MCE mechanism. For magnetic refrigeration to become a reality, we need more groups working on these systems, and we need to develop and demonstrate a high efficiency system for a relevant commercial application to validate this technology and stimulate industrial innovation.

To this end, we have identified an immediate potential application for our MCE/TEC device which utilizes the current state-of-the-art materials that we have developed to prevent boil-off for cryogenic liquid storage. Hydrogen fuel for space platforms is typically stored in liquid form inside highly insulated dewar tanks. In the US, LH2 fuel for space applications is roughly a \$700M/yr market. The current storage tanks cannot completely prevent evaporation or boil-off of the liquid hydrogen to the atmosphere, and in some cases boil-off losses from these tanks can be significant. Incorporating systems using compression based refrigeration cycles are possible to prevent these losses but these systems are expensive, and require enormous amounts of energy. Hydrogen liquefaction using only magnetic refrigeration has been demonstrated, but major issues with these prototypes exist [7]. Our high thermal conductivity MCE structure, and TEC heat switch solve several of these issues. Based on our FY2017 device testing, we would expect MCE/TEC device could provide >10X COP improvement compared to compression only based systems.

For space platforms, a high efficiency system to prevent liquid hydrogen (LH2) fuel boil-off would allow longer flight distances and/or reduction in fuel payloads needed. The system would also be useful for LH2 storage at government laboratories.

Other applications for zero boil-off cryogenic liquid storage include the following:

1) 20K LH2 storage for hydrogen fuel cell vehicles. A major inhibitor to hydrogen fuel cell vehicles is lack of infrastructure which is difficult to build due to LH2 boil-off losses. Economical storage utilizing zero boil-off systems would solve these problems. If successfully implemented, this could have a major impact on the automobile industry.
2) 4K Liquid Helium (LHe). LHe is required for superconducting magnets, which are used in all MRI and NMR machines. Massive amounts of LHe are also used in Nuclear Fusion R&D. Helium is expensive, especially when refrigerated into liquid form, and it is a depletable resource – once it is released to the atmosphere it cannot be re-captured, and is actually light enough that it leaves earth's atmosphere and is lost to space.
3) 77K Liquid Nitrogen (LN2) – Cryogenic preservation of biomaterials is a rapidly growing market requiring massive amounts of LN2.
4) 112K Natural gas (LNG) – Transition to cleaner fossil fuels is increasing however, economical and safe transportation and storage of natural gas requires refrigeration to below 112K.

Accomplishments up through FY2017	- Prototypes for solid state cooling utilizing MCE and TEC were successfully built for both room temperature and 180K and measured performance metrics reported. - Custom built a platform to characterize MCE/TEC device performance at low temperature. - Three patents pending for novel MCE/TEC device structures

Part 5. Research Team

Short biographies of the key personnel for this research effort are provided below.

Principal Investigator – Dr. Robin V. Ihnfeldt, Ph.D., President, GE&R

Dr. Ihnfeldt is the founder of GE&R, which develops and manufactures novel materials and devices for various industries. She has been awarded >$3M in federal grant funding from the National Science Foundation, the Naval Research Laboratory, and the Department of Energy. Her background includes semiconductor manufacturing, pharmaceuticals, and thermoelectric and magnetocaloric materials and devices, with expertise in electrochemistry, colloidal and materials science, and nano-engineering.

Development Engineer – Dr. Xia Xu, Ph.D. GE&R
Dr. Xu is currently working full time for GE&R developing novel thermoelectric and magnetocaloric devices and materials. He has a Ph.D. in chemical engineering with expertise in synthesis and characterization of rare-earth free permanent magnetic materials, nano-material synthesis, and physics of magnetism.

Technical Advisor – Professor Renkun Chen, UCSD
Prof. Chen's research group is focused on synthesis, characterization, and evaluation of nanostructures and materials for high efficiency energy and cooling applications. Chen received his PhD in Mechanical Engineering at UC Berkeley in 2008, and has more than 12 years of experience in advanced materials and technologies for heat transfer, cooling and refrigeration.

Graduate Student Researcher – Jianlin Zheng
Jianlin is currently working on a Ph.D. in materials science and engineering at UCSD. He has successfully setup robust methods to synthesize nano-grained thermoelectric materials and has significant experience in modeling thermoelectric systems.

Consultant – Professor Emeritus Sungho Jin, GE&R
Prof. Jin currently works as a consultant, on an as needed basis, for GE&R. He was the head of the materials science department at UCSD and is a life-time faculty member and distinguished professor of UCSD. He is a Member of US National Academy of Engineering. His research activities include new energy materials, high efficiency thermoelectrics, magnetocaloric materials, new magnetic thin film materials, and unique nanocomposite synthesis. He has ~200 issued or pending US Patents, ~400 publications, and ~140 invited or keynote talks at major professional societies.

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