6

Applications of Rare Earth Magnanites

Research devoted to rare earth manganites (3d-4f oxides) leads to a wide range of applications for example magnetic refrigeration (Environmentally friend technology) and spintronics. Magnetic refrigeration is a revolutionary, efficient, environmentally friend technology, which is on the threshold of commercialization.

6.1 Magnetic Refrigeration

One of Man daily need is environmentally friendly technology, which helps us to decrease pollutions in our world and keep our environment clean and safe. As well known using Freon refrigerators is one of the main sources which increases the Ozone hall and thus the harmful changes in climate. The progress in materials science allowed the appearance of new materials which can be used, in cooling system. Magnetic refrigeration is a cooling technology based on the magneto-caloric properties of these advanced materials to attain extremely low temperatures in ranges used in conventional refrigerators, depending on the design of the system [108]. These new materials are clean and environmentally friendly technology in order to reduce the harmful changing in the climate. From technological point of view, magnetic refrigeration is a revolutionary, efficient, environmentally friend technology, which is on the threshold of commercialization. Magnetic refrigeration was the first method developed to attain the temperature below about 0.3K (a temperature attainable by ^{3}He refrigeration that is pumping on the ^{3}He vapors) [108].

When a magnetic material is subjected to a sufficiently high magnetic field, the reorientation of magnetic moments is taken place as a result to this applied magnetic field. If the magnetic field is applied adiabatically, the raise of temperature of the material is obtained, and if the magnetic field is subsequently removed, the decrease in the temperature is observed. This warming and cooling which related to the application and removal of an external magnetic

field is so called the magneto-caloric effect 'MCE'. The basic idea of magnetic refrigeration is shown in fig. 6.1. When we apply a magnetic field on magneto-caloric material, for example Gadolinium alloy [108-110], thermodynamically process is occurred and resulting in the drastic decrease in temperature as we will see in details. The magneto-caloric effect can be mathematically represented in the following equation form, where ΔT is the change in temperature, ΔH is the change in applied magnetic field, C is the heat capacity of the working magnet (refrigerant), and M is the magnetization of the refrigerant: [1]

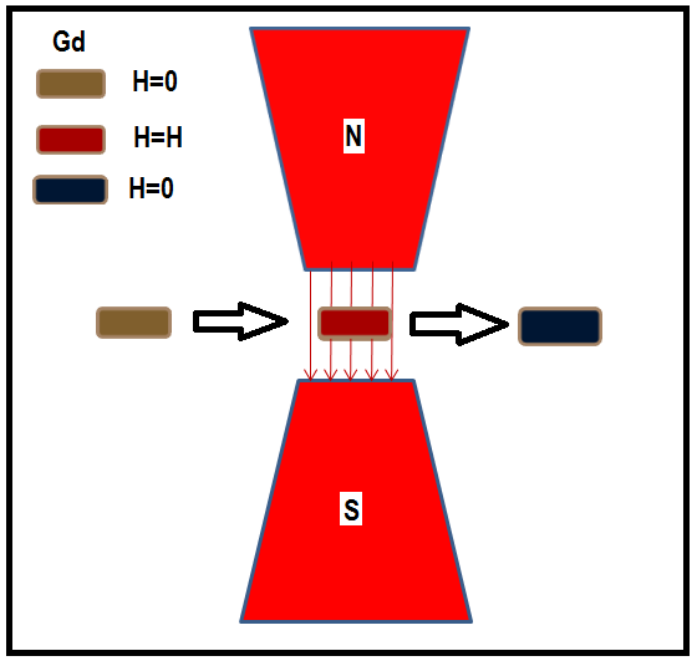


Fig. 6.1 *Gadolinium alloy inside the magnetic field and low temperature output.*

$$\Delta T_{ad} = -\int_0^{H_1} \left(\frac{T}{C(T,H)}\right)_H \left(\frac{\delta M(T,H)}{\delta T}\right) dH \qquad (1)$$

The change in magnetic entropy (ΔS_M) can be defined as the adiabatic change of temperature as a result of the application of the magnetic field. The isothermal entropy change is described by the following relation [4]:

$$\Delta S_M (T,H) = S_M(T,H) - S_M(T, 0) = \int_0^{H_{max}} (\frac{\delta M}{\delta T})_H \, dH \qquad (2)$$

where H_{max} is the maximum external field. ΔS_M can be approximated from magnetization measurements made at discrete field and temperature intervals according to the following relation [5]:

$$\Delta S_M = \sum_i \frac{M_i - M_{i+1}}{T_i - T_{i+1}} \Delta H_i \qquad (3)$$

where M_i and M_{i+1} are the magnetization values measured in a field H, at temperature T_i and T_{i+1}, respectively.

From the above equations one can say that magneto-caloric effect can be enhanced by [108]: applying a large magnetic field, a magnet with a small heat capacity and a magnet with a large change in magnetization vs. temperature, at a constant magnetic field.

THERMODYNAMIC CYCLE

The thermodynamic cycle is performed as a refrigeration cycle that is in analogous to the Carnot refrigeration cycle, where the magnetic refrigerator cycle depends on the increases and the decreases in magnetic field strength in instead of the increases and the decreases in pressure in which the Carnot refrigerator cycle depends [108]. Comparison between magnetic refrigeration and conventional refrigeration cycle is very important to evaluate the magnetic refrigeration and understand how magnetic refrigerator work. As is shown in schematic diagram in Fig. 6.2, there is an analogy between magnetic and conventional refrigeration cycle. [108]

