Magnetic Refrigeration

UMT 401 Term Paper

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Abstract

This term paper describes the phenomenon of magnetocaloric effect (MCE). It addresses the materials used for magnetic refrigeration based on their MCE properties. It also looks at how the device operates and some of its practical challenges. Some of the latest advancements in this topic are also presented.

What is a magnetic refrigerator?

A refrigerator where the working body is the magnetic material instead of gas. Here, the process of magnetization/demagnetization replaces the compression/expansion cycle of conventional refrigerators.

Why do we need a magnetic refrigerator?

High efficiency can be achieved due to the reversible nature of MCE. Magnetic cooling efficiencies can reach up to 30-60% of a Carnot cycle, whereas it is only 5-10% for conventional vapor compression devices. Also, avoidance of volatile refrigeration gases used in conventional vapor compression devices is a plus for this technique. The possibility of recycling materials and magnets at end-of-life, makes the technology attractive from an environmental point of view.

It is among the most promising alternatives to conventional refrigerators.

Brief History

Langevin (1905) demonstrated that change in paramagnet magnetization leads to reversible temperature change. Debye and Giauque (1927) proposed the technique of adiabatic demagnetization to obtain low temperatures. MCE has been used at the lab-scale to obtain sub-4K temperatures for many decades. From the past 30 years, room temperature refrigeration based on MCE has gained prominence due to discovery of material compositions with favorable Curie temperatures.

Concept

MCE is the emission or absorption of heat by a magnetic material under the action of a magnetic field. Under adiabatic conditions, this results in heating/cooling of the material (change in internal energy). In principle, all magnetic substances exhibit MCE. However, it is most pronounced near magnetic phase transitions where a small external field can change the spin state significantly.

The magnetocaloric effect is fully characterized by the two quantities, the adiabatic temperature change, ΔT_{ad} and the isothermal entropy change per unit mass, ΔS mapped out as functions of field and temperature.

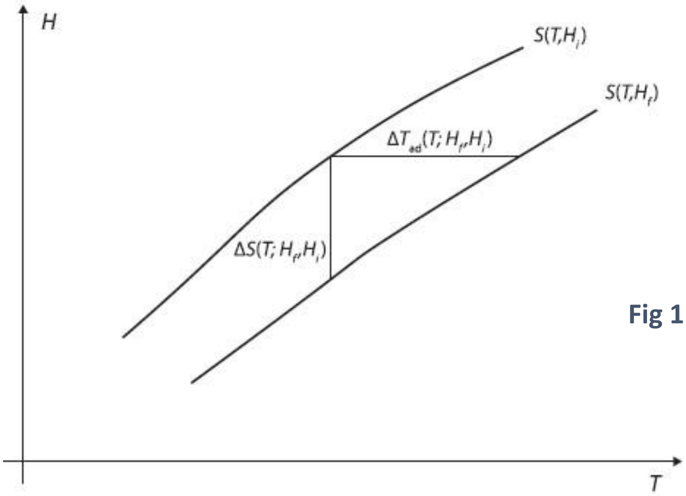

Fig 1: Basic Magnetocaloric Quantities

The total entropy is written as a sum of 'magnetic', 'lattice', and 'electronic' entropies, where it is assumed that the latter two do not depend on the field.

S(T, H) = **S** mag(T, H) + **S** lat(T) + **S** el(T)

S mag is identified with the entropy of the spin system, S lat with the entropy associated with the lattice vibrations (phonons), and S el with that of the conduction electrons. From this it is inferred that the isothermal entropy change is equal to the change in 'magnetic' entropy.

Now, **Δ S mag** (T; H f, H i) = **S** mag (T, H f) − **S** mag (T, H i).

The above equation allows us to derive a fundamental limit on the maximum entropy change. This is done by considering the paramagnetic state as a collection of independent, localized spins with magnitude J, disregarding interactions and any anisotropy. In zero field, each of the (2 J + 1) possible orientations of the spin are equally probable, giving an entropy per spin of k_B ln (2 J + 1).

