Available online at www.sciencedirect.com
SCIENCE DIRECT®
International Journal of Refrigeration 29 (2006) 3–21
REVUE INTERNATIONALE DU FROID
INTERNATIONAL JOURNAL OF
refrigeration
www.elsevier.com/locate/ijrefrig

Review Article

Thermodynamics of magnetic refrigeration

Andrej Kitanovski, Peter W. Egolf*

University of Applied Sciences of Western Switzerland, CH 1401 Yverdon-les-Bains, Switzerland

Received 26 August 2004; received in revised form 21 March 2005; accepted 20 April 2005
Available online 19 August 2005

Abstract

A comprehensive treatment of the thermodynamics of cyclic magnetic refrigeration processes is presented. It starts with a review of the work, heat and internal energy of a magnetized specimen in a magnetic field, and a list of the thermodynamic potentials is given. These are based on the very recent discovery of an alternative Kelvin force. It is shown that this force is compatible with the internal energy proposed by Landau and Lifshitz. New formulas for the specific enthalpies are presented. Cyclic processes are discussed in detail, e.g. the Brayton, Ericsson and Carnot cycles. Magnetic refrigeration and magnetic heat pump cycles are preferably designed by applying the cascade or/and regeneration principle. Cascade systems allow wider temperature ranges to be obtained. The main objective of this article is to yield a theoretical basis for an optimal design of new magnetic refrigeration and heat pump devices.
© 2005 Elsevier Ltd and IIR. All rights reserved.

Keywords: Magnetic refrigerator; Research; Thermodynamic cycle; Brayton; Ericsson; Carnot; Design; Refrigerating system

Froid magnétique: thermodynamique

Mots clés : Réfrigérateur magnétique ; Recherche ; Cycle thermodynamique ; Brayton ; Ericsson ; Carnot ; Conception ; Système frigorifique

1. Introduction

Magnetic refrigeration is a technology which applies the magnetocaloric effect (MCE), akin to gas refrigeration being based on the compressibility of a refrigerant. The MCE was first discovered by Warburg [1], who observed an increase in temperature when he brought an iron sample into a magnetic field and a decrease when the sample was removed from it. Soon after this discovery Edison and Tesla (Rosensweig [2]) independently and unsuccessfully tried to benefit from this effect by running heat engines for power production. In 1918 Weiss and Piccard [3] explained the magnetocaloric effect. Later Debye [4] and Giauque [5] proposed a method of magnetic refrigeration for low-temperature physics in order to obtain sub-Kelvin temperatures. In 1933 Giauque and MacDougall [6] successfully verified the method by experiment. Since the 1930s magnetic refrigeration has been a standard technique in low-temperature physics. It has proved useful to cool down from a few Kelvin to some hundredths, or in very skilful applications to a few thousandths of a Kelvin. In 1976 Brown (Refs. [7,8]) constructed the first magnetic refrigerator to work at room temperature. Subsequently a number of patents describing such refrigerators were registered. The first

* Corresponding author. Tel.: +41 24 426 44 79; fax: +41 24 426 44 77.
E-mail address: peter.egolf@eivd.ch (P.W. Egolf).

0140-7007/$35.00 © 2005 Elsevier Ltd and IIR. All rights reserved.
doi:10.1016/j.ijrefrig.2005.04.007

Nomenclature

A	area (m^2)
$\vec{A}$	vector potential (T m)
B	magnetic induction ($T = N\ A^{-1} m^{-1}$)
c	speed of light ($m\ s^{-1}$)
c	specific heat capacity ($J\ m^{-3}\ K$)
$\vec{D}$	dielectric field ($A\ m^{-1}$)
$\vec{E}$	electric field ($T = N\ A^{-1} m^{-1}$)
f	specific Helmholtz energy ($J\ m^{-3}$)
g	specific Gibbs energy ($J\ m^{-3}$)
h	specific enthalpy ($J\ m^{-3}$)
$\vec{H}$	magnetic field ($A\ m^{-1}$)
j	electrical intensity ($A\ m^{-2}$)
$\vec{M}$	magnetization (vector) ($A\ m^{-1}$)
N	demagnetization factor (–)
$\vec{m}$	magnetic moment ($A\ m^2$)
p	pressure (Pa)
q	specific heat ($J\ m^{-3}$)
Q	heat (J)
S	entropy ($J\ K^{-1}$)
S	surface (m^2)
s	specific entropy ($J\ m^{-3}\ K^{-1}$)
s	displacement (m)
t	time (s)
T	temperature (K)
U	internal energy (J)
u	specific internal energy ($J\ m^{-3}$)
V	volume (m^3)
w	specific work ($J\ m^{-3}$)
W	work (J)
T	temperature (K)

Greek symbols

χ'	(derivative) susceptibility (–)
ϕ	potential ($A^2\ m^{-2}$)
Φ	potential ($A^2\ m$)
Γ	domain of specimen (–)
μ_0	permeability of vacuum ($T\ m\ A^{-1} = N\ A^{-2}$)
μ	relative permeability (–)
ρ	density ($kg\ m^{-3}$)
Ω	total domain (–)
Ψ	potential (T^2)

Subscripts, superscripts

0	free magnetic field
1	normalized
abs	absolute
ad	adiabatic
c	cooling
dem	demagnetization
e	electronic
int	internal
l	lattice
m	magnetic
r	rejected
tech	technical

'room temperature' magnetic refrigerator—containing permanent magnets—was designed and built in 2001 by the Astronautics Cooperation in the USA [9]. A review of such magnetic refrigerators can be found in Refs. [10–12]. Magnetic refrigeration and heat pump technology is considered to be a green technology with the potential to replace conventional vapour compression systems, which at present mainly work with HCFC and CFC refrigerants.

At the end of this article, it will become clear that ferrohydrodynamics (FHD) will play a crucial role in the field of magnetic refrigeration. Research in FHD began in the mid-1960s with the objective of converting heat into work in systems with no moving parts [2]. In 1964 Resler and Rosensweig (Refs. [13,14]) had the idea that magnetic conversion of heat into work (or the reverse process for refrigeration) could be efficiently performed at room temperature or even above by regeneration of heat in the cycle. The first machines based on this idea, which moved magnetocaloric alloys through magnetic fields, were developed. Higher heat transfer from the fluid to the metal and vice versa is obtained by rotating porous structures across magnetic field lines (Kitanovski et al. [15]). Another principle is the creation of suspensions with solid magnetocaloric particles, which are forced to flow through magnetic fields [16]. New developments of fluids, with a characteristic particle size of two orders above the nanoscale, may lead to future improvements in such magnetic refrigeration and heat pump devices. The systems recently proposed are ideal for applications involving an operation in a cascade configuration or/and making use of regeneration.

Research on magneto caloric materials—suitable for magnetic refrigeration near room temperature—increased greatly in the 1980s. The number of reviewed articles shows exponential growth after the invention of alloys based on gadolinium (Gd) at the AMES Laboratory ([17–19]). Since then discoveries of numerous magnetocaloric compounds have been published, based for example on manganese (Mn) (Refs. [20–22]). A review of various magnetocaloric materials can be found in Refs. [23–25]. The development of these materials is still undergoing substantial improvement, which makes the magnetic heating and cooling technology increasingly interesting, including for practical large-scale applications, such as in home refrigerators, heat pump applications, air conditioning systems, process technical systems, automobiles, etc.

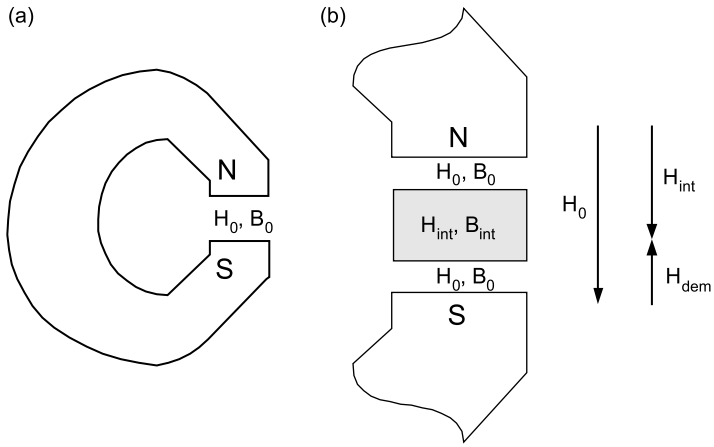

Fig. 1. An electrically induced or permanent magnet (a) without and (b) with a specimen with magnetization M in its gap. The gap field H_0 is assumed to be homogeneous. Because of a demagnetization field in the specimen, H_{dem}, the field there is only H_{int}.

2. Internal energy, heat and work in a magnetic material

The thermodynamics of magnetic refrigeration is introduced by the first law of thermodynamics[1]:

$$dU = dQ + dW \tag{1}$$

where dU is the infinitesimal change of the internal energy. dQ is a small amount of heat added to or removed from the considered system (e.g. Fig. 1), or created by a magnetic internal source (magnetocaloric effect). dW denotes the differential of the work performed on the system, or extracted from it. Magnetic refrigerants are usually alloys, and the conditions:

$$p = \text{const} \tag{2a}$$

$$V = \text{const} \tag{2b}$$

therefore hold very well, and these quantities do not appear in the thermodynamic potentials in this article. To determine the work in the magnetic material, the four Maxwell equations are considered:

$$\text{rot}\vec{E} + \frac{1}{c}\frac{\partial \vec{B}}{\partial t} = 0 \tag{3a}$$

$$\text{div}\vec{B} = 0 \tag{3b}$$

$$\text{rot}\vec{H} - \frac{1}{c}\frac{\partial \vec{D}}{\partial t} - j = 0 \tag{3c}$$

$$\text{div}\vec{D} - \rho = 0 \tag{3d}$$

To obtain the specific (volumetric) energy equation, Eq. (3a) is multiplied by $\vec{H}$ and Eq. (3c) by $\vec{E}$, and the second equation is then subtracted from the first to derive the following result:

$$c(\vec{H}\text{rot}\vec{E} - \vec{E}\text{rot}\vec{H}) + \left(\vec{H}\frac{\partial \vec{B}}{\partial t} + \vec{E}\frac{\partial \vec{D}}{\partial t}\right) + c\vec{E}\cdot\vec{j} = 0 \tag{4}$$

The two terms in the first bracket on the left describe radiation of electromagnetic energy and are of no importance here. The third and fourth terms in the second bracket describe the work per unit of time performed on elementary magnetic moments (ordering of spins) and on charged particles. The charged particles and the electric current are also irrelevant for most of the following considerations. It then follows that (a more detailed derivation is found in Landau and Lifshitz, [26]):

$$dw = -\vec{H}d\vec{B} \tag{5}$$

Reversibly performed or extracted work leads to this alteration of the specific energy of the magnetic system (specimen and surrounding magnetic field to infinity). The induction $\vec{B}$ is a combination of stress $\vec{H}$ and order parameter $\vec{M}$ and defined by:

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) \tag{6}$$

with the magnetic permeability μ_0 of the vacuum. This equation is inserted into (5) to become:

$$dw = -\mu_0\vec{H}d\vec{M} - \frac{\mu_0}{2}d(\vec{H}^2) \tag{7}$$

In Eq. (7) the first term describes the specific energy in the specimen and the second, which can be written by introducing a potential:

$$\phi = \frac{1}{2}\vec{H}^2 \tag{8}$$

denotes the specific energy in the magnetic field. $\vec{H}$ defines a conservative field with the potential ϕ. It then follows that:

[1] This equation is thermodynamically very useful but mathematically a little problematic, because dQ and dW are neither one forms nor total differentials.

$$\mathrm{d}w = -\mu_0 \vec{H}\mathrm{d}\vec{M} - \mu_0 \mathrm{d}\phi \tag{9}$$

At this stage the last term is often neglected with the argument that it does not apply in cyclic processes. In the remainder another normalization is applied. For the differential of the work in a spatial domain Ω we obtain:

$$\mathrm{d}W = -\mu_0 \int_{\Omega} \vec{H}\mathrm{d}\vec{M}\mathrm{d}V - \mu_0 \mathrm{d}\Phi \tag{10a}$$

$$\mathrm{d}\Phi = \int_{\Omega} \mathrm{d}\phi \mathrm{d}V \tag{10b}$$

Only if $\vec{H}$ is constant in the entire specimen does it follow from Eq. (10a) that:

$$\mathrm{d}W = -\mu_0 \vec{H}\mathrm{d}\vec{\mathcal{M}} - \mu_0 \mathrm{d}\Phi \tag{S-11a}$$

$$\vec{\mathcal{M}} = \int_{\Gamma} \vec{M}\mathrm{d}V \tag{S-11b}$$

This now defines the magnetic moment of the specimen. If a result denotes a special case, the equation number is always preceded by the additional letter S. The vector $\vec{H}$ is an intensive variable and $\vec{\mathcal{M}}$ is an extensive variable. For a thermodynamic treatment it is useful to redefine the internal energy u by extracting the field energy, which is contained in the magnetic field without a specimen[2]:

$$\mathrm{d}W_1 = \mathrm{d}W - \mathrm{d}W_0 = -\int_{\Omega} \vec{H}\mathrm{d}\vec{B}\mathrm{d}V + \int_{\Omega} \vec{H}_0 \mathrm{d}\vec{B}_0 \mathrm{d}V \tag{12}$$