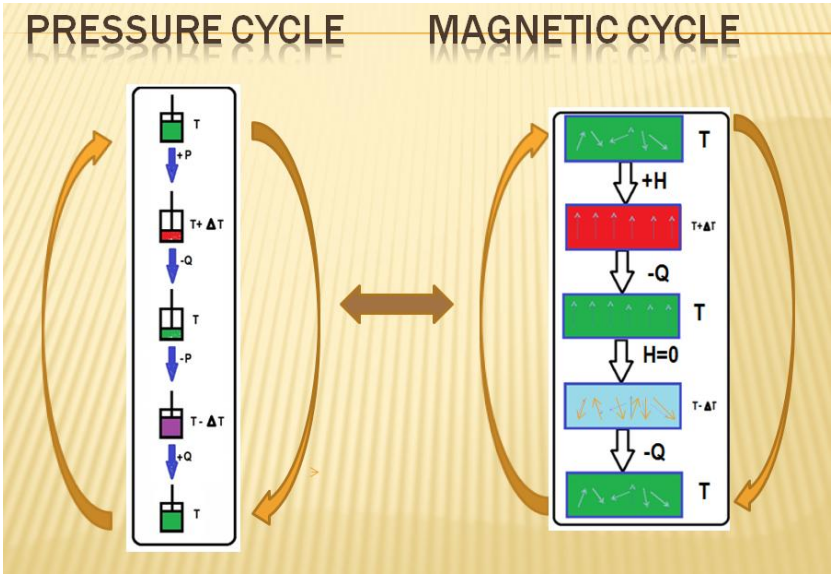


Fig. 6.2 *Conventional vapor refrigeration cycler and magnetic refrigeration cycle.*

In adiabatic magnetization, a magneto-caloric material is placed in an insulated environment, then, as a result of increasing an external magnetic field (+H) the magnetic moments are aligned in the direction which leads to increasing in the material temperature and decreasing in the magnetic entropy and heat capacity of substance. The total entropy does not change because there is no loss in energy and so heating up is observed ($T + \Delta T_{ad}$). [109-115]

For the conventional vapor refrigerator CVR cycle the gas is compressed by applying pressure P and similarly there is no loss in energy and so heating up is observed ($T + \Delta T_{ad}$). In isomagnetic enthalpic transfer: The added heat can then be removed (-Q) by a fluid or gas. To prevent the dipoles from reabsorbing the heat the magnetic field is kept constant and once sufficiently cooled, the magneto-caloric substance and the coolant are separated (H=0). In adiabatic demagnetization: In this stage the total entropy remains constant as a result to return to another adiabatic (insulated) condition. However, this time the decrease in magnetic field is obtained, the thermal energy leads to the magnetic

moments to overcome the field, and thus the sample cools, i.e., an adiabatic temperature change. Energy transfers from thermal entropy to magnetic entropy (as shown in Fig. 6.2, disorder of the magnetic dipoles is appeared). In isomagnetic entropic transfer: The magnetic field is kept constant to prevent the heating up again. Because of the difference in temperature according to our design, heat energy migrates into the working material (+Q). [116-120]

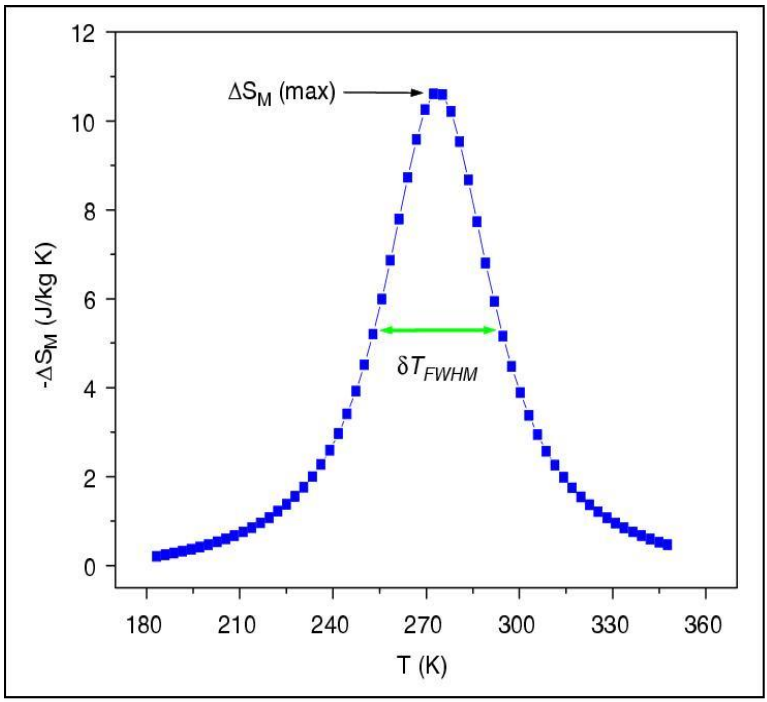


Fig. 6.3 *Magnetic entropy dependence on temperature [6].*

How to evaluate the relative cooling power RCP is an indication to the magnetic cooling efficiency [112] of the magneto-caloric material and it can be simply considered as the magnitude of ΔS_M or ΔT_{ad} multiplied by the full-width at half maximum (δT_{FWHM}) [110, 113]. ΔS_M, ΔT_{ad} and δT_{FWHM} are shown in Fig. 6.3 where the change in entropy is plotted as a function of temperature. The change in entropy could be deduced using equation 3 from

magnetization – temperature dependent measurements. On the time being the conventional vapor compression refrigerators are used for cooling applications; such as refrigerators and air conditioners AC. However, the low efficiency of the compressing and expanding processes of a gas in these refrigerators costs for 25% of residential and 15% of commercial power consumption [6]. In the conventional vapor compression refrigerators, the usage of gases such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) is dangerous because they damage our environment. Searching an alternative to the conventional gas compression (CGC) technique is very important issue to keep our environment safe and clean so that the development of new magnetic refrigeration (MR) technology, based upon the magneto-caloric effect (MCE) [114], has attracted the scientific interest. Now, the question is why MR is promising task for cooling technology. The answer is given in the Phan section in ref. [112] as following;

First, the cooling efficiency in MR is higher than CVR where the magnetic cooling efficiency can be reached up to 30-60% while the cooling efficiency in CVM according to a Carnot cycle is only 5-10%. Second, MR can be more compactly built by using solid substances as working materials and thus does not occupy big place. Third, the MR does not use any global-warming gases and therefore is an environmentally friendly cooling technology. Our main goals in the present proposal are introducing advanced and cheap materials with enhanced properties for cooling systems and developing a new generation of refrigerators and cooling systems environmentally friend to keep our environmental clean and safe.

