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Magnetocaloric materials and the optimization of cooling power density

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ABSTRACT

The magnetocaloric effect is the thermal response of a material to an external magnetic field. This manuscript focuses on the physics and the properties of materials which are commonly used for magnetic refrigeration at cryogenic temperatures. After a brief overview of the magnetocaloric effect and associated thermodynamics, typical requirements on refrigerants are discussed from a standpoint of cooling power density optimization. Finally, a compilation of the most important properties of several common magnetocaloric materials is presented.

1. Magnetic refrigeration

Magnetic refrigeration is employed to provide cooling over many orders of magnitude of temperature, from a few hundred Picokelvin which have been reached with nuclear demagnetization refrigerators [1] to several hundred Kelvin [2,3]. The magnetocaloric effect, which provides the basis for these refrigeration techniques, is discussed by Shirron [4]. For low temperature applications, the reader's attention is also drawn to Ambler's and Hudson's review of magnetic cooling below 1 K [5].

Adiabatic Demagnetization Refrigerators (ADRs) are typically used in the temperature range between a few Millikelvin and a few Kelvin. In this temperature range, ADRs mainly compete with ^{3}He/^{4}He dilution refrigerators and ^{3}He sorption coolers; ADRs have the advantage of more efficient and more accurate temperature control and are thus commonly used to cool low temperature detectors, both in laboratory environments and on spacecraft (e.g. [6,7]). The thermodynamics of ADRs are described in [8].

In Active Magnetic Regenerators (AMRs), the refrigerant material and the regenerator material are combined into one. This concept allows for the construction of efficient and compact refrigerators. AMRs are being researched for gas liquefaction (e.g. hydrogen [9]), as well as for room temperature refrigeration [10]. The working principle and the thermodynamics of AMRs are described in [11].

The basic principles underlying magnetic refrigeration (with the exception of nuclear demagnetization, which is discussed in [12]) will be reviewed in this introductory section. For more details, reference is made to textbooks such as [13–15] or [16].

1.1. The magnetocaloric effect

The entropy of a magnetocaloric material is the sum of three independent constituents, namely the magnetic entropy S_m, the entropy of the lattice S_l and the entropy of the conduction electrons S_e:

$$S = S_m(B,T) + S_l(T) + S_e(T). \quad (1)$$

The magnitude of all constituents depends on the temperature T, while the magnitude of S_m has an additional strong dependence on the external magnetic field density B. S_l and S_e can be neglected at low temperatures, as S_m is much larger than S_l and S_e combined in that regime.

On a microscopic level, the magnetocaloric effect is caused by the interaction of the external magnetic field with magnetic moments in the material. In most cases, the magnetic moments originate from the presence of unfilled electron shells in transition metal or rare earth ions in the refrigerant, which imparts a total electronic angular momentum J on each ion. The magnetic moments thus have $2J+1$ possible orientations, and – assuming

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that the thermal energy k_BT is greater than the splitting between the energy levels of these states – all will be equally occupied and will contribute

$$S_m = R \cdot \ln(2J+1) \tag{2}$$

to the magnetic entropy, where R is the gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$).

If an external magnetic field is applied, the magnetic moments will tend to align with the field, increasing the energy difference between the states, reducing the occupation of higher energy states (those align counter to the field), and thus reducing magnetic entropy. Using statistical mechanics, the field dependence of the magnetic entropy can be derived from the partition function. Assuming that the magnetic moments are completely independent and do not interact with each other, one obtains

$$\frac{S_m}{R} = x \cdot (\coth(x) - (2J+1) \cdot \coth(x \cdot (2J+1))) + \ln\left(\frac{\sinh(x \cdot (2J+1))}{\sinh(x)}\right), \tag{3}$$

where x depends on the temperature T, the magnetic field density B, and properties of the refrigerant.

For a paramagnetic material, x can be calculated with the Bohr magneton μ_B (9.27×10^{-24} J/T), the Boltzmann constant k_B (1.38×10^{-23} J/K) and the Landé factor g (an electronic property of the magnetic refrigerant which will be discussed in more detail in Section 2.1).

$$x = \frac{\mu_B g B}{2 k_B T}. \tag{4}$$

Eqs. 3 and 4 show that the magnetic entropy of a material depends on the ratio B/T. As B approaches 0, Eq. 3 will approach Eq. 2, independent of temperature. In real materials, interaction between ions will always induce some splitting of the energy levels, causing the entropy to approach zero at low temperature. Although these interactions are complex, a rough approximation, useful in ADR design, is to replace B with an effective field B_{eff} in the equations above [13]:

$$B_{\mathrm{eff}} = \sqrt{B^2 + b^2}, \tag{5}$$

where b is a material-dependent parameter.