Note that this is a different normalization process than neglecting the potential in Eq. (10a). From Eq. (6) it is concluded that:

$$\vec{B}_0 = \mu_0 \vec{H}_0 \tag{13}$$

In the following extension, in the last term Eq. (13) is applied:

$$\begin{aligned} &\vec{H}\mathrm{d}\vec{B} - \vec{H}_0\mathrm{d}\vec{B}_0 \\ &\quad = (\vec{H} - \vec{H}_0)\mathrm{d}\vec{B} + \vec{H}_0(\mathrm{d}\vec{B} - \mu_0\mathrm{d}\vec{H}) \\ &\qquad + \mu_0\vec{H}_0(\mathrm{d}\vec{H} - \mathrm{d}\vec{H}_0) \end{aligned} \tag{14}$$

Substituting Eq. (14) into Eq. (12), we obtain:

$$\begin{aligned} \mathrm{d}W_1 = &-\int_{\Omega} (\vec{H} - \vec{H}_0)\mathrm{d}\vec{B}\mathrm{d}V - \int_{\Omega} \vec{H}_0 \mathrm{d}(\vec{B} - \mu_0\vec{H})\mathrm{d}V \\ &- \mu_0 \int_{\Omega} \vec{H}_0 \mathrm{d}(\vec{H} - \vec{H}_0)\mathrm{d}V \end{aligned} \tag{15}$$

A treatment applying vector analysis leads to the following result (Appendix A):

$$\mathrm{d}w_1 = -\vec{B}_0\left(\frac{1}{\mu_0}\mathrm{d}\vec{B} - \mathrm{d}\vec{H}\right) \tag{16}$$

From Eqs. (6) and (13) we conclude that:

$$\mathrm{d}w_1 = \mathrm{d}w_1^{(\mathrm{ext})} = -\mu_0 \vec{H}_0 \mathrm{d}\vec{M} \tag{17}$$

In an application of this relation, the integration takes place only over the domain Γ of the magnetic specimen. Recently, the Kelvin force, which is the force on a magnetic material in a magnetic field, was critically discussed and an alternative version was proposed [27,28]. This force is also the force which has to be overcome to move a magnetocaloric sample out of a magnetic field and to decrease a magnetization. In Appendix B it is shown that the recently discovered Kelvin force leads to the specific internal energy given by Eq. (17). In Ref. [29] this potential is also found to be accurate. It is stated that this is the specific energy related to the specimen only and not including magnetic field energies.

Appendix D/Table A1 and Fig. 2 show an overview of different kinds of work contributions, which occur in magnetic refrigeration by analogy to conventional vapour compression processes. In a vapour compression system the work performed by an external forcing, e.g. a quasi-static reversible movement of a piston, is $\mathrm{d}W_1^{(\mathrm{ext})} = \vec{F}\cdot\mathrm{d}\vec{s} = pA\mathrm{d}s = -p\mathrm{d}V$ (Fig. 2(a)). The analogue work in magnetic refrigeration is given by a forcing of the external magnetic field, which magnetizes the specimen (compare with Fig. 2(b) and Eq. (17)). These two cases correspond to closed systems. The work performed in an open (adiabatic) system, with a fluid transported in and out of the control volume, leads to an alteration of the energy density from $p^{(1)}v^{(1)}$ to $p^{(2)}v^{(2)}$ (Fig. 2(c)). Here the alteration between the two states in the direction of flow is: $\Delta w_1^{(\mathrm{abs})} = -\Delta(pv) = -(p^{(2)}v^{(2)} - p^{(1)}v^{(1)})$, or for an infinitesimally small section: $\mathrm{d}w_1^{(\mathrm{abs})} = -\mathrm{d}(pv)$. The net work of a machine, operating in a steady-state process, also known as shaft or more frequently as technical work is then: $\mathrm{d}w_1^{(\mathrm{tech})} = -(\mathrm{d}w_1^{(\mathrm{abs})} - \mathrm{d}w_1^{(\mathrm{ext})})$. It therefore, follows that: $\mathrm{d}w_1^{(\mathrm{tech})} = \mathrm{d}(pv) - p\mathrm{d}v = v\mathrm{d}p$. This work is available, e.g. at the shaft of a turbine. By analogy it follows for a magnetic refrigeration system that:

$$\begin{aligned} \mathrm{d}w_1^{(abs)} &= -\mu_0\mathrm{d}(\vec{H}_0\vec{M}) \Rightarrow \mathrm{d}w_1^{(tech)} \\ &= -(\mathrm{d}w_1^{(abs)} - \mathrm{d}w_1^{(ext)}) = \mu_0\vec{M}\mathrm{d}\vec{H}_0 \end{aligned} \tag{18}$$

Eq. (18) defines the technical work which has to be performed, e.g. at the shaft of a magnetic refrigerator wheel to drive the magnetic refrigeration process (Fig. 2(d)). Analogous considerations are also valid for the heat, temperature and specific entropy.

We now consider the total differential of the redefined internal energy $u_1(s,M)$:

[2] H_0 is an adjusted external parameter (e.g. a homogeneous field in the gap of an electric magnet created by electric currents).

$$\mathrm{d}u_1 = \mathrm{d}q + \mathrm{d}w_1 = \left(\frac{\partial u_1}{\partial s}\right)_M \mathrm{d}s + \vec{\nabla}_M u_1 \mathrm{d}\vec{M}$$

$$= \left(\frac{\partial u_1}{\partial s}\right)_M \mathrm{d}s + \left(\frac{\partial u_1}{\partial M}\right)_s \mathrm{d}M \tag{19a}$$

$$\vec{\nabla}_M = \left(\frac{\partial}{\partial M_1}, \frac{\partial}{\partial M_2}, \frac{\partial}{\partial M_3}\right) \tag{19b}$$

$$\mathrm{d}\vec{M} = (\mathrm{d}M_1, \mathrm{d}M_2, \mathrm{d}M_3) \tag{19c}$$

where, for simplification, the vectorial notation in (19a) was neglected. Because the volume is also constant, it is written:

$$\left(\frac{\partial u_1}{\partial s}\right)_M = \left(\frac{\partial u}{\partial s}\right)_{M,V} = \left(\frac{\partial u_1}{\partial s}\right)_V = T \tag{20}$$

It is known from the conventional thermodynamics of gas compression (e.g. Ref. [26]) that the derivative of the internal energy in terms of the entropy is identical to the temperature, and this is therefore not proven here. Comparing Eqs. (19) and taking (20) into consideration, it follows that:

$$\mathrm{d}q = T\mathrm{d}s \tag{21}$$

a well-known relation for reversible processes. Now, by comparing again Eq. (19), but this time taking (17) into consideration, the differential of the external work is:

$$\mathrm{d}w_1 = \vec{\nabla}_M u_1 \mathrm{d}\vec{M} = -\mu_0 \vec{H}_0 \mathrm{d}\vec{M} \tag{22}$$

By inserting Eqs. (21) and (22) into Eq. (19a), it follows for the specific internal energy:

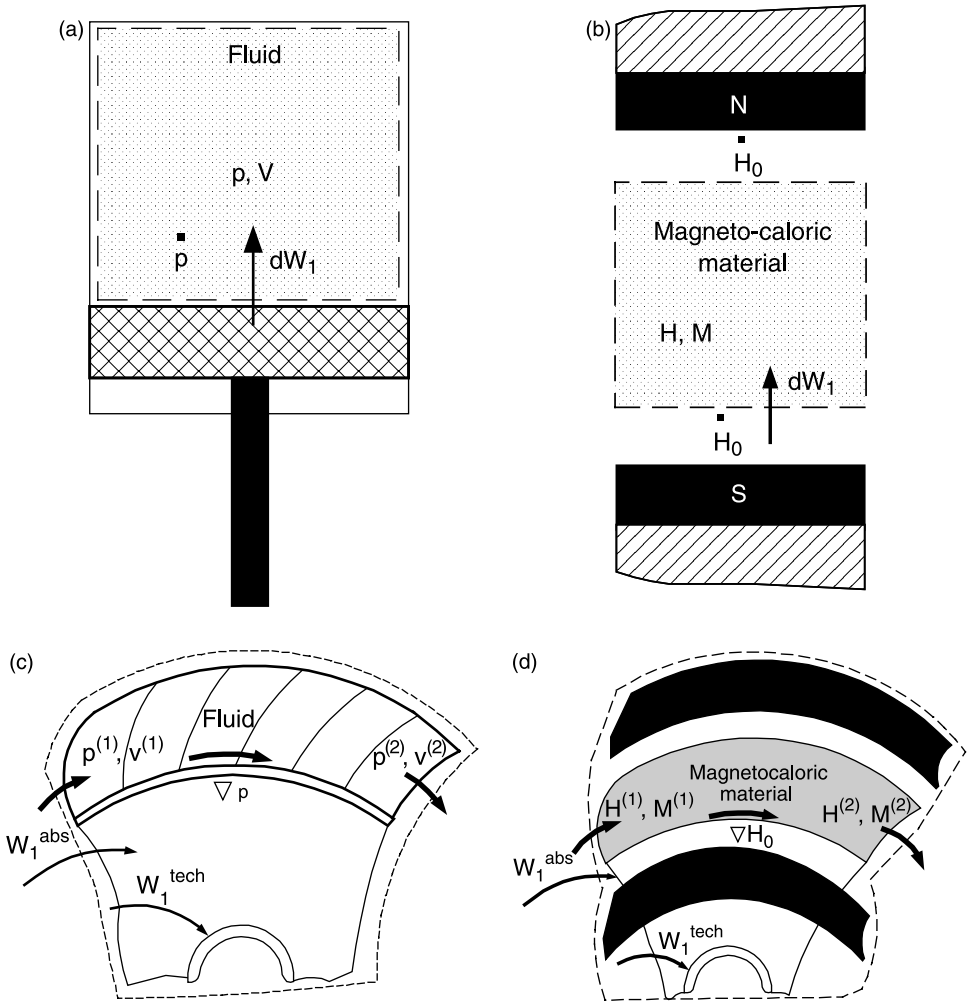

Fig. 2. Analogies of adiabatic processes in conventional systems (a) and (b) with magnetic refrigeration processes (c) and (d). The two processes (a) and (b) occur in closed systems. The first (a) shows a piston compressing a gas, and the second a magnetocaloric sample (e.g. a pendulum) in a magnetic force field. Cases (c) and (d) show an open system each with a flux of refrigerant (gas or magnetocaloric material) over the boundary. In figure (c) only a section of a turbine wheel is shown. The last figure (d), in analogy to (c), presents an equal section of a magnetocaloric double-cylindrical rotary wheel machine. A magnetocaloric alloy flows over the fixed boundaries in the direction of the black arrows.

$$\mathrm{d}u_1 = T\mathrm{d}s - \mu_0\vec{H}_0\mathrm{d}\vec{M} \tag{23}$$

3. Thermodynamic potentials and Maxwell relations

3.1. Brief introduction

The starting point for the study in this chapter is the redefined internal energy, which is presented by Eq. (23). By applying Legendre transformations [30], the thermodynamic potentials which are presented in the following subchapters are obtained.