The data of several typical magnetic materials that could be used in magnetic refrigeration are listed in table below in table 6.1 [121-127].

Table 6.1 *Typical magnetic parameters used for magnetic refrigeration.*

Sample	T_c (K)	$-\Delta S_{max}$ (J/KgK)	ΔH (T)	Reference of data
$La_{0.8}Ca_{0.2}MnO_3$	230	5.5	1.5	Ref [121]
$La_{0.67}Ca_{0.33}MnO_3$	267	6.4	3	Ref [122]
$La_{0.6}Ca_{0.4}MnO_3$	263	5.0	3	Ref [123]
$La_{0.65}Ca_{0.35}Mn_{0.9}Ti_{0.1}O_3$	103	1.3	3	Ref [123]
$La_{0.67}Sr_{0.33}Mn_{0.9}Cr_{0.1}O_3$	328	5.0	5	Ref [124]
$La_{0.87}Sr_{0.13}MnO_3$	197	7.5	8	Ref [125]
$La_{0.84}Sr_{0.16}MnO_3$	244	7.9	8	Ref [125]
Gd	294	4.2	1.5	Ref [121]
$Gd_{0.73}Dy_{0.27}$	265	10	5	Ref [126]
$Gd_5(Si_2Ge_2)$	276	14	2	Ref [127]
$Gd_5(Si_2Ge_2)$	300	7	5	Ref [127]

So the scientific efforts are devoted to get large (reasonable) magnetic entropy at or near room temperature. Different chemical formula is suggested. Large magnetic entropy change (ΔS_M~2.26J/Kg.K) at T_c=354K is observed by Mahn-Huong Phan et al [126] in $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$ in magnetic field range from 0-10KOe. A large magnetocaloric effect in perovskites $(La_{1-x}Nd_x)_{0.7}Sr_{0.3}MnO_3$ at room temperature is reported by N. H. Luong et al. [127]. Magnetocaloric effect in Nd doped perovskite $La_{0.7-x}Nd_xBa_{0.3}MnO_3$ polycrystalline near room temperature was studied by Chen et al, [128]. The large ΔS_M was found in ref. [129] to occur around 300K for investigated manganese perovskites. The manganese perovskites in this work [129] have the large magnetic entropy changes induced by low magnetic field change, which is beneficial for the household application of active magnetic refrigerant (AMR) materials.

The mixed valance manganite perovskites are applied in ref [130] as magnetocaloric materials in a magnetic refrigeration device. The giant magnetocaloric effect with isothermal field-induced entropy change beyond the spin-multiplicity limit gave rise to some indistinctness regarding the

applicability of fundamental thermodynamics in data analysis is one of the important subject we found great number of research in the literature devoted to this subject. Those misleading interpretations concerning, for instance, the rigorousness of phenomenological thermodynamics are reported by Mukherjee et al., [131]. They showed that the Maxwell relation incorporates contributions from the spin degrees of freedom and potential lattice degrees of freedom into the isothermal entropy change. A minimalist model involving pairs of exchange-coupled, mobile Ising spins is investigated. It is explicitly shown that lattice degrees of freedom can be activated via applied magnetic fields and the integrated Maxwell relation contains this lattice contribution. A simple and intuitive analytic expression for the isothermal entropy change in the presence of field-activated lattice degrees of freedom is provided.

The electrocaloric effects accompanied with the ferroelectric to paraelectric phase transitions are investigated in ref [132] within the Landau–Devonshire theory. In this work they found that just changing the nature of the phase transition from the first-order to the second-order reduces the isothermal entropy change, adiabatic temperature change and refrigerant capacity. The isothermal entropy change in the second-order transition is reduced to one half of that in the first-order one, which is confirmed by experiments and is also consistent with the magnetocaloric counterpart.

Understanding the heat transfer phenomena taking place in the regenerator and the impact of the intrinsic properties of the magneto-caloric material will help us to optimize the performance of an active magnetic regenerative system [133]. Legait et al compared and tested three different materials ($Pr_{0.65}Sr_{0.35}MnO_3$, $La(FeCo)_{13-x}Si_x$, and gadolinium) using a permanent magnet based device. They concluded that even with a low δT_{ad}, the oxide $Pr_{0.65}Sr_{0.35}MnO_3$ can provide interesting results and they noted that the layered regenerator presents a better efficiency than the single layer. Moreover, a high

thermal conductivity material allows a great temperature span at high frequency to be obtained. The shape of sample they used in this work and isothermal entropy change in a 1 T field of LaFeCoSi are shown in Fig. 6.4 and Fig. 6.5.

