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Magnetic Solids as Next-Generation Refrigerants: Advancements and Opportunities in Magnetocaloric Materials

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Abstract

This paper explores the challenges of traditional refrigeration methods and the need for environmentally friendly alternatives. It highlights the emergence of magnetic refrigeration, which uses magnetic solids to cool instead of harmful refrigerants. Rare earth alloys and compounds with large magneto-caloric effects at room temperature have gained significant attention for their potential use in this technology. The paper discusses their current application as refrigerant materials and investigates the potential of new materials by comparing their magnetocaloric properties.

KEYWORDS: Magnetic refrigeration, Magnetic material, Magnetocaloric effect

INTRODUCTION

Refrigeration has become an integral part of human life, providing comfort and essential functions such as food and medicine preservation. The most widely used method of refrigeration, the vapour compression method, uses refrigerants that contain chlorofluorocarbons and hydrochlorofluorocarbons. However, due to their adverse environmental impact, their use has been banned under international protocols. This has led to the development of alternative sustainable methods of refrigeration that are environmentally friendly and have low global warming potential (GWP) and zero ozone depletion potential (ODP). Several alternative methods of refrigeration exist, including Magnetic Refrigeration, Thermoelectric Refrigeration, Steam Jet Refrigeration, Vortex Tube Cooling, Thermo Acoustic Refrigeration, Air Cycle Refrigeration, and Aircraft Refrigeration. Among them, Magnetic Refrigeration has made significant progress in recent years due to its many advantages, including the use of solid refrigerant material, zero ODP, less energy consumption, environmental friendliness, and higher efficiency compared to the vapour compression method.

The two main key parameters for magnetic refrigeration are a magnetic source of high strength and a material with a large magnetocaloric effect (MCE). Superconducting magnets can be used to build magnetic refrigerators with high levels of magnetic field, but they are not suitable for domestic refrigerators due to their reliance on liquid

helium or a cryo-cooler. Therefore, the focus is on developing permanent magnet-based magnetic sources that can provide up to 2T of magnetic field[1].

The other part of the research is engaged to find new materials having large MCE and suitable for this new age refrigeration technology[2,3]. In addition to a large MCE, several other properties are essential for effective applications of magnetic refrigeration. In this paper we will discuss the current applications of the existing rare earth alloys and compounds with large magneto-caloric effects at room temperature in this technology. And we will also investigate the potential of new materials by comparing their magnetocaloric properties with the existing one.

MAGNETOCALORIC EFFECT

The magnetocaloric effect is defined as the heating or cooling (i.e., the temperature change) of a magnetic material due to the application of a magnetic field.