In very high fields ($\mu_B \mu_0 H >> k_B T$), all spins are aligned to the field direction, giving an entropy of 0. Thus, the maximum achievable change in magnetic entropy is = N k_B ln (2 J + 1).

Working of the device

The working material (magnetocaloric substance) is the refrigerant and it starts in thermal equilibrium with the refrigerated environment.

1) Adiabatic magnetization: The working material is placed in an adiabatic environment (no heat exchange between system and surroundings). An increasing external magnetic field (+H) causes the magnetic dipoles of the atoms to align, thereby decreasing the material's magnetic entropy and heat capacity (as the overall degrees of freedom decrease). Due to the insulated environment, the total entropy must remain constant and hence, the substance rises to a higher temperature (T + ΔTad) => due to increase in thermal (lattice) entropy.

2) Isomagnetic heat transfer: **A fluid or gas** is used to lower the temperature back to T (by absorbing heat from the working material => -Q), while the magnetic field is held constant to prevent the dipoles from reabsorbing the heat. Once sufficiently cooled, the working substance and the coolant are separated.

3) Adiabatic demagnetization: The magnetic field is decreased, and the magnetic moments become disordered using the thermal energy of the system (since adiabatic conditions are maintained). Energy transfers from thermal entropy to magnetic entropy which is stored in the magnetic dipoles. The decrease in thermal entropy lowers the temperature of the system to (T-ΔTad).

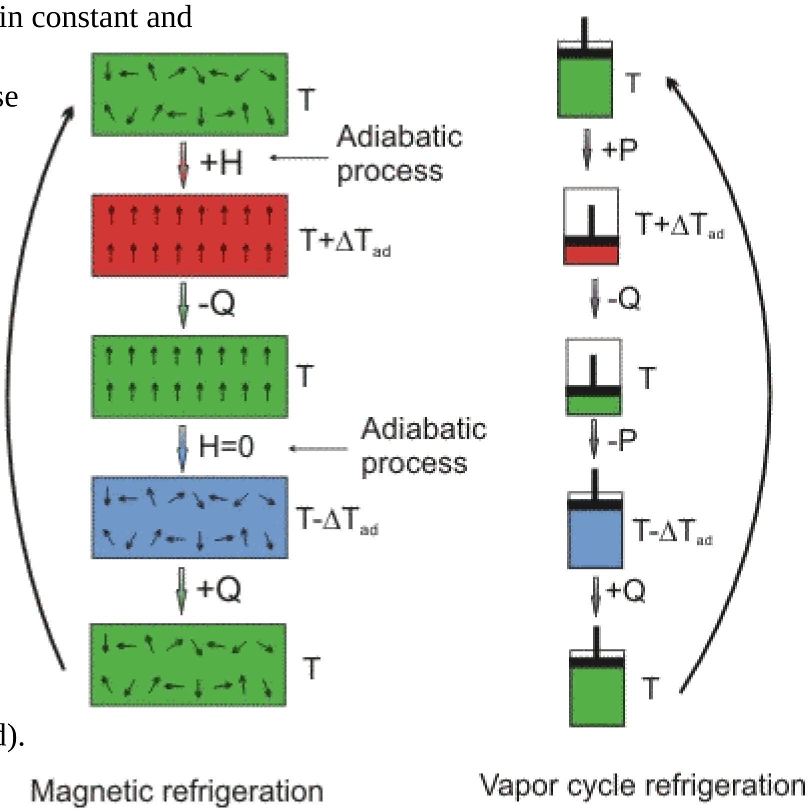

Fig 2: Magnetic Refrigeration Cycle on the left side compared with conventional Vapor cycle refrigeration on the right

4) Isomagnetic heat transfer: The magnetic field is held constant (H=0) to prevent the material from reheating. The material is placed in thermal contact with the environment to be refrigerated. Since the working material is cooler than the refrigerated environment by (ΔTad), heat energy migrates into the working material (+Q).