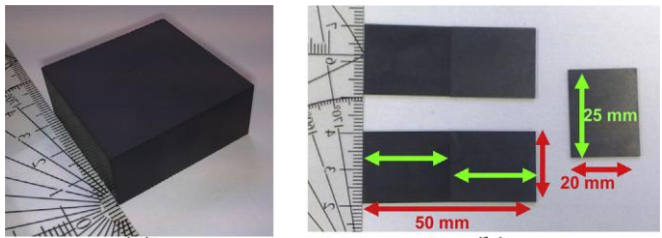


Fig. 6.4 *(a) A block of $Pr_{0.65}Sr_{0.35}MnO_3$ (b) Oxide plates with their dimensions after cutting [72].*

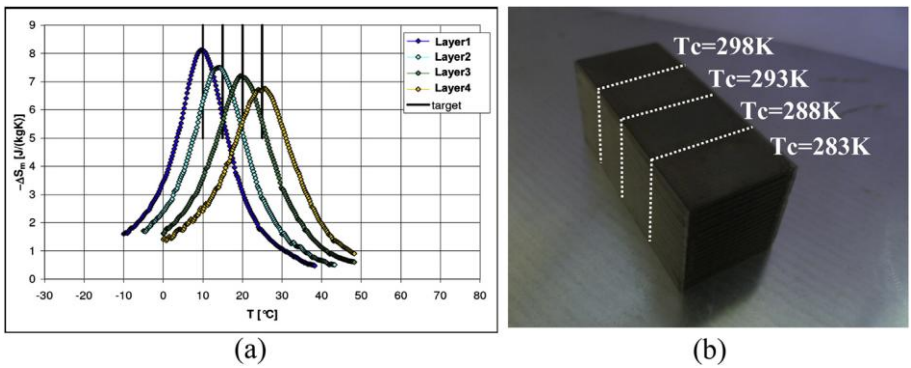


Fig. 6.5 *(a) Isothermal entropy change in a 1 T field variation of the four compounds of LaFeCoSi,. (b) LaFeCoSi regenerator with four different compounds [72].*

Looking at the recent research one can found that there is ongoing work on developing new materials that are both cost effective and operate in the temperature range of normal refrigeration. A giant magnetocaloric effect induced by sodium-deficiency in a Lanthanum manganites polycrystalline is recently reported by Wali et al., [134] where they found that the ability to tune the temperature transition close to room temperature is revealed to be possible by changing the sodium-deficiency content. The most important results in this work

are that a second-order magnetic phase transition from the ferromagnetic to the paramagnetic state at the Curie temperature (T_c) was found to be decreased from 335 to 260 K when the sodium deficiency rate increased. The change in the magnetic entropy increased from 2.38 J kg^{-1} K^{-1} to 3.48 J kg^{-1} K^{-1} under a magnetic field of 2 T when x increased from 0.00 to 0.15. Comparing the values obtained by Wali et al [135] and the values reported before underlines that the proposed oxide material has substantial advantages for magnetic refrigeration. Magnetic, specific heat and magnetocaloric studies have been carried out by Kalipada Das, Tapas Paramanik and I. Das [136] on rare earth calcium manganites; $Ln_{0.5}Ca_{0.5}MnO_3$ (Ln=Gd, Dy). They observed that the isothermal magnetic entropy change is fairly large at low temperature which is attributed to the magnetic precursor effect of rare-earth ions. The impact of the disorder on the magnetocaloric effect in Ti doped manganites was investigated by El. Kossi et al [136] where they found that the magnetic entropy change strongly depends on the Ti concentration. The most promising results are observed by I. A. Abdel-Latif et al., [137] where the $Nd_{0.6}Sr_{0.4}MnO_3$ nanocomposites showed MR of 99.84% at room temperature that makes it is possible to use these materials in fabrication of magnetic devices in the industrial scale.

Theoretical calculations will help us to design new materials with desired properties. Spin-dimer systems are a versatile playground for quantum phase transitions studies by using the magnetic field as the tuning parameter. According to the study of Straßel [138] it is possible to observe a crossover from the characteristic scaling near critical points to the behavior of a finite-temperature phase transition. In this work they studied two-dimensional coupled spin-dimer systems. Moreover, they found that the magnetocaloric behavior of the magnetization with temperature can be used to determine the critical fields with high accuracy. Gharsallah et al studied the magneto caloric effect for

$La_{0.6}Sr_{0.4}MnO_3$ and $La_{0.6}Ca_{0.4}MnO_3$ using theoretical calculations [139-140] which showed large and tunable suggesting their possible applications in moderate magnetic field and near room temperature.

It is quit clear that still great interest and effort that are devoted to studying the magnetocaloric effect in order to develop clean, cheap and environmentally friend refrigerator technology. The main challenge in the current magnetic cooling is that efficiency of cooling needs high magnetic field which is out of use in the industrial scale and very low temperature. So this work is a try to develop magnetic refrigerator materials with reasonable conditions for environmentally friend refrigeration based on the success of our recent work [137] and [134-135].

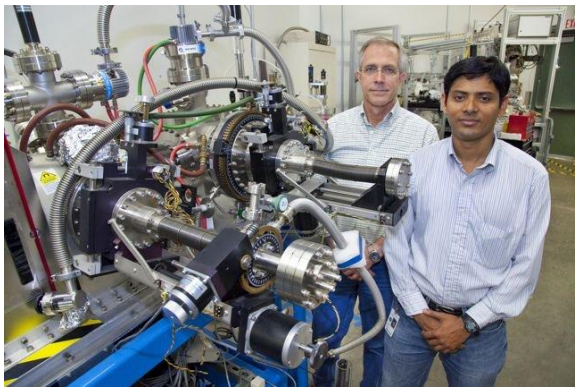


Fig. 6.6 *The Berkeley Lab prototype of magnetic refrigerator.*

(http://www.gizmag.com/giant-magnetocaloric-effect-in-fridges/15624/) [141]

The *Berkeley Lab research* was recently published in the journal *Physical Review* (http://www.gizmag.com/giant-magnetocaloric-effect-in-fridges/15624/) [142]

The magnetic rare earth materials are utilized as the magnetic refrigerants in most cooling devices. Recently, some data on the magnetocaloric effect in hole-doped manganites are reviewed. It is shown that the variation of interaction exchange energy, taking place under the effect of a magnetic field in the vicinity

of the phase transformation, provides a significant contribution to the change of magnetic entropy. Essebti Dhahri et al., reported [143] that different results found for electron-doped manganites $La_{1-x}Ce_xMnO_3$ (x = 0.3, 0.4 and 0.5). These manganites present a large magnetic entropy change induced by low magnetic change, which is beneficial for the household application of active magnetic refrigerant materials. It is believed that the manganite materials with the superior magnetocaloric properties in addition to cheap materials-processing cost will be the option of future magnetic refrigeration technology. So this very important application for perovskite will be one of the future works. Our plan is to synthesize different compounds with different nano-crystalline sizes and study magnetocaloric properties of the proposed compounds.