3.2. Specific enthalpy

The specific enthalpy is the potential to describe the behaviour of an open system with work performed over its boundary:

$$h_1 = u_1 + \mu_0 H_0 M \tag{24}$$

where again for simplicity the vectorial denotation has been substituted by the one-dimensional equivalent. The derivative of this potential is:

$$\mathrm{d}h_1 = \mathrm{d}u_1 + \mu_0 H_0 \mathrm{d}M + \mu_0 M \mathrm{d}H_0 \tag{25}$$

Inserting (23) it follows that:

$$\mathrm{d}h_1(s, H_0) = \left(\frac{\partial h_1}{\partial s}\right)_{H_0}\mathrm{d}s + \left(\frac{\partial h_1}{\partial H_0}\right)_s \mathrm{d}H_0 = T\mathrm{d}s + \mu_0 M \mathrm{d}H_0 \tag{26}$$

The derivatives are:

$$\left(\frac{\partial h_1}{\partial s}\right)_{H_0} = T \tag{27a}$$

$$\left(\frac{\partial h_1}{\partial H_0}\right)_s = \mu_0 M \tag{27b}$$

The Maxwell relation is given by the cross-relation:

$$\left[\frac{\partial}{\partial H_0}\left(\frac{\partial h_1}{\partial s}\right)_{H_0}\right]_s = \left[\frac{\partial}{\partial s}\left(\frac{\partial h_1}{\partial H_0}\right)_s\right]_{H_0} \tag{28}$$

By inserting the results of (27a) and (27b), we obtain:

$$\left(\frac{\partial T}{\partial H_0}\right)_s = \mu_0\left(\frac{\partial M}{\partial s}\right)_{H_0} \tag{29}$$

3.3. Specific Helmholtz energy

The specific free energy or Helmholtz energy is accurate in describing an open system with a flux of heat over its boundary:

$$f_1 = u_1 - Ts \tag{30}$$

Differentiation and inserting (23) leads to:

$$\mathrm{d}f_1(T, M) = -s\mathrm{d}T - \mu_0 H_0 \mathrm{d}M \tag{31}$$

It then follows that:

$$\left(\frac{\partial f_1}{\partial T}\right)_M = -s \tag{32a}$$

and

$$\left(\frac{\partial f_1}{\partial M}\right)_T = -\mu_0 H_0 \tag{32b}$$

By analogy to Eq. (28) in Section 3.1, applying Eqs. (32a) and (32b), the following Maxwell relation is determined:

$$\left[\frac{\partial}{\partial M}\left(\frac{\partial f_1}{\partial T}\right)_M\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial f_1}{\partial M}\right)_T\right]_M \Rightarrow \left(\frac{\partial s}{\partial M}\right)_T = \mu_0\left(\frac{\partial H_0}{\partial T}\right)_M \tag{33}$$

3.4. Specific Gibbs energy

The specific Gibbs energy is the potential to describe a system with some work performed over the boundary and with a heat flux crossing it:

$$g_1 = f_1 + \mu_0 H_0 M \tag{34}$$

Differentiation and inserting (31) leads to:

$$\mathrm{d}g_1(T, H_0) = -s\mathrm{d}T + \mu_0 M \mathrm{d}H_0 \tag{35}$$

The derivatives are:

$$\left(\frac{\partial g_1}{\partial T}\right)_{H_0} = -s \tag{36a}$$

$$\left(\frac{\partial g_1}{\partial H_0}\right)_T = \mu_0 M \tag{36b}$$

From Eqs. (27b) and (36b) it follows that:

$$\left(\frac{\partial h_1}{\partial H_0}\right)_s = \left(\frac{\partial g_1}{\partial H_0}\right)_T \tag{37}$$

By analogy to Section 3.1, with Eqs. (36a) and (36b), a further Maxwell relation is determined:

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial g_1}{\partial H_0}\right)_T\right]_{H_0} = \left[\frac{\partial}{\partial H_0}\left(\frac{\partial g_1}{\partial T}\right)_{H_0}\right]_T \Rightarrow \left(\frac{\partial M}{\partial T}\right)_{H_0} = -\frac{1}{\mu_0}\left(\frac{\partial s}{\partial H_0}\right)_T \tag{38}$$

Numerous further relations may be derived by transforming variables and writing them as functions of other independent variables. But these can be readily found with the existing basic relations, given in the previous subsections.

4. Susceptibilities

The (derivative) adiabatic susceptibility is defined by:

$$\chi'_s = \left(\frac{\partial M}{\partial H_0}\right)_s \tag{39}$$

Now Eq. (27b) is introduced to obtain:

$$\chi'_s = \frac{1}{\mu_0}\left(\frac{\partial^2 h_1}{\partial H_0}\right)_s \tag{40}$$

The (derivative) isothermal magnetic susceptibility is defined in an analogous manner:

$$\chi'_T = \left(\frac{\partial M}{\partial H_0}\right)_T \tag{41}$$

With Eq. (36b) we obtain:

$$\chi'_T = \frac{1}{\mu_0}\left(\frac{\partial^2 g_1}{\partial H_0}\right)_T \tag{42}$$

Only in the case where the magnetization M is proportional to the field H_0, and the demagnetization factor N (Appendix B, Eq. (B.2)) vanishes does it follow that:

$$\chi'_\alpha = \left(\frac{\partial M}{\partial H_0}\right)_\alpha = \text{const}, \quad \alpha \in \{s, T\} \tag{S-43}$$

and

$$B = \mu_0(H + M) = \mu_0\left[H_0 + \left(\frac{\partial M}{\partial H_0}\right)_\alpha H_0\right]$$
$$= \mu_0(1 + \chi'_\alpha)H_0, \quad \alpha \in \{s, T\} \tag{S-44}$$

With the relative magnetic permeabilities, which are also constants of proportionality:

$$\mu_\alpha = (1 + \chi'_\alpha), \quad \alpha \in \{s, T\} \tag{S-45}$$

it follows for adiabatic and isothermal processes that:

$$B = \mu_\alpha \mu_0 H_0, \quad \alpha \in \{s, T\} \tag{S-46}$$

5. Specific heat capacities

Following Ref. [2], the alteration of the heat in a magnetic material in terms of differential increments is written by introducing two specific heat capacities:

$$\mathrm{d}q = c_{H_0}(T, H_0)\mathrm{d}T + c_T(T, H_0)\mathrm{d}H_0 \tag{47}$$

The quantity c_{H_0} denotes the specific heat at constant field H_0. This is (particularly if $H_0 = 0$) the usual specific heat capacity. In cases treated in this article, it is concluded that: $c_{H_0} = c_V = c_p$.

From Eq. (47) it is immediately found that:

$$c_{H_0} = \left(\frac{\partial q}{\partial T}\right)_{H_0} \tag{48}$$

Substituting (21), we obtain:

$$c_{H_0} = T\left(\frac{\partial s}{\partial T}\right)_{H_0} \tag{49}$$

Inserting Eq. (36a) leads to:

$$c_{H_0} = -T\left(\frac{\partial^2 g_1}{\partial T^2}\right)_{H_0} \tag{50}$$

This relation is very similar to the susceptibilities (Eqs. (40) and (42)). A concave Gibbs energy leads also to a positive value of c_{H_0} and guarantees the stability of the thermodynamic system. The second condition is also derived from Eq. (47):

$$c_T = \left(\frac{\partial q}{\partial H_0}\right)_T \tag{51}$$

Again (21) is substituted to obtain:

$$c_T = T\left(\frac{\partial s}{\partial H_0}\right)_T \tag{52}$$

Applying Maxwell relation (38), the following result is derived:

$$c_T(T, H_0) = -\mu_0 T\left(\frac{\partial M}{\partial T}\right)_{H_0} \tag{53}$$

This result was presented earlier by Rosensweig [2], but with an alternative concept for its derivation. Furthermore, he gives the following result:

$$\frac{1}{\mu_0}\left(\frac{\partial c_{H_0}}{\partial H_0}\right)_T = T\left(\frac{\partial^2 M}{\partial T^2}\right)_{H_0} \tag{54}$$

In our presentation this relation is easily obtained by just considering the derivative of c_{H_0} in Eq. (49) in the order of the field H_0 at constant temperature:

$$\frac{1}{\mu_0}\left(\frac{\partial c_{H_0}}{\partial H_0}\right)_T = \frac{1}{\mu_0}\frac{\partial}{\partial H_0}\left[T\left(\frac{\partial s}{\partial T}\right)_{H_0}\right]_T$$
$$= T\frac{\partial}{\partial T}\left[\frac{1}{\mu_0}\left(\frac{\partial s}{\partial H_0}\right)_T\right]_{H_0} = -T\left(\frac{\partial^2 M}{\partial T^2}\right)_{H_0} \tag{55}$$

where Eq. (38) was inserted, q.e.d.

Note that these specific heat capacities are volumetric quantities. In engineering they are usually defined per mass unit. Division by the density ρ of the material leads to the more frequently applied physical properties.

6. Specific entropies and specific heat capacities

The specific entropy s in a magnetocaloric material is a combination of the specific magnetic entropy $s^{(\mathrm{m})}$, the specific lattice subsystem entropy $s^{(\mathrm{l})}$ and the specific entropy of the conduction electrons $s^{(\mathrm{e})}$. If we consider it as a function of T and H_0, it follows [11] that:

$$s(T, H_0) = s^{(\mathrm{m})}(T, H_0) + s^{(\mathrm{l})}(T, H_0) + s^{(\mathrm{e})}(T, H_0) \tag{56}$$

In previous sections we did not focus on each of the entropy contributions and only worked with the total specific entropy s. Separation of the specific entropy into three components is correct for some rare-earth materials, e.g. gadolinium (Gd). But for other substances—e.g. those which show a 3d transition, such as materials based on manganese (Mn)—such a superposition is not accurate. According to Tishin [11] the three entropy contributions depend on the temperature and the magnetic field and cannot be clearly separated. For most engineering applications it is sufficient to work with the total specific entropy. Its differential is:

$$\mathrm{d}s(T,H_0) = \left(\frac{\partial s}{\partial T}\right)_{H_0}\mathrm{d}T + \left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0 \tag{57}$$

The total specific heat capacity at constant magnetic field H_0 (Eqs. (49) and (56)):

$$\begin{aligned} c_{H_0} &= T\left[\frac{\partial}{\partial T}(s^{(\mathrm{m})} + s^{(\mathrm{l})} + s^{(\mathrm{e})})\right]_{H_0} \\ &= T\left(\frac{\partial s^{(\mathrm{m})}}{\partial T}\right)_{H_0} + T\left(\frac{\partial s^{(\mathrm{l})}}{\partial T}\right)_{H_0} + T\left(\frac{\partial s^{(\mathrm{e})}}{\partial T}\right)_{H_0} \\ &= c^{(\mathrm{m})}_{H_0} + c^{(\mathrm{l})}_{H_0} + c^{(\mathrm{e})}_{H_0} \end{aligned} \tag{58}$$

can be also separated into three different specific heats.

7. Some useful relations for the study of cycles

Materials scientists frequently measure and publish specific heat capacities. By application of Eq. (49), the entropy densities at constant magnetic field are derived from these quantities:

$$\left(\frac{\partial s}{\partial T}\right)_{H_0} = \frac{c_{H_0}}{T} \Rightarrow s(T,H_0) = s_0 + \int_0^T \frac{c_{H_0}}{\sigma}\mathrm{d}\sigma \tag{59}$$

where s_0 denotes the specific entropy at the absolute zero point of the temperature ($T=0$ K), which is by definition equal to zero.

In gas thermodynamics the specific heat capacity is defined as the temperature derivative of the specific enthalpy at constant pressure. The analogy for magnetic refrigeration is a derivative of the total specific enthalpy at constant magnetic field H_0 (compare to Eq. (27a)):

$$\mathrm{d}h_1 = T\mathrm{d}s \tag{60}$$

The specific enthalpy at constant magnetic field is calculated by:

$$h_1 = h_1^{(0)} + \int_0^T \left(\frac{\partial h_1}{\partial T}\right)_{H_0}\mathrm{d}T \tag{61}$$

The temperature derivative of the specific enthalpy is:

$$\left(\frac{\partial h_1}{\partial T}\right)_{H_0} = T\left(\frac{\partial s}{\partial T}\right)_{H_0} = c_{H_0} \tag{62}$$

where (49) and (60) were introduced. Now it is straightforward to obtain from (61) with (62):

$$h_1 = h_1^{(0)} + \int_0^T c_{H_0}(\sigma)\mathrm{d}\sigma \tag{63}$$

The enthalpy $h_1^{(0)}$ is usually set equal to zero. The distributions of the specific heat capacities of magnetocaloric alloys are usually not Dirac distributions; they show a finite width. These kinds of continuous phase transitions are very well represented by enthalpy methods. A macroscopic model for continuous phase transitions—based on an enthalpy concept—was published in 1994 by Egolf and Manz [31].