Once the working material and refrigerated environment are in thermal equilibrium, the cycle is repeated. With every cycle, +Q amount of heat energy is removed from our desired environment, thereby decreasing temperature, and causing refrigeration.

Thermodynamic Relations

Writing entropy S(T,H) as a function of 2 independent variables T and H

$$dS = (\frac{dS}{dT})_H \, dT + (\frac{dS}{dH})_T \, dH$$

Along an isentropic curve, we have: ..1

$$0 = (\frac{dS}{dT})_H \, dT + (\frac{dS}{dH})_T \, dH$$

..2

We know by definition:

$$\left(\frac{dS}{dT}\right)_H = \frac{C_H(T,H)}{T}$$

Substituting in equation 2, we get

$$dT = -\frac{T}{C_H(T,H)} (\frac{dS}{dH})_T \, dH$$

The above equation can be integrated to get

$$\Delta T_{ad} = -\int_{H_i}^{H_f} \frac{T}{C_H(T,H)} (\frac{dS}{dH})_T \, dH$$

..3

From the above steps, we see that knowledge of specific heat at constant H allows us to calculate ΔS and ΔT_{ad}

From Maxwell relations between S and M, we have

$$\mu_0 (\frac{dM}{dT})_H = (\frac{dS}{dH})_T$$

Since magnetization measurements are easier to perform than direct measurements of entropy change, this relation helps us to evaluate equation 3 easily.

Materials

Magnetocaloric effect (MCE) is an intrinsic property of a magnetic solid. Materials with a Curie temperature near room temperature are attractive for their possible applications in refrigerators and heat pumps.

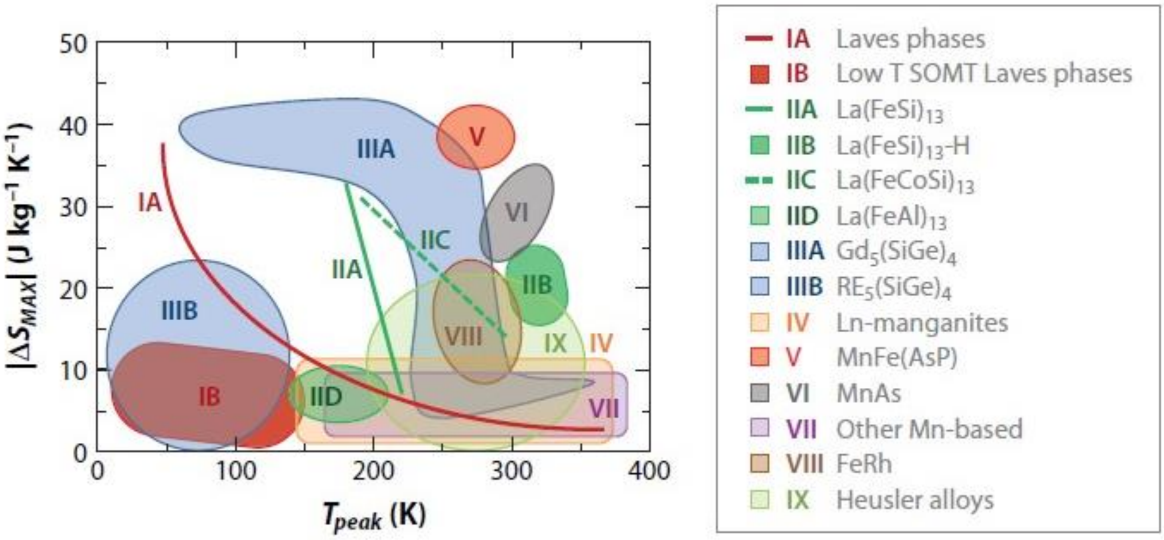

Fig 3: Maximum magnetic entropy change for $\Delta H = 5T$ versus peak temperature for different families of magnetocaloric materials (experimental data)

Gadolinium (Gd):

It is the only pure element with a Curie temperature near room temperature. In many ways it can be considered as the best performing material available for room temperature refrigeration: the adiabatic temperature change is large, the specific heat is fairly low (around 300 J/kgK at room temperature) and the thermal conductivity is high.