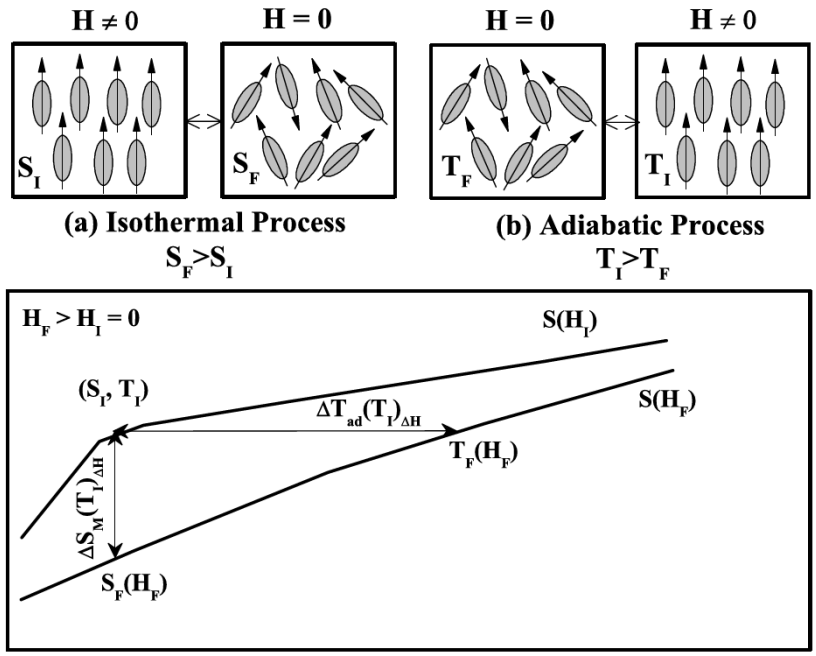

Fig1: Schematic picture that shows the two basic processes of the magnetocaloric effect when a magnetic field is applied or removed in a magnetic system:(a) the isothermal process, which leads to an entropy change, and (b) the adiabatic process, which yields a variation in temperature. Lower panel shows S-T diagram showing the MCE. The horizontal arrow shows ΔT_{ad} and the vertical arrow shows ΔS_M, when the magnetic field is changed from H_I to H_F.

In order to explain the origin of the magnetocaloric effect, using thermodynamics, the magnetic variables (M and H) is to be related to entropy (S) and temperature. All

magnetic materials intrinsically show MCE, although the intensity of the effect depends on the properties of each material. The physical origin of the MCE is the coupling of the magnetic sublattice to the applied magnetic field, H, which changes the magnetic contribution to the entropy of the solid. At constant pressure the entropy of a magnetic solid, S(T, H), which is a function of both the magnetic field strength (H) and the absolute temperature (T), is the combined total of the magnetic (S_M), lattice (S_{lat}), and electronic (S_{el}) contributions such as $S(T,H) = S_M + S_{lat} + S_{lat.}$ As shown in figure 1, in case of isothermal magnetization if we apply H to a magnetic material the magnetic entropy decreases and in case of adiabatic demagnetization (shown in figure 1(b)) as we remove H, the total entropy remains constant and temperature decreases since the magnetic entropy increases. In the lower panel of figure 1, S-T diagram is shown for a ferromagnetic material in two constant magnetic fields (zero magnetic field, $H_I = 0$, and a non-zero magnetic field, H_F. When the magnetic field is applied adiabatically (i.e., when the total entropy of the system remains constant during the magnetic field change) in a reversible process, the magnetocaloric effect (i.e., the adiabatic temperature rise, $\Delta T_{ad} = T_F - T_I$ can be visualized as the isentropic difference between the corresponding S(T,H) functions as shown in the figure by the horizontal arrow. The MCE can be also expressed by means of the isothermal magnetic entropy change (or simply magnetic entropy change), $\Delta S_M = S_F - S_I = S_M(T,H) - S_M(T,0)$, when the magnetic field is applied isothermally. Therefore ΔT_{ad} and ΔS_M represent the two quantitative characteristics of the magnetocaloric effect.

MAGNETIC COOLING EFFICIENCY

The magnetic cooling efficiency of a magnetocaloric material can be, in simple cases, evaluated by considering the magnitude of ΔT_{ad} and ΔS_M and its full-width at half maximum (ΔT_{FWHM})[5]. It is easy to establish the product of the ΔS_M maximum and the full-width at half maximum $\Delta T_{FWHM} = T_2 - T_1$) as $RCP(S) = \Delta S_M (T, H) \times \Delta T_{FWHM}$ which stands for the so-called relative cooling power (RCP) based on the magnetic entropy change. Similarly, the product of the maximum adiabatic temperature change ΔT_{ad} and the full-width at half-maximum ΔT_{FWHM} is expressed by $RCP(T) = \Delta T_{ad} (T, H) \times \Delta T_{FWHM}$ which stands for the so-called RCP based on the adiabatic temperature change.

THE CRITERIA FOR SELECTING MAGNETIC REFRIGERANTS MATERIALS

Most research on the magnetocaloric effect (MCE) has focused on either soft ferromagnetic material ordering between 4 to 77 K for applications such as helium, hydrogen ($\sim$ 20K), and nitrogen liquefaction, or materials ordering near room temperature for applications such as conventional air conditioning and refrigeration.

However, the intermediate temperature range has not been extensively studied due to the lack of applications in this range.