By applying Eq. (62) the specific entropy is determined from the specific heat in a constant magnetic field:

$$s = s_0 + \int_0^T \left(\frac{\partial s}{\partial \sigma}\right)_{H_0}\mathrm{d}\sigma = s_0 + \int_0^T \frac{c_{H_0}}{\sigma}\mathrm{d}\sigma \tag{64}$$

where the specific entropy s_0 at the zero point is also set equal to zero.

8. Isothermal magnetization and demagnetization

There are a large number of possible magnetic refrigeration cycles. The three basic cycles, the Brayton, Ericsson, and Carnot cycles are described in the succeeding chapters. Some preparatory work on partial processes of cycles is presented in the present section and the next section.

In the Ericsson cycle—and partly in the Carnot cycle—magnetization and demagnetization are isothermal processes. The temperature does not change during the alteration of the volumetric magnetic flux. Substituting the derivative of the specific entropy for $T=$const (Eq. (57)) into Eq. (26) leads to:

$$\mathrm{d}h_1(s,H_0) = T\left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0 + \mu_0 M \mathrm{d}H_0 \tag{65}$$

By applying Eqs. (38) and (53) this equation is rewritten:

$$\begin{aligned} \mathrm{d}h_1(s,H_0) &= \mu_0\left[-T\left(\frac{\partial M}{\partial T}\right)_{H_0} + M\right]\mathrm{d}H_0 \\ &= (c_T + \mu_0 M)\mathrm{d}H_0 \end{aligned} \tag{66}$$

The alteration of the specific entropy during an isothermal alteration of the volumetric magnetic flux is calculated by applying Eqs. (38) and (53):

$$\Delta s = s(2) - s(1) = \int_{s(1)}^{s(2)} \mathrm{d}s(T) = \int_{H_0^{(1)}}^{H_0^{(2)}} \left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0$$

$$= -\int_{H_0^{(1)}}^{H_0^{(2)}} \mu_0 \left(\frac{\partial M}{\partial T}\right)_{H_0} \mathrm{d}H_0 = \int_{H_0^{(1)}}^{H_0^{(2)}} \frac{c_T}{T} \mathrm{d}H_0 \tag{67}$$

where $s(1)$ is the specific entropy at the field $H_0^{(1)}$ and $s(2)$ at $H_0^{(2)}$. Eq. (67) was derived with the assumption that the lattice and the electronic entropy are not functions of the magnetic field. The specific magnetic entropy alteration then corresponds to the alteration of the total specific entropy.

9. Adiabatic magnetization and demagnetization

For adiabatic magnetization—as occurs in the Brayton and in the Carnot cycle—the differential of the specific enthalpy is derived from Eq. (26):

$$\mathrm{d}h_1(s, H_0) = \mu_0 M \mathrm{d}H_0 \tag{68}$$

In an adiabatic process the total specific entropy does not alter ($\mathrm{d}s = 0$). From Eq. (57) it follows that:

$$\left(\frac{\partial s}{\partial T}\right)_{H_0} \mathrm{d}T = -\left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0 \tag{69}$$

By substituting Eqs. (49) and (52) into (69) a further relation is obtained:

$$\mathrm{d}T = -\frac{c_T}{c_{H_0}} \mathrm{d}H_0 \tag{70}$$

Inserting Eq. (53) into (70) the magnetization is introduced:

$$\frac{\mathrm{d}T}{T} = \frac{\mu_0}{c_{H_0}} \left(\frac{\partial M}{\partial T}\right)_{H_0} \mathrm{d}H_0 \tag{71}$$

According to Pecharsky and Gschneidner [32] the integration of Eq. (71) is problematic, because the thermodynamic measurement of c_{H_0} has a much longer characteristic time than the magnetic measurement of M. With knowledge of the temperature as a function of the specific entropy for different isomagnetic fields, it is more convenient to perform the following integration:

$$\Delta T = \int_{T^{(1)}}^{T^{(2)}} \mathrm{d}T = T^{(2)}(s, H_0^{(2)}) - T^{(1)}(s, H_0^{(1)}) \tag{72}$$

where $T^{(2)}(s, H_0^{(2)})$ is the temperature of the magnetocaloric material at the higher magnetic field $H_0^{(2)}$ and $T^{(1)}(s, H_0^{(1)})$ at the lower field intensity, both evaluated at the same specific entropy. Eq. (71) shows that the temperature will increase in the case where the magnetocaloric material is moved from a lower to a higher field and vice-versa. Note that there are antiferromagnetic materials which exhibit an inverse magnetocaloric effect [11]. As noted by Gschneidner and Pecharsky [32], application of Eq. (71) may lead to small errors, because the specific entropy at the zero point is neglected. A comprehensive description of this effect and other errors which occur can be found in [32]. It should be noted that in most articles only the temperature increase ΔT of the heating case is presented, because the cooling case may be derived from these data. In Fig. 3 the absolute values of the positive and the negative temperature difference $|\Delta T_{\mathrm{ad}}|$ of an adiabatic magnetization and demagnetization process are presented. The data were taken from Ref. [17]. For example, if the temperature occurring without a magnetic field ($H_0 = 0$) is $T^{(1)} = 286$ K, then the adiabatic temperature increase due to the adjustment of a magnetic field $H_0^{(2)} = 7.958 \times 10^5$ A/m (this corresponds to $\mu_0 H_0^{(2)} = 5T$) will lead to a temperature of approximately $T^{(2)} = 301$ K. On the other hand, if the magnetocaloric material is initially in a magnetic field of strength $H_0^{(2)} = 7.958 \times 10^5$ A/m, at $T^{(2)} = 301$ K, the alteration of $H_0^{(2)}$ to $H_0^{(1)} = 0$ cools the sample to $T^{(1)} = 286$ K.

10. Cyclic processes

To build new continuously operating magnetic refrigerators and heat pumps, it is favourable to begin with the study of the work, the heat fluxes and coefficients of performance of cyclic processes. For any kind of magnetic refrigeration cycles, the cyclic integral of the equivalent of Eq. (1) for specific properties leads to:

$$\oint \mathrm{d}u_1 = \oint \mathrm{d}q + \oint \mathrm{d}w_1 = 0 \tag{73}$$

where w_1 without a further superscript always refers to the external work. The reason for the validity of Eq. (73) is that the internal energy is a state function and that after a cycle it

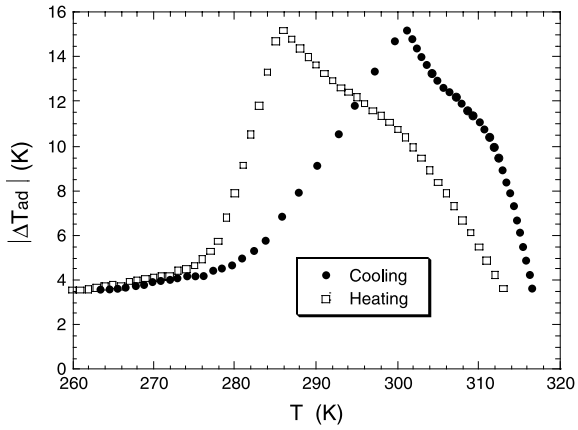

Fig. 3. Heating of the magnetocaloric material $Gd_5(Si_{1.985}Ge_{1.985}Ga_{0.03})$ is shown by the curve with a maximum on the left-hand side (from Ref. [17]). The cooling case, with a negative adiabatic temperature difference (presented with the opposite sign), has its maximum on the right. This second case was created with the data of the heating case.

reaches the same point and, therefore, must show the same value again. It then follows that:

$$\oint \mathrm{d}w_1 = -\oint \mathrm{d}q \tag{74}$$

In the following treatments only the work contributions for the magnetization of the magnetocaloric material are investigated. Other contributions—e.g. the work performed to accelerate a rotating wheel, etc.—are not referred to, because in most systems these contributions are negligible or do not occur. Then, by applying Eq. (22), the cyclic work is given by:

$$\oint \mathrm{d}w_1 = -\mu_0 \oint H_0 \mathrm{d}M \tag{75}$$

In a cyclic process the following total differential also vanishes:

$$\oint \mathrm{d}(M, H_0) = \oint M \mathrm{d}H_0 + \oint H_0 \mathrm{d}M = 0 \tag{76}$$

Eq. (75) is therefore rewritten:

$$\oint \mathrm{d}w_1 = \mu_0 \oint M \mathrm{d}H_0 \Rightarrow \oint \mathrm{d}w_1^{(ext)} = \oint \mathrm{d}w_1^{(tech)} \tag{77}$$

Eq. (77) follows by comparing (75) with (77) and remembering Eqs. (17) and (18). For a reversible process the cyclic work can be also represented by the temperature and specific entropy by substituting (21) into (74):

$$\oint \mathrm{d}w_1 = -\oint T \mathrm{d}s \tag{78}$$

11. The Brayton cycle

Fig. 4 shows the Brayton cycle, which is one of the most basic cycles of magnetic refrigeration. A machine based on this cycle operates between two isofields (constant magnetic fields H_0) and two isentropic curves (constant total specific entropy s). When a magnetocaloric material is moved into a magnetic field (process 1–2), the total entropy remains constant. But due to the adiabatic magnetization ($\Delta H_0 = H_0^{(2)} - H_0^{(1)}$), the temperature in the magnetocaloric material increases. At this higher temperature heat is rejected from the material (2–3). In the adiabatic demagnetization process (3–4) the magnetocaloric material cools down. In the last stage (4–1) heat can be absorbed from a heat source, leading to the cooling of an external device. The cyclic work of the Brayton cycle is described by applying Eq. (77):

$$w_1 = \oint \mathrm{d}w_1 = \mu_0 \oint M \mathrm{d}H_0$$

$$= \mu_0 \int_1^2 M \mathrm{d}H_0 + \mu_0 \int_3^4 M \mathrm{d}H_0 \tag{79}$$

Eq. (79) follows, because the analogous integrals of the

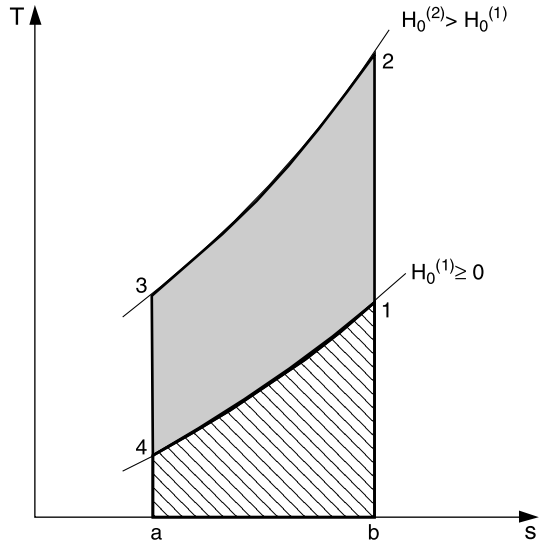

Fig. 4. The Brayton cycle follows two isomagnetic field lines (H_0 = const) and two adiabatic curves (s = const).

two isofield processes (2–3) and (4–1) vanish. Note that the integral boundaries are actually defined by their physical states, e.g. $H_0^{(1)}$ and $H_0^{(2)}$, and not simply by the corresponding integer numbers 1 and 2, which here have been introduced as abbreviations.