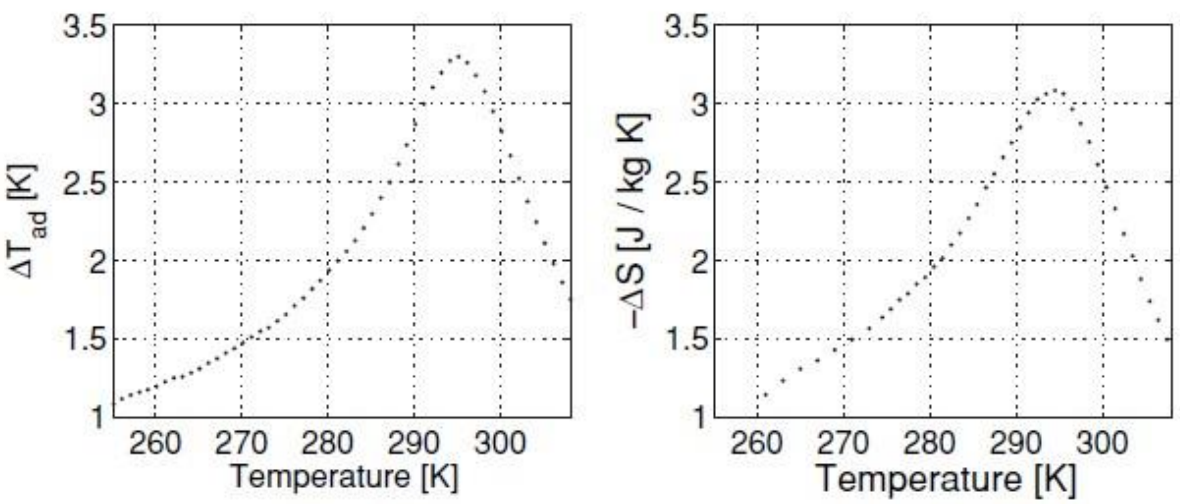

Fig 4: MCE in commercial grade Gadolinium in a field of 1 T (experimental)

The main drawback of Gd-based devices is the cost, both materials cost and shaping cost. 1kg of Gadolinium costs approximately 4000 US dollars.

$Gd_5(Si_{4-x}Ge_x)$ family:

$Gd_5Si_2Ge_2$ was the first 'giant' magnetocaloric material to be discovered (2 times higher MCE than pure Gd). Increasing x from 0 to 2 changes the Curie temperature from 336K to 300K.

Perovskite Manganites ($R_{1-x}A_xMnO_3$):

The perovskite manganites show many magnetic properties, including colossal magnetoresistance and multiferroic phases. They have also been widely investigated for their magnetocaloric properties. For these materials the maximum adiabatic temperature change is about 1-1.5 K at an applied field of 1 T, while ΔS is 2-3 J/kgK. (values lower compared to Gd)

However, lower price, corrosion resistance, easy tunability of the Curie temperature, and good processability still make them relevant for device application.

Alternative Materials without rare earths:

Ni–Mn–Ga alloys, Mn–As–Sb alloys, La–Fe–Co–S alloys, Mn–Fe–P–As alloys, La–Ca–Sr–Mn–O manganites and exhibiting large MCEs in the room-temperature range are of practical importance.