A MATERIAL CAN BE USED AS A MAGNETIC REFRIGERANT WITH THE FOLLOWING PROPERTIES

- It should have a large magnetic entropy changes and adiabatic temperature changes throughout a wide temperature region.
- Ferromagnets with large values of effective magnetron number $P = \sqrt{J(J+1)}$ are selected as they have large density of magnetic entropy (it is an important factor contributing to the working efficiency of materials).
- Materials with high Debye temperature or small lattice entropy is more suitable for room-temperature magnetic refrigerators.
- Working efficiency of a magnetic refrigerant material increases having no magnetic hysteresis.
- Materials with small thermal hysteresis is required for the reversibility of the MCE.
- Small specific heat and large thermal conductivity ensures remarkable temperature change and rapid heat exchange.
- Large electric resistance for lowering eddy current heating or the small eddy current loss.
- High chemical stability and simple sample synthesis route are also required for magnetic refrigerant materials i.e, materials should be of low cost.

DIFFERENT ALLOYS AND COMPOUNDS USED AS A MAGNETIC REFRIGERANT MATERIAL

Magnetic refrigeration has been used for cooling below 1K with paramagnetic salts such as $Gd_2(SO_4)_3,8H_2O$[4]. However, its applications at temperatures around room temperature are not yet commercially available, although this technology is believed to have great potential for new global business opportunities[5]. Until recently a gadolinium (Gd) rare-earth metal with large MCE has been considered as the most active magnetic refrigerant in room-temperature magnetic refrigerators[5]. However, its usage is somehow commercially limited because Gd is quite expensive. Therefore, research in the magnetic cooling field has been focused on finding new materials that are cheaper but display larger MCEs[5-10]. As a remarkable breakthrough occurred in 1997 when Pecharsky and Gschneidner[6] discovered that the giant magnetocaloric (GMC) effect in a $Gd_5Si_2Ge_2$ alloy was twice larger than in Gd MCE (15 J/Kg-K around 277 K with application of 5 T magnetic field). More importantly, this alloy could not only improve the efficiency of large-scale magnetic refrigerators but also open the door to new small-scale applications, such as home and automotive air conditioning [5]. Nonetheless, the Curie temperature of $Gd_5Si_2Ge_2$ is about 276 K, which is much lower than that of Gd of 294 K, making this alloy difficult to be used in room-temperature magnetic refrigerators. Another disadvantage is the large thermal and field hysteresis near the phase transition. The gadolinium metal (Gd) is the initial material for room

temperature magnetic refrigerators (From 1974) having T_C at 294K. However, using alloys in magnetic refrigeration presents several problems, including the presence of thermal hysteresis, brittleness, and very high cost.

The unique magnetocaloric properties of rare-earth manganites were not reported until 1996, despite being known for over 50 years[12]. However, these materials offer advantages over previously studied materials due to their lack of thermal and field hysteresis and lower cost. Such a proposition was made more than 10 years ago by Zhang et al. who performed magnetocaloric measurements in $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.60}Ca_{0.33}Y_{0.07}MnO_3$[13]. Since then, many other manganites have been examined from this point of view and MCEs of hole doped manganites have been heavily studied[14] and they are proved to be compatible having large MCE and also of lower cost than any other materials, particularly those based on Gd. The perovskite and related structures of manganites also make them suitable for carrier-doping procedures, which can modify their magnetic properties such as Curie temperature and saturation magnetization, making them good candidates for magnetic refrigeration at various temperatures.

For example, self-doped $La_{0.9}MnO_3$, has been reported to have a $-\Delta S_M$ value of 4.9 J/kg-K at 254 K and at 20 kOe[15]. The value of adiabatic temperature change (ΔT_{ad}) is ~ 2.1 K at its Curie temperature (T_C). A hole doped single crystalline manganite with composition $Pr_{0.52}Sr_{0.48}MnO_3$ was investigated where a significant negative entropy change (~3.8 J/kg K) associated with the considerably large refrigerant capacity (293 J/kg) is observed close to T_C. For nanocrystalline $Pr_{0.52}Sr_{0.48}MnO_3$, around paramagnetic to ferromagnetic (FM) transition temperature (T_C) maximum negative change in magnetic entropy ΔS_{Max} occurs and around FM to antiferromagnetic (AFM) transition (T_N) a maximum positive change in magnetic entropy ΔS_{Min} is observed. With the increase of Cr doping both the Curie temperature (T_C) and the Néel temperature (T_N) decrease. The ΔS_{Max} and ΔS_{Min} at T_C and T_N respectively increase for x = 0.02 and then they decrease for x = 0.035[16]. The symmetric nature of the MCE curve with a large full width half maxima 110 K makes this material a very good refrigerant.