The adiabatic magnetization or demagnetization process has been examined in Section 9. In the adiabatic case ($\mathrm{d}s = 0$) it follows from Eq. (68) that:

$$\int \mathrm{d}h_1 = \mu_0 \int M \mathrm{d}H_0 \tag{S-80}$$

Comparing this equation with Eq. (77), it is concluded that the work is equal to the enthalpy difference:

$$\int \mathrm{d}w_1 = \int \mathrm{d}h_1 \tag{S-81}$$

An alteration of the magnetic field only occurs in the processes (1–2) and (3–4). By applying Eqs. (69) and (79) it follows:

$$w_1 = \int_1^2 \mathrm{d}h_1 + \int_3^4 \mathrm{d}h_1 = [h_1^{(2)} - h_1^{(1)}] + [h_1^{(4)} - h_1^{(3)}] \tag{82}$$

In another approach, following Eq. (78), we obtain:

$$w_1 = -\int_2^3 T \mathrm{d}s - \int_4^1 T \mathrm{d}s \tag{83}$$

because now the other pair of integrals, namely those of the processes (1–2) and (3–4), are zero. The processes (2–3) and (4–1) are isomagnetic field processes ($\mathrm{d}H_0 = 0$). The derivative of the specific entropy (Eq. (57)) is:

$$\mathrm{d}s = \left(\frac{\partial s}{\partial T}\right)_{H_0} \mathrm{d}T \tag{84}$$

Substituting (49) and (84) into (83) results in:

$$w_1 = -\int_2^3 c_{H_0}\mathrm{d}T - \int_4^1 c_{H_0}\mathrm{d}T \tag{85}$$

Eq. (62) shows that the cyclic work may be also described by the specific enthalpy:

$$w_1 = -\int_2^3 \left(\frac{\partial h_1}{\partial T}\right)_{H_0}\mathrm{d}T - \int_4^1 \left(\frac{\partial h_1}{\partial T}\right)_{H_0}\mathrm{d}T \tag{86}$$

Because the enthalpy difference in an isomagnetic field is only temperature-dependent, it follows that:

$$\begin{aligned} w_1 &= [h_1^{(2)} - h_1^{(3)}] - [h_1^{(1)} - h_1^{(4)}] \\ &= [h_1^{(2)} - h_1^{(1)}] + [h_1^{(4)} - h_1^{(3)}] \end{aligned} \tag{87}$$

in agreement with (82). An important criterion to evaluate technical systems is the coefficient of performance (COP), which in a refrigeration application represents the ratio of the cooling energy q_c to the work w_1 which has to be performed:

$$\mathrm{COP} = \frac{q_c}{w_1} \tag{88}$$

Applying this to the Brayton cycle, it follows that:

$$q_c = \int_4^1 T\mathrm{d}s \tag{89a}$$

$$q_r = \int_2^3 T\mathrm{d}s \tag{89b}$$

$$w_1 = -q_r - q_c \tag{89c}$$

where (89c) is a consequence of Eqs. (83), (89a) and (89b). Here q_r describes the heat rejected from the system ($q_r < 0$). Applying partial results of Eqs. (83)–(87), the following final result is obtained:

$$\mathrm{COP}_{\mathrm{Brayton}} = \frac{[h_1^{(1)} - h_1^{(4)}]}{[h_1^{(2)} - h_1^{(1)}] + [h_1^{(4)} - h_1^{(3)}]} \tag{90}$$

12. The Ericsson cycle

A machine based on the Ericsson cycle operates along two isotherms and two isomagnetic field lines. This process requires heat regeneration. During the isomagnetic field process (1–2) heat is absorbed by regeneration from the opposite side (3–4). Therefore, in ideal regeneration—the area (2–1–b–d), representing thermal energy absorption from the magnetocaloric material has to correspond to (3–4–a–c), representing the heat extraction of the refrigerant material. The regeneration can only be driven by a temperature difference. The heat transfer represents an irreversible process and, therefore, decreases the efficiency of the Ericsson machine. A simultaneous alteration of the magnetic field and heat absorption, or rejection, leads to the isothermal processes (2–3) and (4–1). The area (1–2–3–4) represents the work required for the Ericsson cycle and the area (1–4–a–b) is identical to the cooling energy.

In Fig. 5 an ideal Ericsson magnetic refrigeration cycle is presented. Its cyclic work is derived by applying Eq. (77):

$$\oint \mathrm{d}w_1 = \mu_0 \int_2^3 M\mathrm{d}H_0 + \mu_0 \int_4^1 M\mathrm{d}H_0 \tag{91}$$

Two integrals, namely those related to the isomagnetic field processes (1–2) and (3–4), again vanish. Since the integrals presented in Eq. (91) refer to isotherms, it is concluded that:

$$w_1 = \mu_0 \int_1^4 [M(H_0, T^{(2)}) - M(H_0, T^{(1)})]\mathrm{d}H_0 \tag{92}$$

Substituting the integrands in Eq. (91) by Eq. (27b) the work is also:

$$\begin{aligned} w_1 &= \int_2^3 \left(\frac{\partial h_1}{\partial H_0}\right)_s \mathrm{d}H_0 + \int_4^1 \left(\frac{\partial h_1}{\partial H_0}\right)_s \mathrm{d}H_0 \\ &= [h_1^{(3)} - h_1^{(2)}] - [h_1^{(4)} - h_1^{(1)}] - T^{(2)}[s^{(3)} - s^{(2)}] \\ &\quad - T^{(1)}[s^{(1)} - s^{(4)}] \end{aligned} \tag{93}$$

An alternative approach to calculating the cyclic work of the Ericsson cycle involves application of the cyclic integral of heat, Eq. (78), and by substituting Eq. (57):

$$\begin{aligned} w_1 &= -\int_1^2 T\left(\frac{\partial s}{\partial T}\right)_{H_0}\mathrm{d}T - \int_2^3 T\left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0 \\ &\quad - \int_3^4 T\left(\frac{\partial s}{\partial T}\right)_{H_0}\mathrm{d}T - \int_4^1 T\left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0 \end{aligned} \tag{94}$$

Furthermore, it follows with Eqs. (49) and (52) that:

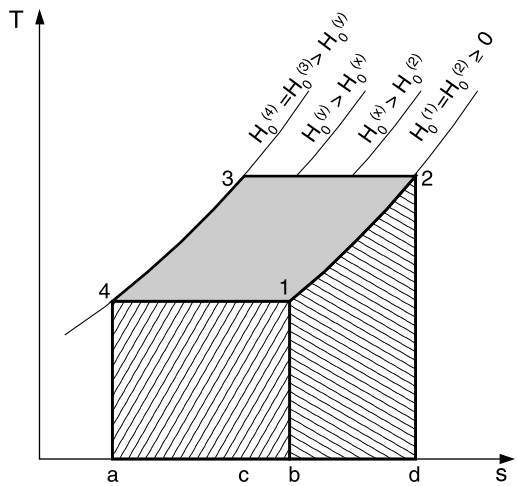

Fig. 5. The Ericsson cycle may operate with heat regeneration. In an ideal case no heat losses occur.

$$w_1 = -\int_1^2 c_{H_0}\mathrm{d}T - \int_2^3 c_T\mathrm{d}H_0 - \int_3^4 c_{H_0}\mathrm{d}T - \int_4^1 c_T\mathrm{d}H_0 = -\int_1^2 \mathrm{d}h_1 - \int_3^4 \mathrm{d}h_1 - \int_2^3 c_T\mathrm{d}H_0 - \int_4^1 c_T\mathrm{d}H_0 \quad (95)$$

Inserting c_T given by Eq. (66), we obtain:

$$w_1 = -\int_1^2 \mathrm{d}h_1 - \int_3^4 \mathrm{d}h_1 - \int_2^3 \mathrm{d}h_1 + \mu_0\int_2^3 M\mathrm{d}H_0 - \int_4^1 \mathrm{d}h_1 + \mu_0\int_4^1 M\mathrm{d}H_0 \quad (96)$$

The four integrals with specific enthalpy differentials add up to the cyclic integral of the specific enthalpy and are therefore disregarded:

$$w_1 = -\mu_0\int_1^4 M\mathrm{d}H_0 + \mu_0\int_2^3 M\mathrm{d}H_0 \quad (97)$$

which is identical to Eq. (91). The specific cooling energy is calculated by substituting Eqs. (52) and (53) into (89a):

$$q_\mathrm{c} = T^{(1)}\int_4^1 \left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0 = \int_4^1 c_T\mathrm{d}H_0 = -\mu_0 T^{(1)}\int_4^1 \left(\frac{\partial M}{\partial T}\right)_{H_0}\mathrm{d}H_0 \quad (98)$$

Because the temperature in isothermal magnetization and demagnetization is constant, and therefore not a function of the specific entropy, the specific cooling energy is calculated by:

$$q_\mathrm{c} = T^{(1)}[s^{(1)} - s^{(4)}] = T^{(1)}[s(T^{(1)}, H_0^{(1)}) - s(T^{(4)}, H_0^{(4)})], \quad T^{(4)} = T^{(1)} \quad (99)$$

In an analogous manner the rejected specific heat of the system is determined (Eq. (89b)):

$$q_\mathrm{r} = T^{(2)}\int_2^3 \left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0 = \int_2^3 c_T\mathrm{d}H_0 = -\mu_0 T^{(2)}\int_2^3 \left(\frac{\partial M}{\partial T}\right)_{H_0}\mathrm{d}H_0 \quad (100)$$

and

$$q_\mathrm{r} = T^{(2)}[s^{(3)} - s^{(2)}] = T^{(2)}[s(T^{(3)}, H_0^{(3)}) - s(T^{(2)}, H_0^{(2)})], \quad T^{(3)} = T^{(2)} \quad (101)$$

From Eqs. (52) and (94) we derive:

$$w_1 = [h_1^{(1)} - h_1^{(4)}] - T^{(1)}[s^{(1)} - s^{(4)}] + [h_1^{(3)} - h_1^{(2)}] - T^{(2)}[s^{(3)} - s^{(2)}] \quad (102)$$

The COP of the Ericsson cycle is obtained by substituting (99) and (102) into (88):

$$\mathrm{COP}_\mathrm{Ericsson} = \frac{q_\mathrm{c}}{w_1} = \frac{T^{(1)}[s^{(1)} - s^{(4)}]}{[h_1^{(1)} - h_1^{(4)}] - T^{(1)}[s^{(1)} - s^{(4)}] + [h_1^{(3)} - h_1^{(2)}] - T^{(2)}[s^{(3)} - s^{(2)}]} \quad (103)$$

An alternative formula, containing the magnetization, is developed by substituting Eqs. (92) and (98) into (88):

$$\mathrm{COP}_\mathrm{Ericsson} = \frac{T^{(1)}\int_4^1 \left(\frac{\partial M}{\partial T}\right)_{H_0}\mathrm{d}H_0}{\left|\int_1^4 [M(H_0,\ T^{(1)}) - M(H_0, T^{(2)})]\mathrm{d}H_0\right|} \quad (104)$$

In the case that processes (1–2) and (3–4) refer to ideal regeneration, it follows with Eq. (49) that:

$$\int_1^2 T\left(\frac{\partial s}{\partial T}\right)_{H_0}\mathrm{d}T = -\int_3^4 T\left(\frac{\partial s}{\partial T}\right)_{H_0}\mathrm{d}T \Rightarrow \int_1^2 c_{H_0}\mathrm{d}T = -\int_3^4 c_{H_0}\mathrm{d}T \quad (S\text{-}105)$$

By introducing the specific enthalpies, we obtain:

$$h_1^{(2)} - h_1^{(1)} = h_1^{(3)} - h_1^{(4)} \quad (S\text{-}106)$$

With this result Eq. (103) is simplified:

$$\mathrm{COP}_\mathrm{Ericsson} = \frac{q_\mathrm{c}}{w_1} = \frac{T^{(1)}[s^{(1)} - s^{(4)}]}{-T^{(1)}[s^{(1)} - s^{(4)}] - T^{(2)}[s^{(3)} - s^{(2)}]} \quad (S\text{-}107)$$

Studying the following limit:

$$\lim_{T^{(2)}\to T^{(1)}} \mathrm{COP}_\mathrm{Ericsson} = \frac{T^{(1)}}{T^{(2)} - T^{(1)}} = \mathrm{COP}_\mathrm{Carnot} \quad (S\text{-}108)$$

because $s^{(2)}$ approaches $s^{(1)}$ and $s^{(3)}$ tends toward $s^{(4)}$, so that the brackets in (S-107) cancel out. Within this limit the work performed vanishes and the COP becomes infinitely large. The Carnot system will be discussed in more detail in the next section.[3]

13. The Carnot cycle

In the Carnot cycle an adiabatic magnetization occurs in process (1–2) (Fig. 6). It continues with a further magnetization in stage (2–3), which is now an isothermal

[3] If the regeneration is reversible (ideal) then in Fig. 5 the processes (1, 2) and (4, 3) are parallel. This also leads to a limit of $\mathrm{COP}_\mathrm{Brayton}$ equal to $\mathrm{COP}_\mathrm{Carnot}$, which in this case may even be finite.