Criteria for selecting materials as Magnetic Refrigerants

- Large magnetic entropy change and large adiabatic temperature change (i.e., the large MCE).
- Large density of magnetic entropy (it is an important factor contributing to the working efficiency of materials); ferromagnets with large values of effective magnetron number P = {J(J+1)} ^1/2 are selected.
- Small lattice entropy (high Debye temperature).
- Nearly zero magnetic hysteresis (it is related to the working efficiency of a magnetic refrigerant material). (M v/s H)
- Very small thermal hysteresis (this is related to the reversibility of the MCE of a magnetic refrigerant material). (M v/s T)
- Small specific heat and large thermal conductivity (these ensure remarkable temperature change and rapid heat exchange).

Types of MCE materials:

Regular: The material heats up upon magnetization and cools down upon demagnetization. The corresponding isothermal entropy change is negative upon magnetization.

Inverse: The material cools down upon magnetization and heats upon demagnetization. The corresponding isothermal entropy change is positive upon magnetization. Examples include antiferromagnets and ferrimagnets.

<u>Classification based on order of the transition:</u>

Observations from figure 1:

For second order materials:

The specific heat curve is sharply peaked as a function of temperature at low fields. As the field increases, the peak lowers, broadens and shifts to higher temperatures. This implies that the phase transition happens more gradually over a wider range of temperatures, while experiencing higher H.The corresponding curves for the entropy change and adiabatic temperature change increase in height and width, while the peak positions also change weakly.

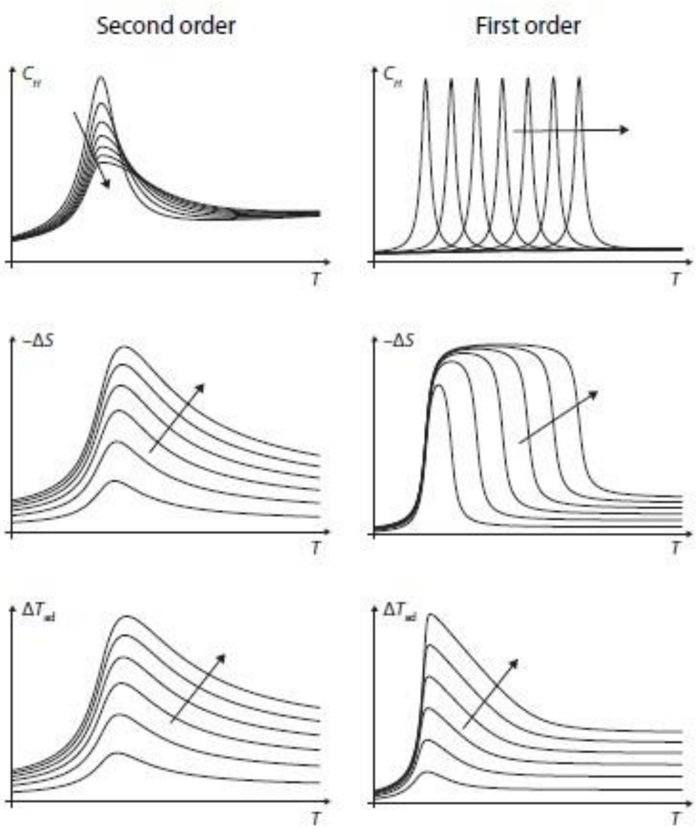

Fig 5: The arrow indicates direction of increasing H. Generic curves for second order and first-order materials

For first order materials: The peak in the specific heat moves significantly with field while the width of the peak hardly increases. This is intuitively understood in terms of a first-order transition between a low temperature ferromagnetic state and a high temperature paramagnetic state: the effect of increased field will be to stabilize the low temperature state (i.e. shifting the transition temperature up) but the phase transition will still be first order (i.e., still sharp)

The peak height of $-\Delta S$ is not sensitive to the size of the external field (for large fields) while the width of the peak scales nearly linearly with magnetic field.