At low enough temperature, most paramagnetic materials undergo a phase change to an ordered state, usually ferromagnetic or antiferromagnetic (see Section 2.2). Entropy drops sharply below the critical temperature. Fig. 1 shows the dependence of the entropy S on the magnetic field density B and temperature T for Ferric Ammonium Alum (a common paramagnetic refrigerant). The phase change can be clearly seen by the sharp change in slope at 26 mK.

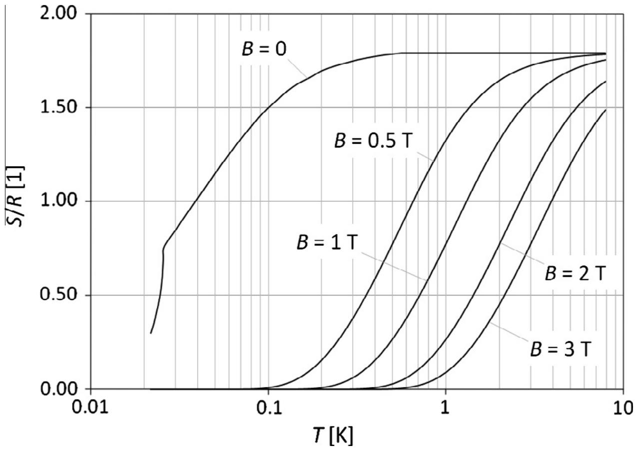

Fig. 1. Entropy vs. temperature curves of Ferric Ammonium Alum (FAA) for different values of the external field density B. The entropy is normalized to the gas constant R.

1.2. Thermodynamics of the magnetocaloric effect

The magnetocaloric effect can also be described using formalisms from classical thermodynamics. The total differential of the entropy $S(T,B)$ of an isobaric system is

$$dS = \left(\frac{\partial S}{\partial T}\right)_B \cdot dT + \left(\frac{\partial S}{\partial B}\right)_T \cdot dB. \tag{6}$$

In an adiabatic system, $dS = 0$. Using the definition of the specific heat C_B at constant magnetic field,

$$C_B = T \cdot \left(\frac{\partial S}{\partial T}\right)_B, \tag{7}$$

and Maxwell's relation for the magnetization M,

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B, \tag{8}$$

one obtains the following relation for the adiabatic temperature change dT/dB, which is often used to characterize the magnitude of the magnetocaloric effect:

$$\frac{dT}{dB} = -\frac{T}{C_B} \cdot \left(\frac{\partial M}{\partial T}\right)_B. \tag{9}$$

Eq. 9 shows that the magnetocaloric effect is large if the temperature T is high, if the specific heat C of the refrigerant is small, and if the magnetization changes rapidly with temperature; the latter condition is fulfilled around magnetic phase transitions in the refrigerant.

Knowledge of entropy as a function of temperature and magnetic field is essential for the design of magnetic coolers, and the above relations are useful in determining entropy from measurements of refrigerant properties. Measurements of either the specific heat $C(T,B)$ or the magnetization $M(T,B)$ allow the calculation of ΔS_B. It is not possible to measure the three constituents of the entropy (magnetic, lattice and electronic) separately; only the total entropy change ΔS_B is accessible by experiment.

If the specific heat $C(T,B)$ is measured on a sample of a magnetocaloric material, the entropy can be derived with the following equation:

$$S(T,B) = \int_0^T \left(\frac{C(T',B)}{T'}\right)_B dT'. \tag{10}$$

In some cases, it is difficult to measure the specific heat to temperatures low enough such that $C(T',B)$ can be easily extrapolated to $T = 0$. Then, the entropy from Eq. 10 is best separated into two parts,

$$S(T,B) = \int_0^{T_0} \left(\frac{C(T',B)}{T'}\right)_B dT' + \int_{T_0}^T \left(\frac{C(T',B)}{T'}\right)_B dT', \tag{11}$$

where T_0 is the lowest temperature achieved in the specific heat measurements. Usually, the specific heat data at high magnetic fields can be extrapolated to $T = 0$, because the specific heat peak due to phase transitions is suppressed in high fields. For many materials, the specific heat can be extrapolated with a T^3 dependence for the lattice entropy and a linear dependence on T for the electronic specific heat.

If the magnetization is measured, the change in magnetic entropy induced by field B, $\Delta S(T,B) = S(T,B) - S(T,0)$, can be calculated by integrating the Maxwell relation (Eq. 8), which gives