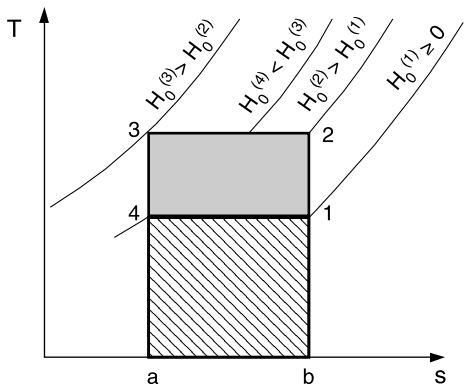

Fig. 6. The Carnot cycle operates with mixed processes of alteration of the magnetization in an altering field and heat absorption or rejection.

magnetization. During this process generated heat is extracted from the system. The next process step, namely (3–4), is an adiabatic demagnetization process. Connecting the system with a heat source leads to an isothermal demagnetization, resulting in process (4–1). It becomes clear that the Carnot cycle can only be run, if a minimum of four different magnetic fields occur, through which the magnetocaloric material is moved. In the vertical process 1–2 the alteration of the magnetic field has to apply quickly, not allowing heat to diffuse away or be transported out by convection. In (2–3) the isothermal magnetization requires an alteration of the magnetic field and simultaneous rejection of heat. This process will therefore be slower. The area between (1–2–3–4) represents the work required and the area (1–4–a–b) is related to the thermal cooling energy.

In Fig. 6 a Carnot cycle is presented. The cyclic work is calculated by:

$$w_1 = \mu_0 \int_1^2 M \mathrm{d}H_0 + \mu_0 \int_2^3 M \mathrm{d}H_0 + \mu_0 \int_3^4 M \mathrm{d}H_0 + \mu_0 \int_4^1 M \mathrm{d}H_0 \tag{109}$$

With Eq. (27b) (107) is transformed to:

$$w_1 = \int_1^2 \left(\frac{\partial h_1}{\partial H_0}\right)_s \mathrm{d}H_0 + \int_2^3 \left(\frac{\partial h_1}{\partial H_0}\right)_s \mathrm{d}H_0 + \int_3^4 \left(\frac{\partial h_1}{\partial H_0}\right)_s \mathrm{d}H_0 + \int_4^1 \left(\frac{\partial h_1}{\partial H_0}\right)_s \mathrm{d}H_0 \tag{110}$$

Because the derivative of specific enthalpy in an adiabatic magnetization or demagnetization process is not dependent on the specific entropy, we obtain:

$$w_1 = \int_1^2 \mathrm{d}h_1 + \int_2^3 \left(\frac{\partial h_1}{\partial H_0}\right)_s \mathrm{d}H_0 + \int_3^4 \mathrm{d}h_1 + \int_4^1 \left(\frac{\partial h_1}{\partial H_0}\right)_s \mathrm{d}H_0 \tag{111}$$

Now the second and the fourth terms are replaced, using the total differential of the specific enthalpy (Eq. (26)). Because the cyclic integral of the specific enthalpy vanishes, Eq. (111) simplifies to:

$$w_1 = -\int_2^3 \left(\frac{\partial h_1}{\partial s}\right)_{H_0} \mathrm{d}s - \int_4^1 \left(\frac{\partial h_1}{\partial s}\right)_{H_0} \mathrm{d}s \tag{112}$$

Because the partial derivatives in Eq. (112) are identical to the temperature T (Eq. (27a)), and the temperature in an isothermal process is not dependent on the specific entropy, it follows that:

$$\begin{aligned} aw_1 &= -\int_2^3 T \mathrm{d}s - \int_4^1 T \mathrm{d}s \\ &= [T^{(2)} - T^{(1)}][s^{(1)} - s^{(4)}], \quad s^{(1)} - s^{(4)} \\ &= s^{(2)} - s^{(3)} \end{aligned} \tag{113}$$

Now the cyclic work is developed with the circle integral of the specific heat (compare with Eq. (74)). Additionally, Eq. (52) is substituted:

$$\begin{aligned} w_1 &= -\int_2^3 T \left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0 - \int_4^1 T \left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0 \\ &= -\int_2^3 c_T \mathrm{d}H_0 - \int_4^1 c_T \mathrm{d}H_0 \end{aligned} \tag{114}$$

Eq. (114) is rewritten:

$$w_1 = \int_1^4 [c_T(H_0, T^{(1)}) - c_T(H_0, T^{(2)})] \mathrm{d}H_0 \tag{115}$$

Combining Eq. (114) with (52) leads to:

$$\begin{aligned} w_1 &= T^{(1)} \int_1^4 \mathrm{d}s - T^{(2)} \int_2^3 \mathrm{d}s \\ &= [T^{(2)} - T^{(1)}][s^{(1)} - s^{(4)}] \end{aligned} \tag{116}$$

Eq. (116) is identical to Eq. (113). The specific cooling energy is (compare with Eq. (52)):

$$q_c = \int_4^1 T \left(\frac{\partial s}{\partial H_0}\right)_T \mathrm{d}H_0 = \int_4^1 c_T \mathrm{d}H_0 \tag{117}$$

By analogy to the Ericsson cycle (Eqs. (98) and (99)), the following relation is obtained:

$$q_c = T^1 [s^{(1)} - s^{(4)}] \tag{118}$$

The COP of the Carnot cycle is therefore obtained by inserting Eqs. (116) and (118) into (88):

$$\mathrm{COP}_{\mathrm{Carnot}} = \frac{q_c}{w_1} = \frac{T^{(1)}}{T^{(2)} - T^{(1)}} \tag{119}$$

All the cycles previously discussed are ideal cycles. At present the existing magnetocaloric materials do not show sufficiently wide temperature differences for some frequently occurring refrigeration and heat pump applications. For example, a heat pump for a new building with floor heating does not require as great a temperature rise as one designed for a conventional heating system in a renovated building. If the temperature difference between the heat source and the heat sink at present is more than twenty degrees, a one-stage machine is not able to fulfil the task. A solution to this problem is to build magnetic refrigerators and heat pumps, which take advantage of cascades. However, both—the regeneration and the cascade systems—show additional irreversibilities in their cycles. These lead to lower coefficients of performance.

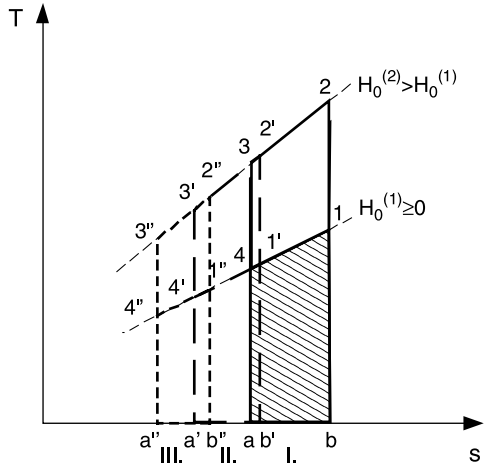

Fig. 8. Overlaps in a cascade system lead to dissipation of energy and decrease the COP.

14. Cascade systems

Cascade systems are well known from conventional refrigeration technology. A cascade system is a serial connection of some refrigeration apparatuses. They may be packed into one housing to give the impression of having only a single unit. Each of these apparatuses has a different working domain and temperature range of operation. This can be seen in Fig. 7(a) by the decreasing temperature domains of stages I–III. In this figure the cooling energy of stage I (surface: ef14) is applied for the heat rejection of stage II (surface cd23). Analogously, the cooling energy of stage II (surface cd14) is responsible for the heat rejection in stage III. The cooling energy of the entire cascade system is represented by the surface ab14 of the last stage (white domain). The total work performed in the total cascade system is given by the sum of the areas 1234 of all present stages I, II, and III.

The magnetocaloric effect is maximal at the Curie temperature. It is large only in the temperature interval around this temperature, with decreasing effect in the case of greater (temperature) differences. It is therefore, advantageous that the operating point of the refrigeration plant and this temperature interval of optimal magnetocaloric effect coincide. If the temperature span of the refrigeration process is too wide, a decrease in efficiency occurs. A solution to this problem is to work with a cascade system, where each internal unit has its own optimally adapted working temperature. Each stage of a cascade system contains a different magnetocaloric material (Fig. 7(a)) or it contains the same (Fig. 7(b)).

The disadvantage of a cascade system is that the cycles of each stage must be designed to avoid overlaps (Fig. 8). An overlap leads to a narrower temperature span and reduced efficiency.

A major advantage of a magnetic refrigeration cascade system over a conventional one is that in the magnetic refrigeration machine no heat exchangers are required between the cooling process of the higher stage and the heat rejection process of the lower stage. This is due to the fact that the magnetocaloric material is solid and a single fluid may be transferred to both stages.

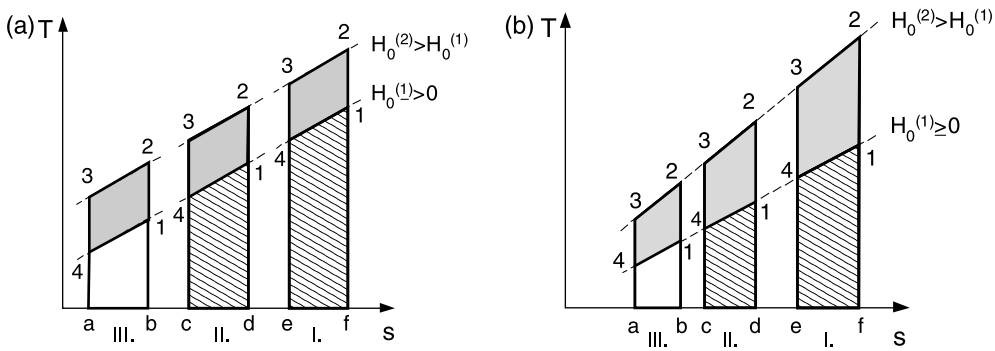

Fig. 7. Two cascade systems based on the Brayton cycle. In case (a) all stages (I, II and III) are designed to have a different optimally adapted material, whereas in case (b) they are produced with the same material.

15. Systems with regeneration

There are three different types of regenerators: the external, internal and active types. Further information on these regenerators is given for example in the review paper by Yu [10] or the book by Tishin [11]. In this presentation only active magnetic regenerators are considered, where the magnetocaloric material itself acts as a regenerator.

Fig. 9 shows a multi-stage regeneration process. Here the heat rejection from the system is represented by surface: cd22′. Magnetocaloric material is therefore cooled in a (constant) magnetic field from 2 to 2′. From 2′ to 2″ the same magnetocaloric material continues its path in the magnetic field. At the same time the 'regeneration' fluid—which was cooled down in process 11′—passes through it (the first regeneration). Then the magnetocaloric material continues to move through the magnetic field in a further stage, namely 2″3, where another 'regeneration' fluid from stage 1′1″ passes through it. After reaching point 3 the specimen is moved out of the magnetic field (or a region of lower magnetic field intensity). Simultaneously an adiabatic cooling effect occurs. Finally surface ab1″4 represents the cooling 'capacity' of this regeneration process. After that the magnetocaloric material is heated and occurs at point 1″. Because between 1″1′ and 2″3 there is a regeneration due to the fluid circulating through the magnetocaloric material, this material warms up and arrives at point 1′. The same regenerative process occurs between 1′1 and 2″2′, so finally the magnetocaloric material reaches point 1 again. After that it is adiabatically magnetized, and so the temperature increases to point 2. The work, which is performed in this system, is represented by the surface 1234.

As has probably become apparent, in the regeneration systems there is no overlapping of the 'cycles', as is usually the case in a cascade system. On the other hand, it is difficult to perform a multi-stage regeneration system with different magnetocaloric materials, because each of them has to pass through all the cycles of the entire system. The multi-regeneration process cannot be as flexible as a cascade process, because in the latter each stage may be adjusted with another 'mass flow' of solid refrigerant. Attempts are currently being made to find hybrid materials or multi-layer materials to improve regeneration systems [11].

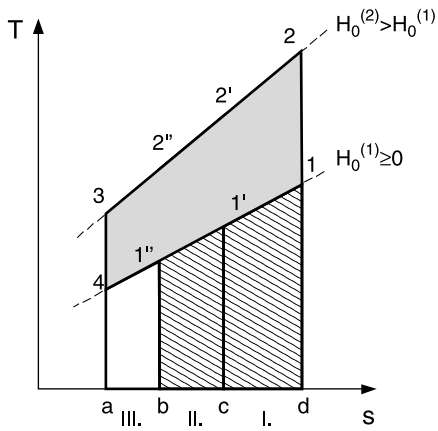

Fig. 9. A system with regeneration based on the Brayton cycle.

16. Conclusions and outlook

The magnetic refrigeration and heat pump technology at room temperature is still in an early stage of development. Materials scientists have produced promising new materials with 'giant' magnetocaloric effects, leading to refrigeration 'capacities', which are promising even for targeting real-scale applications in buildings, industry, automobiles, etc. Because the temperature spans of these materials are not so wide, it is advantageous to design new prototypes with cascades. Regeneration is also very favourable. Rotary-wheel-type magnetic refrigerators with porous magneto-caloric cylinders lead to a very simple system configuration. Furthermore, slurries—containing magnetocaloric particles, just above the nanoscale, which avoid the occurrence of sedimentation—open up a wide field for new system developments. The present article aims to yield a basis for sophisticated (numerical) magnetic refrigerator and heat pump system calculations.