Other types of MCE materials include: Transitions from a ferromagnetic state to a non-magnetic state: with a different structure (martensitic type) where there is a diffusionless transition between the two structures; examples are found among Heusler alloys. Such alloys may also exhibit the inverse magnetocaloric effect if they have a martensitic transformation from a low-temperature paramagnetic phase to a high-temperature ferromagnetic phase.

Characterization methods

A Vibrating Sample Magnetometer is used to measure bulk magnetization. Specific spatial variation of magnetization is determined using a Hall probe. This allows better resolution for studying magnetic phase transitions.

The adiabatic temperature change measurement requires custom-built equipment. The idea is to apply time varying magnetic field and record temperature of the sample. The sample needs to be kept in adiabatic conditions.

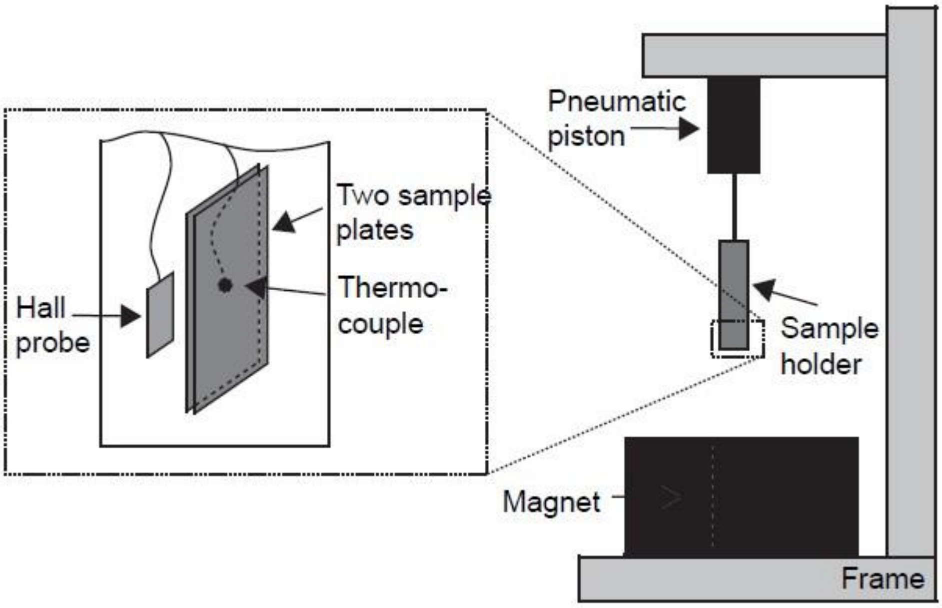

Fig 6: Custom Built set-up for measuring magnetocaloric properties

The sample is made by sandwiching a thermocouple between two identical plates of the magnetocaloric material, to ensure good thermal contact. The sample is wrapped in insulating foam to reduce heat losses and placed in a sample holder such that the orientation of the sample is fixed and known relative to the sample holder. A Hall probe, which measures the flux density of the magnetic field orthogonal to the surface of the probe, is also placed inside the sample holder. The sample holder is then mounted on a pneumatic piston rod, which is used to move the sample in and out of a static magnetic field. This allows the applied field in the central bore to be adjusted between 0 and 1.5 T. The piston is automatically moved in and out of the magnetic field, while the temperature of the thermocouple is recorded. The time to move the piston in or out of the field is less than 100ms. To measure the entire ΔT curve as a function of temperature, the sample temperature is varied by controlling the temperature of the sample environment. As the sample is not completely adiabatic it will slowly follow the temperature of the environment. If this temperature change is very slow compared to the movement time of the pneumatic piston, this approach can be used to determine the adiabatic temperature change.

Device Performance and Challenges

The three magnetocaloric quantities, ΔS, ΔT_{ad} and C_H are important for the performance of a given material. There have been a few attempts to quantify a material's potential as a refrigerative material with a single number.