6.2 Magnetoresistive Random Access Memory (MRAM)

MRAM is a random access memory (RAM) technology (based on Spintronics) that uses electron spin to store information. MRAM has been called "the ideal memory", potentially combining the density of DRAM with the speed of SRAM and non-volatility of FLASH memory or hard disk, and all this while consuming a very low amount of power [144-146]. MRAM can resist high radiation, and can operate in extreme temperature conditions, very suited for military and space applications.

Transistors and other components with nanoscale dimensions, processors and memories are becoming so dense that even their infinitesimal individual currents are combining to produce scorching heat. Furthermore, quantum effects that were negligible before are now so pronounced that they're threatening to render circuits inoperable. The upshot is that we're fast approaching the point when moving charge is not going to be enough to keep Moore's Law chugging along.

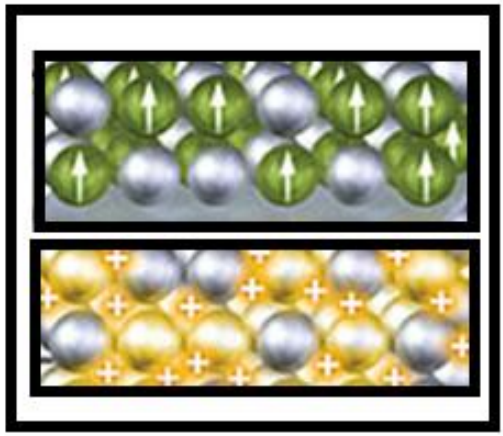


Fig. 6.7 *How a spin memory works (http://spectrum.ieee.org/image/MTcxODEyNg).*

In anticipation of that day, researchers all over the world are already working on a promising alternative. We have set our sights on a different property of electrons, which we hope to exploit for storing and processing data. This property is spin.

Spin is a fundamental yet elusive quantum attribute of electrons and other subatomic particles. It is often considered as a bizarre form of nano world angular momentum, and it underlies permanent magnetism. What makes spin interesting for electronics is that it can assume two states relative to a magnetic field, typically referred to as spin up or spin down. In other words you can use these two states to represent the two values of binary logic—to store a bit.

The development of spin-based electronics, or spintronics, promises to open up remarkable possibilities in the field of electronics. In principle, manipulating spin is faster and requires far less energy than pushing charge around, moreover it can take place at smaller scales. Chips built out of spin transistors would be faster and more powerful than traditional ones and, farther down the road, may feature such new and remarkable properties as the ability to change their logic functions on the fly. It is still decades away from being able to build such a

thing. But chips that exploit spin in a more modest way are already available. At least one company is now selling magnetoresistive random access memory, or MRAM, a kind of spintronic memory. And many others—including Free scale, Honeywell, IBM, Infineon, Micron, and Toshiba, as well as start-ups and university research groups—are busy investigating MRAM technology. The reason for all this interest is clear. Today's computers often use four kinds of storage. Dynamic random access memory, or DRAM, has high density but needs to be constantly refreshed and in addition to consuming lots of power. Static random access memory, or SRAM is used in caches. It is fast to read and write but from another side it takes up considerable space on a chip. Flash, unlike SRAM and DRAM, is nonvolatile but is quite slow to write to. And then there are hard disk drives; these have high density but rely on moving parts, which impose size and speed limitations. MRAM is attractive because it could, in principle, replace all other kinds of memory.

Rather than representing a bit as charge in a capacitor or as the state of an interconnected set of transistors, MRAM stores data using the spin of electrons in a ferromagnetic substance by creating a magnetic alignment in one direction or the other. In a tiny region of that material, spin up ↑ means 0, and spin down ↓ means 1. Proponents say that as MRAM improves, it could combine all the advantages of SRAM, DRAM, flash, and hard disks—with none of their shortcomings. MRAM would be a compact, speedy, low-power, and nonvolatile "universal memory." Using MRAM, a computer wouldn't have to juggle data between main memory, cache, and disk; instead, it could load all data into its working memory. This capability would change the way we think about computer architecture because it makes possible instant-on.

The challenge at the moment is that MRAM suffers from two problems: The density of bits is low, and the cost of chips is high. The early MRAM designs needed lots of current to change a 1 to a 0 or vice versa. This requirement

prevented their further miniaturization. Improved designs might overcome that hurdle using novel techniques and materials, but they would operate at only liquid-nitrogen temperatures. This is not going to work for your PC. This problem—the need for cryogenic temperatures to reduce the write current of MRAM—has been under the focus of the research. It's a major challenge, but there is hope to significant breakthrough. Recently, a device that shows potential as an MRAM memory cell was demonstrated. We can write using conventional voltage levels and almost no current at all. The key is a material called gallium manganese nitride, a semiconductor whose magnetic properties we can manipulate electrically. And here's the best part: It works at room temperature. Typical “classic” or “conventional” MRAM uses spin-dependent tunnel junction memory cells and magnetic row and column write lines.

