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Review

Advanced magnetocaloric materials: What does the future hold?

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Abstract

Recent achievements in the design of robust near room temperature magnetic cooling devices signify paradigm shift in refrigeration, liquefaction and freezing technologies, and call for a much broader base of advanced magnetocaloric materials to support quick materialization of this environmentally friendly, energy efficient technology in a variety of markets. The latest material discoveries are reviewed and current trends in engineering of advanced magnetocaloric compounds have been identified.

Keywords: Magnetic refrigerator; Survey; Material; Alloy

Matériaux magnétocaloriques de pointe: le futur que réserve-t-il?

Mots clés : Réfrigérateur magnétique ; Enquête ; Matériau ; Alliage

1. Introduction

Our society is highly dependent on reliable cooling technology. Without refrigeration, the food supply would still be seasonal and limited to locally produced non-perishable items; comfortable living conditions would be impossible everywhere causing overpopulation in areas with modest climates; certain medical advancements, e.g. organ transplantation, organ and tissue cryo-storage, and cryo-surgery would be impossible. It is startling that all these and other advancements are supported by the technology, which remains essentially unchanged from the time it has evolved as a freon-based refrigerator in the late 1920s.

Modern refrigeration is almost entirely based on a compression/expansion refrigeration cycle. It is a mature, reliable and relatively low cost technology. Over the years, all parts of a conventional refrigerator (i.e. compressor, heat exchanger, refrigerant, packaging, and insulation) were considerably improved due to extended research and developmental efforts. Anticipated improvements, however, are incremental since modern refrigeration is already near its fundamental limit of energy efficiency. Furthermore, some liquids used as refrigerants are hazardous chemicals, while

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Nomenclature

AMR	active magnetic regeneration
C_H	heat capacity in constant magnetic field (J mol^{-1} K^{-1}, J kg^{-1} K^{-1}, or J cm^{-3} K^{-1})
E	enthalpy (J kg^{-1}, J mole^{-1}, or J cm^{-3})
GMCE	giant magnetocaloric effect (J kg^{-1} K^{-1}, J mole^{-1} K^{-1}, J cm^{-3} K^{-1}, or K)
H	magnetic field (Oe, T)
H_i	initial magnetic field (Oe, T)
H_f	final magnetic field (Oe, T)
M	magnetization (emu g^{-1})
MCE	magnetocaloric effect (J kg^{-1} K^{-1}, J mole^{-1} K^{-1}, J cm^{-3} K^{-1}, or K)
MR	magnetic refrigeration
S	total entropy (J mol^{-1} K^{-1}, J kg^{-1} K^{-1}, or J cm^{-3} K^{-1})
S_E	electronic entropy (J mol^{-1} K^{-1}, J kg^{-1} K^{-1}, or J cm^{-3} K^{-1})
S_{HF}	entropy of the high magnetic field polymorph (J mol^{-1} K^{-1}, J kg^{-1} K^{-1}, or J cm^{-3} K^{-1})
S_i	total entropy in the initial magnetic field (J mol^{-1} K^{-1}, J kg^{-1} K^{-1}, or J cm^{-3} K^{-1})
S_f	total entropy in the final magnetic field (J mol^{-1} K^{-1}, J kg^{-1} K^{-1}, or J cm^{-3} K^{-1})
S_L	lattice entropy (J mol^{-1} K^{-1}, J kg^{-1} K^{-1}, or J cm^{-3} K^{-1})
S_{LF}	entropy of the low magnetic field polymorph (J mol^{-1} K^{-1}, J kg^{-1} K^{-1}, or J cm^{-3} K^{-1})
S_M	magnetic entropy (J mol^{-1} K^{-1}, J kg^{-1} K^{-1}, or J cm^{-3} K^{-1})
T	temperature (K)
T_C	Curie temperature (K)
T_{cold}	cold end temperature (K)
T_{hot}	hot end temperature (K)
ΔE	enthalpy change or latent heat (J kg^{-1}, J mole^{-1}, or J cm^{-3})
ΔH	magnetic field change (Oe, T)
ΔM	change of magnetization (emu g^{-1})
ΔS	isothermal entropy change (J kg^{-1} K^{-1}, J mole^{-1} K^{-1}, or J cm^{-3} K^{-1})
ΔS_M	isothermal magnetic entropy change (J kg^{-1} K^{-1}, J mole^{-1} K^{-1}, or J cm^{-3} K^{-1})
ΔS_{st}	isothermal structural entropy change (J kg^{-1} K^{-1}, J mole^{-1} K^{-1}, or J cm^{-3} K^{-1})
ΔT_{ad}	adiabatic temperature change (K)
μ_0	permeability of vacuum (dimensionless)

other eventually escape into the environment contributing toward ozone layer depletion and global warming, and therefore, conventional refrigeration ultimately promotes deleterious trends in the global climate.

Magnetic refrigeration is an emerging technology that has the potential for high energy efficiency [1–6]. The high efficiency arises because the analogues to the compression and expansion parts of the vapor cycle are accomplished by the magnetization and demagnetization, respectively, of a magnetic material [7]. In a magnetically soft ferromagnetic compound, these magnetic processes can be essentially dissipation free, thus approaching 100% of Carnot efficiency. Furthermore, the magnetic refrigerant is a solid and will generally present a negligible environmental hazard. Heat transfer is done by a reciprocating flow of an inert fluid; for example, water can be used above 273 K.

Magnetic refrigeration is based on the magnetocaloric effect (MCE). Originating from coupling of a magnetic field with magnetic moments carried by itinerant or localized electrons and quantified in terms of temperature and/or entropy changes, the MCE reflects field-induced, reversible variations of internal energy and the effect itself represents one of the most basic properties of magnetic solids [8–10]. The phenomenon covers length, energy and time scales spanning over many orders of magnitude: from quantum mechanics to micromagnetics, from statistical to macroscopic thermodynamics and from spin dynamics to heat flow, yet prior to recent discoveries of the giant MCE in $Gd_5(Si_xGe_{1-x})_4$ [11] and, soon after, in several other families of intermetallic compounds [12–15], it was all but ignored by mainstream materials physics. Understanding and ultimately exploiting this multidimensional landscape is an enormously challenging task, yet every success along the way facilitates a better control over the design of novel compounds exhibiting a desirable combination of magnetic and thermal properties, thus expanding the base of advanced magnetocaloric materials.

Throughout its ~120 years history – counting from the discovery of the magnetocaloric effect in iron by Warburg [8] – experimental measurements of MCE were combined with a general thermodynamic theory, or the Landau theory of phase transitions, or the mean field approximation, which resulted in the notion that both the rate of change of the magnetization with temperature at constant field, $|(\partial M/\partial T)_H|$, and/or the magnetic field change, ΔH, must be maximized in order to maximize the MCE [16]. The first quantity is material-dependent and, in principle, it may be adjusted over several orders of magnitude, but a much better understanding of the composition-structure-magnetic property relationships of solids is required. As far as practical applications of the magnetic refrigeration are of concern, increasing ΔH beyond 2 T without using a superconducting magnet is unrealistic considering the current state-of-the art of permanent magnets. Therefore, maximizing $|(\partial M/\partial T)_H|$ via the proper design of a magnetocaloric material is the only rational approach to improve performance of a magnetic refrigerant, yet this presents a formidable basic science challenge that