Wood and Potter introduced the concept of 'refrigerant capacity' RC , which they suggest should be maximized in a magnetic refrigeration cycle:

$$RC = \Delta S_{cold}(T_{hot} - T_{cold})$$

It is defined for a refrigeration cycle between a cold side and a hot side; ΔS_{cold} is the entropy absorbed at the cold side per cycle which is then identified with the magnitude of the material's isothermal entropy change at the temperature T_{cold}. Maximizing the refrigerant capacity is equivalent to finding the largest area rectangle which fits a ΔS vs. T curve.

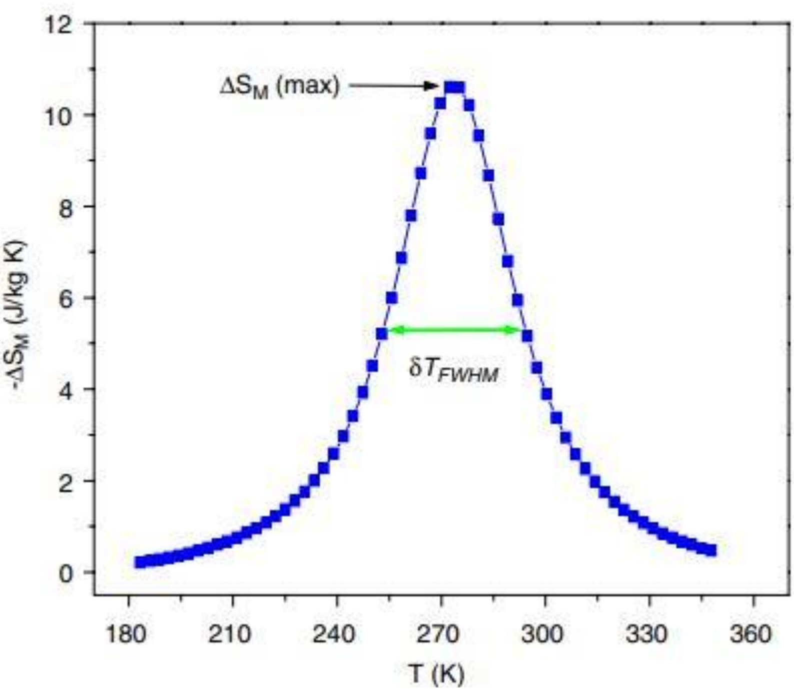

Fig 7: Maximizing the area under the del S v/s T curve

Assumptions/Limitations of this concept:

In practical applications, the hot and cold temperatures are determined by specific device requirements. Hence a high RC does not imply suitability of a material for a particular application.

It is assumed that the entire magnetocaloric material is at the same temperature throughout (and any regeneration is done by the heat transfer fluid).

RC is usually quoted in gravimetric units (J/kg). However, Pecharsky and Gschneidner argue that from an applications point of view it is much more relevant to use volumetric (J/m3) units. Materials with low volumetric refrigeration capacity will require a higher volume of the magnet gap to achieve the same potential magnetic work per cycle, compared to materials with a higher volumetric refrigeration capacity (even though gravimetrically the latter may be worse). However, the amount of magnet material required to produce a given maximum field in a certain volume increases exponentially with the volume. Since the most significant component cost-wise of a refrigeration device is the permanent magnet, this will have a direct impact on the practical applicability of a given material.

Other Factors

In a magnetic refrigerator, the magnetocaloric material shaped in a particular geometry is subjected to periodically varying magnetic fields while being in contact with a flowing heat transfer fluid. Hence additional factors which determine the device performance are the shape of the regenerator, thermal conductivity of the magnetocaloric materials and thermal, viscous properties of the heat transfer fluid. Since heat transfer is necessary, entropic losses are unavoidable.

The objective is to maximize the heat transfer between solid matrix and fluid, while keeping the pressure drop and demagnetization as small as possible. The available geometries for a given choice of magnetocaloric material are to some extent constrained by processing issues. For example, the cost of Gd increases tenfold for processing into thin plates. On the other hand, manganites and other ceramic materials may be processed into a variety of different geometries using cheap standard ceramic forming processes such as tape-casting or extrusion.