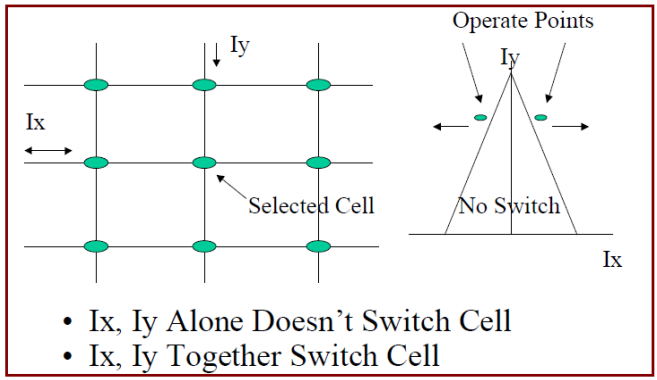
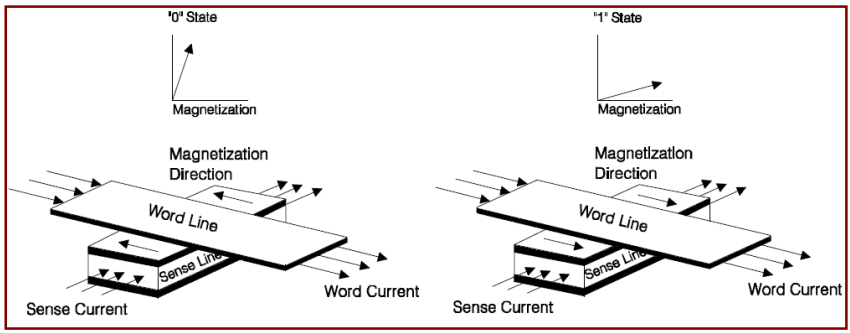


Fig. 6.8 *Magnetic Memory Cell Array.*



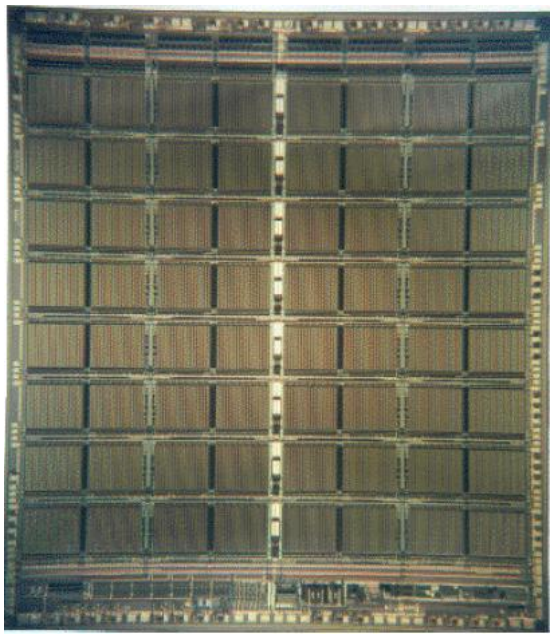


Fig. 6.9 *MRAM memory cell.*

The spin-dependent tunnel junction produces a large change in resistance depending on the predominant electron spin in a storage layer. The tunnel barrier is as thin as a few atomic layers--so thin that electrons can "tunnel" through the normally insulating material, causing a resistance change. Row and column magnetic write lines allow data to be written to a selected cell in a two-dimensional array.

Data are written by small electrical currents in the write lines that create magnetic fields, which flip electron spins in the spin-dependent tunnel junction storage layer, thus changing the junction's resistance. Data is read by the tunneling current or resistance through the tunnel junction.

Next-generation MRAM could reduce cell size and power consumption. Potential next-generation designs include Spin-Momentum Transfer, Magneto-Thermal MRAM, and Vertical Transport MRAM. Spin-Momentum

Transfer (also “Spin-Transfer,” “Spin Injection,” or “Spin Torque Transfer”) MRAM is based on changing the spin of storage electrons directly with an electrical current rather than an induced magnetic field. This method has the potential to significantly reduce MRAM write currents, especially with lithographic feature sizes less than 100 nanometers. M-T MRAM uses a combination of magnetic fields and ultra-fast heating from electrical current pulses to reduce the energy required to write data. Vertical Transport MRAM (VMRAM) is a high-density type of MRAM that employs current perpendicular to the plane to switch spintronic memory elements.

6.3 Magnetic Sensor

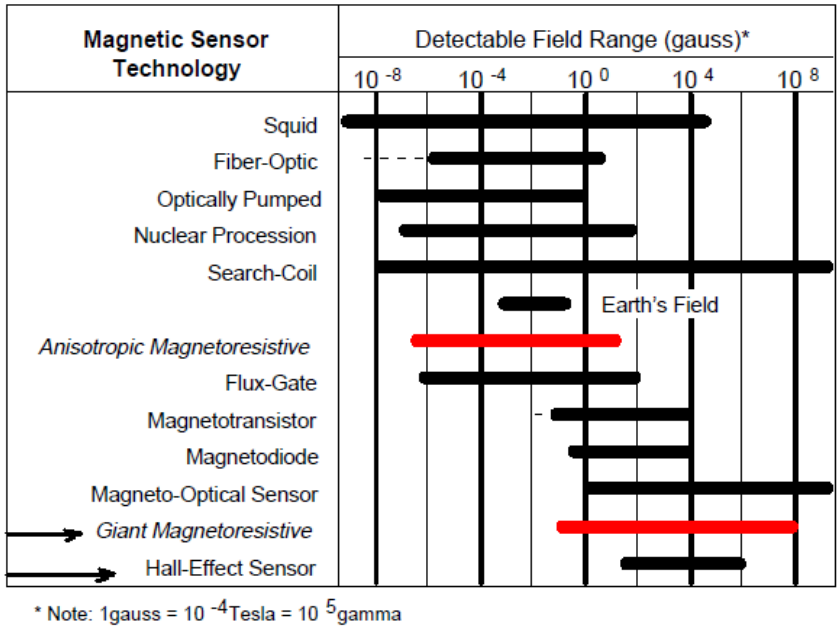
The earliest magnetic field detectors allowed navigation over trackless oceans by sensing the Earth's magnetic poles. Magnetic field sensing has vastly expanded as industry has adapted a variety of magnetic sensors to detect the presence, strength, or direction of magnetic fields not only from the Earth, but also from permanent magnets, magnetized soft magnets, vehicle disturbances, brain wave activity, and fields generated from electric currents. Magnetic sensors can measure these properties without physical contact and have become the eyes of many industrial and navigation control systems. This paper will describe the current state of several methods of magnetic sensing and how the sensors are used—many with integrated functions. Finally, several applications will be presented for magnetic sensing in systems.