Following ideas of Tesla and Edison the magneto caloric effect can also be applied for power generation. The use of low-level-temperature heat sources makes this method highly attractive. This method may even become competitive with photovoltaics. The authors propose a reinvestigation of these methods with recently developed materials.

Acknowledgements

Helpful scientific comments have been made by Ch. Besson, A. Poredos, A. Sarlah, E. Brück, R.E. Rosensweig, and V.K. Pecharsky. We are grateful to the Swiss Federal Office of Energy (F. Rognon, Th. Kopp), the Gebert Rüf Stiftung (Ph. Egger and P. Martinoli) and Arçelik A.S. (F. Oezkadi) for their interest in our research work.

Appendix A. Auxiliary derivation to the introduction of the internal energy

By regrouping Eq. (15) the next equation is obtained:

$$\mathrm{d}W_1 = \underbrace{-\int_{\Omega}(\vec{H}-\vec{H}_0)\mathrm{d}\vec{B}\mathrm{d}V}_{A} \underbrace{-\mu_0\int_{\Omega}\vec{H}_0\mathrm{d}(\vec{H}-\vec{H}_0)\mathrm{d}V}_{B} \underbrace{-\int_{\Omega}\vec{H}_0\mathrm{d}(\vec{B}-\mu_0\vec{H})\mathrm{d}V}_{C} \tag{A.1}$$

At first it is shown that term A vanishes. In electromagnetism it is well known that the divergence-free magnetic induction $\vec{B}$ possesses a vector potential $\vec{A}$:

$$\vec{B} = \mathrm{rot}\vec{A} \Rightarrow \mathrm{d}\vec{B} = \mathrm{rot}\mathrm{d}\vec{A} \tag{A.2}$$

After substituting (A.2) into term A of (A.1) with the vector identity:

$$\mathrm{div}(\vec{a} \times \vec{b}) = \vec{b}\mathrm{rot}\vec{a} - \vec{a}\mathrm{rot}\vec{b} \tag{A.3}$$

it follows that:

$$\int_{\Omega}(\vec{H} - \vec{H}_0)\mathrm{d}\vec{B}\mathrm{d}V = -\int_{\Omega}\mathrm{div}[(\vec{H} - \vec{H}_0) \times \mathrm{d}\vec{A}]\mathrm{d}V + \int_{\Omega}\mathrm{rot}(\vec{H} - \vec{H}_0)\mathrm{d}\vec{A}\mathrm{d}V \tag{A.4}$$

With the divergence theorem the first integral on the right-hand side of Eq. (A.4) can be transformed to the surface integral:

$$\int_{\Omega}(\vec{H} - \vec{H}_0)\mathrm{d}\vec{B}\mathrm{d}V = -\int_{\partial\Omega}[(\vec{H} - \vec{H}_0) \times \mathrm{d}\vec{A}]\mathrm{d}\vec{S} + \int_{\Omega}\mathrm{rot}(\vec{H} - \vec{H}_0)\mathrm{d}\vec{A}\mathrm{d}V, \quad \mathrm{d}\vec{S} = \vec{n}\mathrm{d}S \tag{A.5}$$

with the normal vector $\vec{n}$ of the surrounding surface domain $\partial\Omega$. This surface can be transformed to infinity and then the first integral in (A.5) vanishes:

$$\int_{\Omega}(\vec{H} - \vec{H}_0)\mathrm{d}\vec{B}\mathrm{d}V = \int_{\Omega}\mathrm{rot}(\vec{H} - \vec{H}_0)\mathrm{d}\vec{A}\mathrm{d}V \tag{A.6}$$

From Maxwell Eq. (3c) it follows that:

$$\mathrm{rot}\vec{H} - \mathrm{rot}\vec{H}_0 = \mathrm{rot}(\vec{H} - \vec{H}_0) = \vec{j} - \vec{j}_0 = 0 \tag{A.7}$$

because both fields $\vec{H}$ and $\vec{H}_0$ are created by the same currents $\vec{j} = \vec{j}_0$, which do not depend on the existence and distribution of magnetic material in the considered domain (see also Ref. [26]). Therefore, both integrals in (A.4) vanish and the total term A in (A.1) is zero, q.e.d.

The second term B in (A.1) is:

$$\mu_0\int_{\Omega}\vec{H}_0\mathrm{d}(\vec{H} - \vec{H}_0)\mathrm{d}V = \int_{\Omega}\vec{B}_0\mathrm{d}(\vec{H} - \vec{H}_0)\mathrm{d}V \tag{A.8}$$

From Eq. (A.2) it is concluded that:

$$\vec{B}_0 = \mathrm{rot}\vec{A}_0 \tag{A.9}$$

This equation is substituted into (A.8) and, furthermore, (A.3) is applied:

$$\int_{\Omega}\mathrm{rot}\vec{A}_0\mathrm{d}(\vec{H} - \vec{H}_0)\mathrm{d}V = \int_{\Omega}\mathrm{div}[\vec{A}_0 \times \mathrm{d}(\vec{H} - \vec{H}_0)]\mathrm{d}V + \int_{\Omega}\vec{A}_0\mathrm{rot}[\mathrm{d}(\vec{H} - \vec{H}_0)]\mathrm{d}V = 0 \tag{A.10}$$

The arguments are the same as before. The first integral on the right-hand side is transformed by the divergence theorem to a surface integral, which at an infinite distance vanishes. The second integral is also zero, because of Eq. (A.7), q.e.d.

Now only term C is left:

$$\mathrm{d}W_1 = -\int_{\Omega}\vec{H}_0\mathrm{d}(\vec{B} - \mu_0\vec{H})\mathrm{d}V = -\int_{\Omega}\vec{B}_0\mathrm{d}\left(\frac{1}{\mu_0}\vec{B} - \vec{H}\right)\mathrm{d}V \tag{A.11}$$

The term in the integral is just the specific external work presented by Eq. (16).

Appendix B. Derivation of the magnetic internal energy by applying the alternative Kelvin force (Liu force)

The following Kelvin force has to date been believed to apply in a very general manner:

$$\vec{F}_{\mathrm{K}}^{(1)} = \mu_0\int_{T}M_i\nabla H_i\mathrm{d}V, \quad N \ll 1, \quad \chi \ll 1 \tag{B.1}$$

where Einstein's summation rule has to be applied to identical indices. An alternative representation is also valid (Appendix C). In this appendix, after each formula of a force, its correct application domain is given. From the derivation in this section, it will become clear that this force is related to the technical work of an open system in the case that $H = H_0$ (compare with Eq. (18)). This is identical to the relation (Fig. 1):

$$N = \frac{H_{\mathrm{dem}}}{M} \ll 1, \quad \vec{H}_{\mathrm{int}} = \vec{H}_0 + \vec{H}_{\mathrm{dem}} \Rightarrow H = H_0 = H_{\mathrm{int}} \tag{B.2}$$

Odenbach and Liu [28] performed precise measurements on a ferromagnetic fluid sample, which was prepared as a pendulum in a magnetic field with a spatial derivative and showed that the alternative Kelvin force:

$$\vec{F}_{\mathrm{K}}^{(2)} = \int_{T}M_i\nabla B_i\mathrm{d}V, \quad N \ll 1, \quad \chi \in \Re^{+} \tag{B.3}$$

is more accurate for high susceptibilities. The two forces are only identical for small susceptibilities. The experiments were performed for $H = H_0$. Thus small adaptations are proposed:

$$\vec{F}_{\mathrm{K}}^{(3)} = -\int_{\Gamma} M_i \nabla B_i(H_0, M)\mathrm{d}V, \quad N \in \Re^+, \quad \chi \in \Re^+ \tag{B.4}$$

The introduction of the zero field in this equation is consistent with the knowledge that the internal magnetic field is a reaction field and on the basis of momentum considerations cannot contribute to the force [26]. Applying Eq. (6) it follows that:

$$\vec{F}_{\mathrm{K}}^{(3)} = -\frac{1}{\mu_0}\int_{\Gamma} B_i \nabla B_i \mathrm{d}V + \mu_0 \int_{\Gamma} H_{0i}\nabla H_{0i}\mathrm{d}V + \mu_0 \int_{\Gamma} H_{0i}\nabla M_i \mathrm{d}V \tag{B.5}$$

First it is shown that the first two integrals cancel out:

$$\frac{1}{\mu_0}\int_{\Gamma} B_i \nabla B_i \mathrm{d}V - \mu_0 \int_{\Gamma} H_{0i}\nabla H_{0i}\mathrm{d}V = \frac{1}{2\mu_0}\int_{\Gamma} \nabla B_i^2 \mathrm{d}V - \frac{\mu_0}{2}\int_{\Gamma} \nabla H_{0i}^2 \mathrm{d}V \tag{B.6}$$

Now Eq. (B.6) is multiplied from the left with $2\mu_0$ times a constant vector $\vec{C}$:

$$\int_{\Gamma} \vec{C}\cdot(\nabla B_i^2 - \mu_0^2 \nabla H_{0i}^2)\mathrm{d}V = \int_{\Gamma} \vec{C}\cdot\nabla\Psi \mathrm{d}V \tag{B.7a}$$

$$\Psi = (B_i^2 - \mu_0^2 H_{0i}^2) \tag{B.7b}$$

The following identity of vector analysis is applied:

$$\mathrm{div}(\vec{C}\cdot\Psi) = \mathrm{div}\vec{C}\cdot\Psi + \vec{C}\cdot\nabla\Psi = \vec{C}\cdot\nabla\Psi \tag{B.8}$$

Eq. (B.8) can be reduced because the divergence of a constant vector is zero. Now, with Eqs. (B.7a) and (B.8) it is concluded that:

$$\int_{\Gamma} \vec{C}\cdot\nabla\Psi \mathrm{d}V = \int_{\Gamma} \mathrm{div}(\vec{C}\cdot\Psi)\mathrm{d}V \tag{B.9}$$

Now the divergence theorem is applied to obtain:

$$\int_{\Gamma} \mathrm{div}(\vec{C}\cdot\Psi)\mathrm{d}V = \int_{\partial\Gamma} \Psi\vec{C}\cdot\vec{n}\cdot\mathrm{d}S = \int_{\partial\Gamma} \Psi\vec{C}\mathrm{d}\vec{S} \tag{B.10}$$

where surface integrals are taken over the border of the specimen $\partial\Gamma$ with the normal vector $\vec{n}$. On this border surface the following conditions hold:

$$B_i = \mu_0 H_{0i} \quad i \in \{1,2,3\} \Rightarrow \Psi = 0 \tag{B.11}$$

Therefore, (B.4) reduces to:

$$\vec{F}_{\mathrm{K}}^{(3)} = \mu_0 \int_{\Gamma} H_{0i}\nabla M_i \mathrm{d}V \tag{B.12}$$

The work performed on a specimen relates to the reaction force of this magnetic force:

$$\vec{F} = -\vec{F}_{\mathrm{K}}^{(3)} = -\mu_0 \int_{\Gamma} H_{0i}\nabla M_i \mathrm{d}V \tag{B.13}$$

Because the pendulum experiment is isothermal, $\mathrm{d}q = 0$, and this force relates to the potential:

$$\vec{F} = \nabla U_1 \tag{B.14}$$

Then it follows that:

$$\mathrm{d}U_1 = \vec{F}\cdot\mathrm{d}\vec{s} = -\mu_0 \int_{\Gamma} H_{0i}\nabla M_i \mathrm{d}V \mathrm{d}\vec{s} = -\mu_0 \int_{\Gamma} H_{0i}\nabla M_i \mathrm{d}\vec{s}\mathrm{d}V \tag{B.15}$$

and

$$\mathrm{d}u_1 = -\mu_0 H_{0i}\nabla M_i \mathrm{d}\vec{s} \tag{B.16}$$

For a clear demonstration of this relation the following treatment is performed by writing all the components. The spatial vector increment is also given in components:

$$\mathrm{d}\vec{s} = \begin{pmatrix} \mathrm{d}x_1 \\ \mathrm{d}x_2 \\ \mathrm{d}x_3 \end{pmatrix} \tag{B.17}$$