Also, while using first-order materials, there may be a significant volume change associated with the phase transition which may induce cracks and other mechanical defects.

Current Research

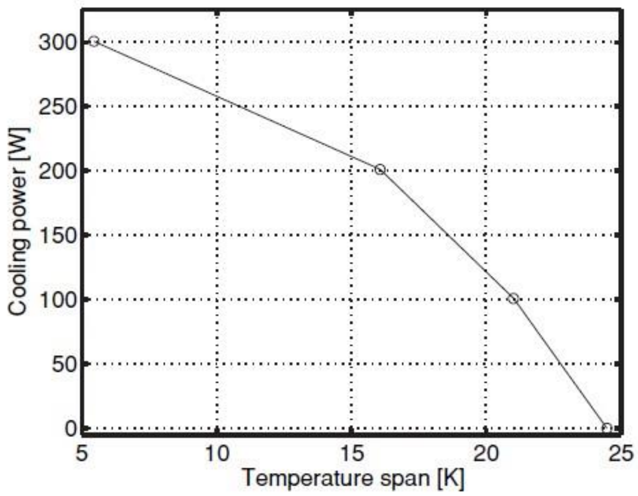

Fig 8: A lab device constructed in TU Denmark achieved a 100W cooling load a temperature span of 20.5K using Gd-spheres. The device can be operated at cycle frequencies up to 10 Hz

Nuclear Demagnetization Refrigeration (NDR)

The principle is similar to adiabatic demagnetization, the only difference being cooling arises due to magnetic dipoles of the nuclei of the refrigerant atoms, rather than their electron configurations. Since these dipoles are of much smaller magnitude, they are less prone to self-alignment and have lower intrinsic minimum fields. This allows NDR to cool the nuclear spin system to very low temperatures (1 μK or below). But, the small magnitudes of nuclear magnetic dipoles also make them less inclined to align to external fields. Magnetic fields of 3 T or greater are needed for the initial magnetization step of NDR.

In NDR systems, the initial heat sink must sit at very low temperatures (10–100 mK). This precooling is provided by adiabatic demagnetization.

Improving Thermal Conductivity and Performance

An interesting idea is to tailor the thermal conductivity by impregnating small amounts of silver into porous manganites and in this way increase the thermal conductivity of the magnetocaloric material. This will degrade the magnetocaloric performance compared to a fully dense sample, as one is replacing magnetocaloric material with non-magnetocaloric material. But device performance overall improves.

Several devices have been tested with Gd in combination with its alloys, in a graded (layered) regenerator configuration, showing that they can outperform single material regenerators. Arnold et al. found that the largest temperature span is obtained when each material during operation has an average temperature close to its Curie temperature.

Outlook

- The general aim is to find cost-effective magnetic materials with a large MCE (over a wide range of temperatures) suitable for magnetic refrigerators.
- The significance of the two fundamental magnetocaloric quantities is : ΔS is a measure of how much heat can be moved (at a given temperature) by magnetic means, while ΔT_{ad} is a measure of how high a temperature difference is available to achieve the transfer of the heat to and from the heat transfer fluid. It is not possible to evaluate the performance of a magnetocaloric material based on only one of these quantities. If for instance a material has a high ΔS but a low ΔT_{ad} the heat transfer from matrix to fluid will be slow, limiting the operation frequency and giving rise to significant internal losses.
- The present stage of device development experience shows that the performance of a given device depends very much on the entire design and not only on the material performance. This makes it difficult to compare the detailed performance of different materials if they are not tested in the same device and with comparable geometry.
- Paramagnets exhibit the magnetocaloric effect but since the associated relative entropy change is small, it becomes relevant only at very low temperatures (<1K)
- The inter-relation between microstructure, shaping and performance must be explored in more detail for existing material candidates.

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