Magnetic sensors have been in use for well over 2,000 years. Early applications were for direction finding, or navigation. Today, magnetic sensors are still a primary means of navigation but many more uses have evolved. The technology for sensing magnetic fields has also evolved driven by the need for improved sensitivity, smaller size, and compatibility with electronic systems. This paper will overview various types of magnetic sensors and their

applications. It is not intended as a how-to description of building sensor systems but more of what is this sensor and how does it detect magnetic fields. The newest types of silicon based magnetic sensors will be emphasized—anisotropic magnetoresistive (AMR) and giant magnetoresistive (GMR) sensors. Applications for AMR and GMR magnetic sensors are presented.

A unique aspect of using magnetic sensors is that measuring magnetic fields is usually not the primary intent. Another parameter is usually desired such as wheel speed, presence of a magnetic ink, vehicle detection, or heading determination. These parameters cannot be measured directly, but can be extracted from Figure 6.8. Conventional vs. Magnetic Sensing changes, or disturbances, in magnetic fields. Scheme 6.1 shows other sensors, such as temperature, pressure, strain, or light that can be detected using an appropriate sensor. The output of these sensors will directly report the desired parameter. On the other hand, using magnetic sensors to detect direction, presence, rotation, angle, or electrical currents only indirectly detect these parameters. First, the enacting input has to create, or modify, a magnetic field. A current in a wire, a permanent magnet, or sensing the Earth's magnetic field can create this field. Once the sensor detects that field, or change to a field, the output signal requires some signal processing to translate the sensor output into the desired parameter value. This makes magnetic sensing a little more difficult to apply in most applications, but it also allows for reliable and accurate sensing of parameters that are difficult to sense otherwise. One way to classify the various magnetic sensors is by the field sensing range. These sensors can be arbitrarily divided into three categories—low field, medium field, and high field sensing. Sensors that detect magnetic fields less than 1 microgauss will be classed low field sensors. Sensors with a range of 1 microgauss to 10 gauss will be considered Earth’s field sensors and sensors that detect fields above 10 gauss will be considered bias

magnet field sensors for this paper. In scheme 6.1 the various sensor technologies are listed and illustrates the magnetic field sensing ranges [1].



Scheme 6.1 *Various sensor technology.*

http://www.sensorsmag.com/sensors/electric-magnetic/a-new-perspective-magnetic-field-sensing-855

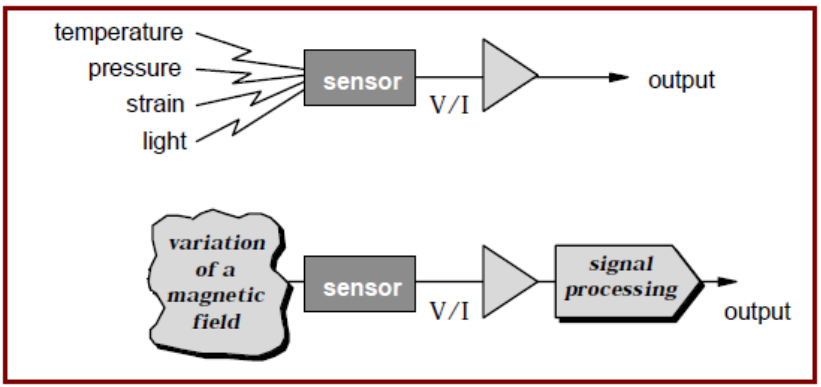


Fig. 6.10 *The magnetic field sensing.*

6.4 Hydrogen Storage

The use of hydrogen as the basis for a future sustainable energy economy with low carbon emissions is one of the worldwide interest in the time being. Production, Storage and utilization of hydrogen are the main factors for considering the economy of using these materials. It is significant scientific and technological challenges to satisfy these main factors. For hydrogen-fuel cell transportation use a suitable material for on-board storage should be able to store a high weight-percent and high volume density of hydrogen and rapidly discharge and charge the same amount of hydrogen at acceptable temperatures (typically around 50–100 ℃). This represents a particular challenging set of credentials for an ideal storage material and at present no known material meets these critical requirements.

According to Chen et al work [145] in 2002 the system Li_3N-Li_2NH-$LiNH_2$ could reversibly cycle hydrogen with a theoretical maximum of over 11wt% H_2. In practice, only cycling between lithium imide and amide is feasible at realistic pressures and temperatures. Ammonia, NH_3, is formed as portion of the H_2 desportion process. This dispotion occurred in two steps:

$$2LiNH_2+LiH \Rightarrow (Li_2NH+NH_3)+LiH$$

$$Li_2NH+(NH_3+LiH) \Rightarrow Li_2NH+LiNH_2+H_2$$

NH_3 absorption by LiH is a rapid and efficient process. However, in practice it is difficult to reduce NH_3 levels to below 200 ppm, a value that still is high enough to poison current fuel-cell operation.

David et al, [146] demonstrated from synchrotron X-ray diffraction refinement that the mechanism of the transformation between lithium amide and lithium imide during hydrogen cycling in the important Li-N-H hydrogen storage system is a bulk reversible reaction that occurs in a non-stoichiometric manner within the cubic anti-fluorite-like Li-N-H structure.