Then Eq. (B.16) transforms to:

$$\mathrm{d}u_1 = -\mu_0 \begin{pmatrix} H_{01}\frac{\partial M_1}{\partial x_1} + H_{02}\frac{\partial M_2}{\partial x_1} + H_{03}\frac{\partial M_3}{\partial x_1} \\ H_{01}\frac{\partial M_1}{\partial x_2} + H_{02}\frac{\partial M_2}{\partial x_2} + H_{03}\frac{\partial M_3}{\partial x_2} \\ H_{01}\frac{\partial M_1}{\partial x_3} + H_{02}\frac{\partial M_2}{\partial x_3} + H_{03}\frac{\partial M_3}{\partial x_3} \end{pmatrix} \begin{pmatrix} \mathrm{d}x_1 \\ \mathrm{d}x_2 \\ \mathrm{d}x_3 \end{pmatrix} \tag{B.18}$$

The vector multiplication leads to:

$$\mathrm{d}u_1 = -\mu_0 \Big(H_{01}\frac{\partial M_1}{\partial x_1}\mathrm{d}x_1 + H_{02}\frac{\partial M_2}{\partial x_1}\mathrm{d}x_1 + H_{03}\frac{\partial M_3}{\partial x_1}\mathrm{d}x_1 + H_{01}\frac{\partial M_1}{\partial x_2}\mathrm{d}x_2 + H_{02}\frac{\partial M_2}{\partial x_2}\mathrm{d}x_2 + H_{03}\frac{\partial M_3}{\partial x_2}\mathrm{d}x_2 + H_{01}\frac{\partial M_1}{\partial x_3}\mathrm{d}x_3 + H_{02}\frac{\partial M_2}{\partial x_3}\mathrm{d}x_3 + H_{03}\frac{\partial M_3}{\partial x_3}\mathrm{d}x_3 \Big) \tag{B.19}$$

By regrouping the terms we obtain:

$$\mathrm{d}u_1 = -\mu_0 \Big(H_{01}\frac{\partial M_1}{\partial x_1}\mathrm{d}x_1 + H_{01}\frac{\partial M_1}{\partial x_2}\mathrm{d}x_2 + H_{01}\frac{\partial M_1}{\partial x_3}\mathrm{d}x_3 + H_{02}\frac{\partial M_2}{\partial x_1}\mathrm{d}x_1 + H_{02}\frac{\partial M_2}{\partial x_2}\mathrm{d}x_2 + H_{02}\frac{\partial M_2}{\partial x_3}\mathrm{d}x_3 + H_{03}\frac{\partial M_3}{\partial x_1}\mathrm{d}x_1 + H_{03}\frac{\partial M_3}{\partial x_2}\mathrm{d}x_2 + H_{03}\frac{\partial M_3}{\partial x_3}\mathrm{d}x_3 \Big) \tag{B.20}$$

Note that the index 1 in du_1 has a different meaning than in the other quantities relating to the coordinate system. For a steady state motion one obtains:

$$du_1 = -\mu_0(H_{01}dM_1 + H_{02}dM_2 + H_{03}dM_3) \tag{B.21}$$

Now the result is:

$$du_1 = -\mu_0\vec{H}_0 d\vec{M} \tag{B.22}$$

the internal energy alteration of an adiabatic closed system (compare with Eq. (23)).

Appendix C. Different representations of the Kelvin force

The Kelvin force density is:

$$f_K = M_i \nabla H_i \tag{C.1}$$

It is very often written in a different manner, namely:

$$f_K = (\vec{M}\cdot\nabla)\vec{H} \tag{C.2}$$

In the following it is proven that these two representations are identical:

$$f_K = M_i \nabla H_i = \begin{bmatrix} M_1\frac{\partial}{\partial x_1}H_1 + M_2\frac{\partial}{\partial x_1}H_2 + M_3\frac{\partial}{\partial x_1}H_3 \\ M_1\frac{\partial}{\partial x_2}H_1 + M_2\frac{\partial}{\partial x_2}H_2 + M_3\frac{\partial}{\partial x_2}H_3 \\ M_1\frac{\partial}{\partial x_3}H_1 + M_2\frac{\partial}{\partial x_3}H_2 + M_3\frac{\partial}{\partial x_3}H_3 \end{bmatrix} \tag{C.3}$$

From Maxwell Eq. (3c), because electricity is not involved and the currents are zero, it follows that:

$$\mathrm{rot}\vec{H} = \begin{bmatrix} \frac{\partial H_3}{\partial x_2} - \frac{\partial H_2}{\partial x_3} \\ \frac{\partial H_1}{\partial x_3} - \frac{\partial H_3}{\partial x_1} \\ \frac{\partial H_2}{\partial x_1} - \frac{\partial H_1}{\partial x_2} \end{bmatrix} = 0 \tag{C.4}$$

we conclude that:

$$\frac{\partial H_3}{\partial x_2} = \frac{\partial H_2}{\partial x_3} \tag{C.5a}$$

$$\frac{\partial H_1}{\partial x_3} = \frac{\partial H_3}{\partial x_1} \tag{C.5b}$$

$$\frac{\partial H_2}{\partial x_1} = \frac{\partial H_1}{\partial x_2} \tag{C.5c}$$

Substituting some terms in Eq. (C.3) by these relations leads to:

$$f_K = \begin{bmatrix} M_1\frac{\partial}{\partial x_1}H_1 + M_2\frac{\partial}{\partial x_2}H_1 + M_3\frac{\partial}{\partial x_3}H_1 \\ M_1\frac{\partial}{\partial x_1}H_2 + M_2\frac{\partial}{\partial x_2}H_2 + M_3\frac{\partial}{\partial x_3}H_2 \\ M_1\frac{\partial}{\partial x_1}H_3 + M_2\frac{\partial}{\partial x_2}H_3 + M_3\frac{\partial}{\partial x_3}H_3 \end{bmatrix} = \begin{bmatrix} M_1\frac{\partial}{\partial x_1} + M_2\frac{\partial}{\partial x_2} + M_3\frac{\partial}{\partial x_3} \\ M_1\frac{\partial}{\partial x_1} + M_2\frac{\partial}{\partial x_2} + M_3\frac{\partial}{\partial x_3} \\ M_1\frac{\partial}{\partial x_1} + M_2\frac{\partial}{\partial x_2} + M_3\frac{\partial}{\partial x_3} \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = (\vec{M}\cdot\nabla)\vec{H} \tag{C.7}$$

q.e.d.

Appendix D. Analogy

Table A1
Analogy of the driving force and order parameter of a conventional gas compression system with a magnetic refrigeration or heating system

Quantity	Gas thermodynamics	Magneto-thermodynamics
Driving and 'force' (stress parameter)	Pressure p	Field H_0
Order parameter (reaction of system)	Specific volume v	Magnetization M (orientation of spins)
External work (closed system)	$dw_1^{(ext)} = -pdv$	$dw_1^{(ext)} = -\mu_0 H_0 dM$[a] (related to force of Liu)
Technical work (open system)	$dw_1^{(tech)} = vdp$	$dw_1^{(tech)} = \mu_0 M dH_0$ (related to old Kelvin force)

[a] This follows by the vector analytical treatment in Appendix B.

References

[1] E. Warburg, Magnetische Untersuchungen über einige Wirkungen der Koerzitivkraft, Ann Phys 13 (1881) 141–164.
[2] R.E. Rosensweig, Ferrohydrodynamics, Dover Publications, Mineola, NY, 1997.
[3] P. Weiss, A. Piccard, Sur un nouveau phénomène magnéto-calorique, Compt Rend Ac Sci 166 (1918) 352.
[4] P. Debye, Einige Bemerkungen zur Magnetisierung bei tiefer Temperatur, Ann Phys 81 (1926) 1154–1160.
[5] W.F. Giauque, A thermodynamic treatment of certain magnetic effects. A proposed method of producing temperatures considerably below 1° absolute, J Am Chem Soc 49 (1927) 1864–1870.

[6] W.F. Giauque, D.P. MacDougall, Attainment of temperatures below 1° absolute by demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$, Phys Rev Lett 43 (9) (1933) 768.
[7] G.V. Brown, Magnetic heat pumping. US Patent 4.069.028; 1978.
[8] G.V. Brown, Magnetic heat pumping near room temperature, J Appl Phys 47 (1976) 3673–3680.
[9] C.B. Zimm, A. Sternberg, A.G. Jastrab, A.M. Boeder, L.M. Lawton, J.J. Chell, Rotating bed magnetic refrigeration apparatus. US Patent 6.526.759.4; 2003.
[10] B.F. Yu, Q. Gao, B. Zhang, X.Z. Meng, Z. Chen, Review on research of room temperature magnetic refrigeration, Int J Refrigeration 26 (2003) 1–15.
[11] A.M. Tishin, Y.I. Spichkin, The magnetocaloric effect and its applications, Series in condensed matter physics, Institute of Physics Publishing, Bristol and Philadelphia, 2003.
[12] V.K. Pecharsky, K.A. Gschneidner Jr, Magnetocaloric effect and magnetic refrigeration, J Magn Magn Mater 200 (1999) 44–56.
[13] E.L. Resler Jr, R.E. Rosensweig, Magnetocaloric power, AIAA J 2 (8) (1964) 1418–1422.
[14] E.L. Resler Jr, R.E. Rosensweig, Regenerative thermomagnetic power, J Eng Power 89 (3) (1967) 399–406.
[15] A. Kitanovski, P.W. Egolf, O. Sari, Method and device for the generation of cold and heat by the magnetocaloric effect. WO/059222; 2004.
[16] A. Kitanovski, P.W. Egolf, O. Sari, Method and device for a continuous generation of cold and heat by means of the magnetocaloric effect. WO/059221; 2004.
[17] V.K. Pecharsky, K.A. Gschneidner Jr, Tunable magnetic regenerator alloys with a giant magnetocaloric effect for magnetic refrigeration from $\sim$20 to $\sim$290 K, Appl Phys Lett 70 (24) (1997) 3299–3301.
[18] V.K. Pecharsky, K.A. Gschneidner Jr, Effect of alloying on the giant magnetocaloric effect of $Gd_5(Si_2Ge_2)$, J Magn Magn Mater 167 (1997) 179–184.
[19] K.A. Gschneidner Jr, V.K. Pecharsky, Active magnetic refrigerants based on Gd–Si–Ge material and refrigeration apparatus and process. US Patent 5.743.095; 1998.
[20] O. Tegus, Novel materials for magnetic refrigeration. PhD Thesis Van der Waals-Zeeman Institute, Printer Partners. Ipskamp BV, Enschede; 2003.
[21] O. Tegus, E. Brúck, K.H. Buschow Jr, F.R. de Boer, Transition-metal-based magnetic refrigerants for room-temperature applications, Nature (Lett) 415 (2002) 150–152.
[22] E. Brück, O. Tegus, X.W. Li, F.R. de Boer, K.H.J. Buschow, Magnetic refrigeration towards room-temperature applications, Physica B 327 (2003) 431–437.
[23] H. Wada, S. Hirosawa, Magnetic refrigerant material, regenerator and magnetic refrigerator. PCT Patent WO 03/009314 A1; 2003.
[24] H. Wada, Y. Tamabe, Giant magnetocaloric effect of $MnAs_{1-x}Sb_x$, Appl Phys Lett 79 (20) (2001) 3302–3304.
[25] K.A. Gschneidner Jr, V.K. Pecharsky, Magnetic refrigeration, Intermetallic compounds principles and practice, vol. 3, Wiley, New York, 2002. [chapter 25, p. 519–39].
[26] L.D. Landau, E.M. Lifshitz, Statistische Physik, Lehrbuch der Theoretischen Physik, Teil 1, Band V. Akademie-Verlag, Berlin, 1979.
[27] A. Lange, Kelvin force in a layer of magnetic fluid, J Magn Mater 241 (2002) 327–329.
[28] S. Odenbach, M. Liu, Invalidation of the Kelvin force in ferrofluids, Phys Rev Lett 86(2) (2001) 328–331.
[29] A. Adib, Free energies for magnetic system: http://www.physics.brown.edu/physics/userpages/students/Artur_Adib/docs/thermomagnets.pdf.
[30] V.I. Arnold, Mathematical methods of classical mechanics, Springer, Berlin, 1980. [Second corrected printing].
[31] P.W. Egolf, H. Manz, Theory modeling of phase change materials with and without mushy regions, Int J Heat Mass Transfer 37 (18) (1994) 2917–2924.
[32] V.K. Pecharsky, K.A. Gschneidner Jr, Magnetocaloric effect from indirect measurements: magnetization and heat capacity, J Appl Phys 86 (1) (1999) 565–575.