CONCLUSION

Besides value of MCE around room temperature with application of low field, very small field and thermal hysteresis (almost nil) also make the manganites excellent candidates for working materials in magnetic refrigeration. The main advantages of magneto caloric effect (MCE) principle as compared with classical VCRS are that it does not release any ozone layer depleting or global warming gases and possesses high energy efficiencies.

REFERENCES:

1. Masche M., J. Liang, K. Engelbrecht and C.R.H. Bahl (2023):" Efficient modulation of the magnetocaloric refrigerator capacity". International Journal of Refrigeration. 145: 59–67.
2. Gschneidner K.A., Jr., V. K. Pecharsky (2008): "Thirty years of near room temperature magnetic cooling: Where we are today and future prospects". International Journal of Refrigeration. 31: 945-961.
3. Alahmer A., M. Al-Amayreh, A. O. Mostafa, M. Al-Dabbas and H. Rezk (2021): "Magnetic Refrigeration Design Technologies: State of the Art and General Perspectives" Energies. 14: 4662.
4. Giauque W.F. and D.P. MacDougall (1933): "Attainment of Temperatures Below 1° Absolute by Demagnetization of $Gd_2(SO_4)3{\cdot}8H_2O$". Phys. Rev. 43: 768.
5. Pecharsky V.K., K.A. Gschneidner and A.O. Tsokol (2005).:" Recent developments in magnetocaloric materials". Rep. Prog. Phys. 68: 1479.
6. Pecharsky V.K. and K.A. Gschneidner(1997): "Giant Magnetocaloric Effect in Gd5(Si2Ge2)". Phys. Rev. Lett. 78: 4494.
7. Hu F.X., B.G. Shen, J.R. Sun and G.H. Wu (2001): "Large magnetic entropy change in a Heusler alloy $Ni_{52.6}Mn_{23.1}Ga_{24.3}$ single crystal".Phys. Rev. B. 64: 132412.
8. Wada H. and Y. Tanabe (2001): "Giant magnetocaloric effect of $MnAs_{1-x}Sb_x$". Appl. Phys. Lett. 79: 3302.
9. Fujieda S., A. Fujita, K. Fukamichi (2002): "Large magnetocaloric effect in $La(Fe_xSi_{1-x})_{13}$ itinerant-electron metamagnetic compounds". Appl. Phys. Lett. 81: 1276.
10. Tegus Q., E. Bruck, K.H. Buschow, F.R. de Boer (2002): "Transition-metal-based magnetic refrigerants for room-temperature applications". Nature. 415: 150.
11. Goodenough J. B., (2003) Handbook on the Physics and Chemistry of Rare Earths 33, ed K. A. Gschneidner Jr. et al, (Amsterdam: Elsevier) 249.
12. Gschneidner Jr. K. A. and V. K. Pecharsky (2000): "Magnetocaloric materials". Annu. Rev. Mater. Sci. 30: 387.
13. Zhang X. X., J. Tejada, Y. Xin, G. F. Sun, K. W. Wong and X. Bohigas (1996):" Magnetocaloric effect in $La_{0.67}Ca_{0.33}MnO_{\delta}$ and $La_{0.60}Y_{0.07}Ca_{0.33}MnO_{\delta}$ bulk materials" Appl. Phys. Lett. 69: 3596.
14. M. H. Phan, S. C. Yu (2007): "Review of the magnetocaloric effect in manganite materials". J. Magn. Magn. Mater. 308: 325-340.
15. Patra M., K. De, S. Majumdar, S. Giri (2009): "Multifunctionality attributed to the self-doping in polycrystalline $La_{0.9}MnO_3$: Coexistence of large magnetoresistance and magnetocloric effect". Appl. Phys. Lett. 94: 092506.
16. Patra M, S. Majumdar, S. Giri (2014): "Tuning of magnetocaloric effect in $Pr_{0.5}Sr_{0.5}MnO_3$ with minimal Cr substitution". 448(1): 297-299.