The hydrogen desorption and structural properties of the Li−Mg−N−H systems with different LiH/$Mg(NH_2)_2$ ratios are systemically investigated by Haiyan Leng et al. [147] The system with the LiH/$Mg(NH_2)_2$ ratio of 6/3 transforms into Li_2NH and MgNH, and then, the mixture forms an unknown phase by a solid−solid reaction, which presumably is the ternary imide $Li_2Mg(NH)_2$; the system with the LiH/$Mg(NH_2)_2$ ratio of 8/3 transforms into $4Li_2NH$ and Mg_3N_2 after releasing H_2 at T < 400 ℃; the system with the LiH/$Mg(NH_2)_2$ ratio of 12/3 transforms into $4Li_3N$ and Mg_3N_2 after releasing H_2 at T > 400 ℃, where the LiMgN phase is formed by the reaction between Li_3N and Mg_3N_2. The characteristics of the phase transformations and the thermal gas desorption behaviors in these Li−Mg−N−H systems could be reasonably explained by the ammonia mediated reaction model, irrespective of the difference in the LiH/$Mg(NH_2)_2$ ratios.

The combination of X-ray and neutron diffraction studies (see Fig. 6.11) led to a precise determination of the full crystal structure, which has been independently corroborated by computational studies as the most precise determination of a number of recent studies [149].

The maximum available weight percentage and the hydrogen capacity per volume are 10.6 wt.% and 96 kgm^{-3}, respectively. Chen *et al.* [150] recently showed that titanium chloride-doped LiAlH4 lowered the decomposition temperature of $LiAlH_4$, which resulted from the enhanced kinetics for a dehydriding cycle. Thus development of catalysts for the enhanced kinetics of LiAlH4 is very attractive since it can eliminate the need for high temperature and high pressure previously required for the rehydriding/dehydriding cycle.

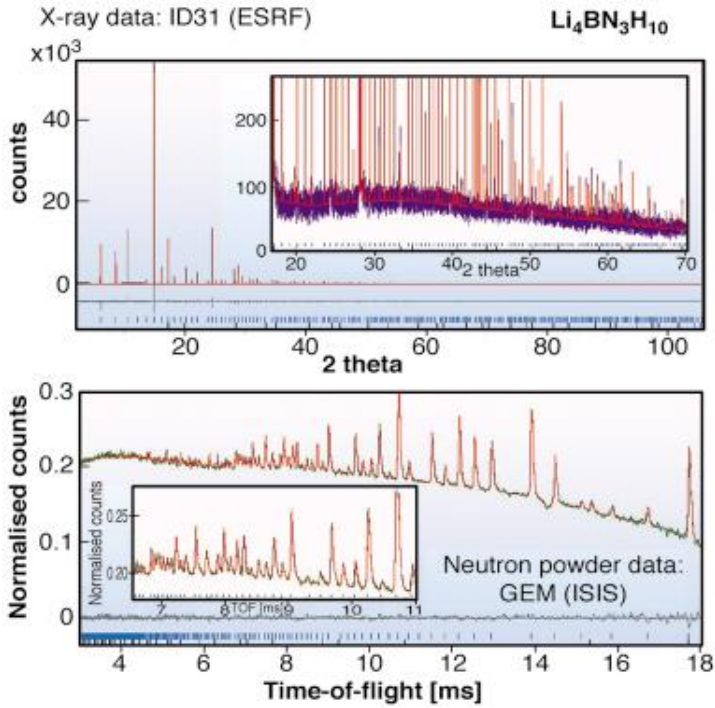


Fig. 6.11 *X-ray and neutron powder diffraction patterns of $Li_4BN_3H_{10}$. Both datasets are fitted simultaneously to high precision providing strong validation of all aspects of the crystal structure including hydrogen positions.*

Most promising future scenario is the hydrogen economy especial concerning ideal replacement in the transportation application. Hydrogen is the ideal means of energy storage, transportation and conversion in a comprehensive clean-energy concept. [151] It is non-polluting as its combustion only generates water. It is abundant and can be produced from a variety of conventional and renewable energy resources, mainly water which covers 71% of earth planet area. For these reasons, there is now world widespread agreement that hydrogen will play a key role in the developed countries energy policy towards the middle of the century. [152-154] However, the storage of hydrogen is still the bottleneck problem which faces its commercial application. Inefficient storage in liquid form is because of hydrogen very low boiling point around -250 ℃.

Add to that, its low density in the gaseous state requires storage in risky high-pressure vessels not accepted by safety regimes for mobile applications and in particular in the future "zero-emission vehicle" [155-160].

Hydrogen car fueling Material hydride design

Fig. 6.12 *Hydrogen fuel.*

Alternative safe offer has been introduced by storing hydrogen storage in matter for transportation. Several promising systems are under discussion: adsorbed hydrogen on nano-structures (nano tubes, metal organic frameworks), and hydrogen absorbed in metal hydrides (transition metal based hydrides, complex hydrides). [156-159] Requirements for hydrogen fuel tanks to be used in vehicles is put down by US Department Of Energy (DOE) which have been taken as international target for onboard application, at least 6 mass% hydrogen has to be stored (6.5 mass% and 62 kg H_2/m^3) in a time as short as 5-10 minutes which allows the vehicle to cut a distance of about 500Km. [160-170] Qualification for the carrier matter is to have high gravimetric and volumetric density, to be suitable for the already designed transport technologies. Achieving all of these targets in one hydrogen storage material system is not available in the present nevertheless, studding different storage material systems with different treatments,

like doping a catalyst and structure treatments already have improved some of them that they become promising for application. [161, 163] Examples are adsorbed nano-structures like carbon nanotubes and other carbon materials as well as absorbed in transition metal-based materials. Recently, intense interest has developed in light-weight complex hydrides such as alanates and borohydrides beside the peroviskites which newly appear on the scene of the hydrogen energy storage field. The above mentioned materials still need to adjust thermodynamics and kinetics properties to technical needs for on board application.

The peroviskite crystal structure is associated with unique octahedral with hydrogen atoms prefer to occupy. The noticed high mobility of hydrogen atoms in the peroviskite crystal structure can be used to improve the slow hydrogenation kinetics of some strongly bound light-metal-hydride system such as MgH_2 and possibly to design new alloy hydrides with desirable hydrogen-storage properties. [164-198]