

Material-based figure of merit for caloric materials

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The efficient use of reversible thermal effects in magnetocaloric, electrocaloric, and elastocaloric materials is a promising avenue that can lead to a substantially increased efficiency of refrigeration and heat pumping devices, most importantly, those used in household and commercial cooling applications near ambient temperature. A proliferation in caloric material research has resulted in a wide array of materials where only the isothermal change in entropy in response to a handful of different field strengths over a limited range of temperatures has been evaluated and reported. Given the abundance of such data, there is a clear need for a simple and reliable figure of merit enabling fast screening and down-selection to justify further detailed characterization of those material systems that hold the greatest promise. Based on the analysis of several well-known materials that exhibit vastly different magnetocaloric effects, the Temperature averaged Entropy Change is introduced as a suitable early indicator of the material's utility for magnetocaloric cooling applications, and its adoption by the caloric community is recommended. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5004173>

INTRODUCTION

Magnetocaloric materials exhibit a substantial and, in the absence of hysteresis, reversible change of entropy (temperature) when exposed to a change in the external magnetic field isothermally (adiabatically), commonly referred to as the magnetocaloric effect (MCE).^{1–3} The magnetocaloric functionality is most commonly characterized by calculating the isothermal entropy change, ΔS , from either isothermal or isofield magnetization data,⁴ and the resulting $\Delta S(T)_{\Delta H, T}$ is typically reported as a function of temperature for one or several different, fixed field strengths in the vicinity(ies) of spontaneous magnetic phase transition(s), where the entropy changes reach the maximum.^{5,6} When the magnetic ordering/disordering transformation is second-order, the absolute value of the cusp-like entropy change peaks at the Curie (Neel) temperature, broadening and increasing in magnitude with the values of $|\Delta S|$ often being proportional to $\Delta H^{2/3}$.⁷ In first order materials, on the other hand, a rapidly rising, narrow peak in the entropy change observed at the transition temperature in low fields becomes a broad plateau spanning a widening range of temperatures as ΔH increases, exhibiting only a minor rise in the $|\Delta S|$.⁸

The majority of laboratory-scale devices demonstrated for cooling around room temperature employ an active magnetic regenerative cycle.⁹ In this mode of operation, the material itself acts as a regenerator. The (simplified, without considering the variable temperature profile across the regenerator) operating cycle for an active magnetic regenerator constructed from a material exhibiting a direct magnetocaloric effect, i.e., for which $\Delta S < 0$ when $\Delta H > 0$, has four steps:

1. The material is adiabatically magnetized, which decreases field-sensitive component(s) of the total entropy of the material and causes its temperature to rise by $+\Delta T(T)_{\Delta H, S}$;

2. A heat exchange fluid is pumped from the cold side of the device to the hot, carrying the heat generated in the magnetization step to the hot side of the device, simultaneously cooling the regenerator itself;
3. The material is adiabatically demagnetized, which increases its entropy and causes the temperature of the material to fall by $-\Delta T(T)_{\Delta H, S}$;
4. A heat exchange fluid is pumped from the hot side of the device to the cold, where the chilled fluid absorbs heat from the source on the cold side of the device while returning the regenerator temperature to the initial state.

The amount of heat moved from the cold end to the hot end in one cycle depends on $\Delta S(T)_{\Delta H}$ and $\Delta T(T)_{\Delta H}$ of the magnetocaloric material, heat capacities and thermal conductivities of both the magnetocaloric material and heat exchange fluid, the cycle frequency, the amount of heat exchange fluid pumped during the cycle, and the geometry of the device and the magnetocaloric material.⁹ The efficiency depends on all of the above properties, as well as the thermodynamic cycle, the amount of work done to magnetize/demagnetize the material and pump the fluid, and the efficiency of heat exchangers.

Due to the relative ease with which the operating parameters of the device can be changed compared with the material properties, optimization studies typically focus on which operating parameters yield the optimum performance for a given refrigerant and magnet assembly.¹⁰ This work is far from trivial, given the highly temperature dependent properties of the magnetocaloric refrigerant itself. The dependence of regenerator performance on material properties is demonstrated by improved performance of multi-layer regenerators over single-layer regenerators^{11–14} and explored in further detail using 1-D regenerator models, which allow the material properties to be varied systematically.^{15,16} In addition to studying the device performance, Eriksen *et al.* set out to

make a device operate as efficiently as possible¹⁷ while also characterizing how the work is distributed in the device.¹⁸

Generally, device-related studies demonstrate that there is a long list of desired properties for the magnetocaloric refrigerant material. It must have the following:

- A large $|\Delta S|$, since this determines the amount of heat that will be generated (absorbed) in the material during adiabatic magnetization (demagnetization);
- A moderate heat capacity so the heat generated by the magnetization results in a large temperature change in the material, hence accelerating heat exchange;
- High thermal conductivity so the heat generated or absorbed through changes in entropy of the material can be transported to the heat exchange fluid, and
- Chemical and mechanical stability so it can last for millions of cycles.

Fundamental physics restricts the extent to which some of the properties relevant to magnetocalorics can possibly be tuned. For example, there is a well-known fundamental limit, also known as the Dulong-Petit rule,¹⁹ which establishes molar lattice heat capacity as $3R$ (R is the universal gas constant) above the corresponding Debye temperature, which for most metals is below room temperature. Further, the total available molar magnetic entropy is limited to $R \ln(2J + 1)$, where J is the total angular momentum for the lanthanides, or the total spin for the 3d transition metals.²⁰ Also, the sum rule²¹ shows that the change in thermal energy, given by $\Delta S(T)_{\Delta H, T}$ integrated over all temperatures, can be no larger than the change in magnetic energy imparted to the material by the magnetic field, given by the product of the magnetic field strength, H , and the saturation magnetization, M_0 ,

$$\int_0^\infty |\Delta S(T)_{\Delta H, T}| dT \leq HM_0. \quad (1)$$

It should also be noted that this rule represents a trade-off in the shape of the magnetic entropy change curve. Since the integral in the above equation [i.e., the total area under the $\Delta S(T)_{\Delta H, T}$ curve] is limited by the available magnetic energy, if a high entropy change is desired, then it must occur over a narrow temperature window. Conversely, if a wide temperature window is desired, then the maximum entropy change must be sacrificed.

With the discovery of several materials that exhibit the giant magnetocaloric effect,^{22–24} a popular strategy for constructing devices is to use multiple layers of materials with very high entropy change, arranged in such a way that their temperature ranges overlap.^{9,11,14,25–27} This circumvents the material limitation, providing both a high value of magnetic entropy change and a large temperature span for the device. A typical value for a temperature span for a single layer in such a device is about 2–3 K.^{26–28}

Continued development of materials for caloric heat pumps can be accelerated with guidance from an appropriate figure of merit (FOM). To be useful for accelerating development, a FOM should provide as much predictive power as possible from as little information as possible. In the following sections, several FOMs suggested and employed in the

past are reviewed. The challenges of using the FOMs are discussed, and a new FOM, the Temperature averaged Entropy Change (*TEC*), which overcomes these challenges is proposed. Advantages of *TEC* as an early indicator of material's potential are demonstrated through comparison of well-known materials using *TEC* and some of the earlier FOMs. Although the bulk of this discussion is rooted in magnetocaloric materials, *TEC* can also be easily calculated and employed for initial assessment of electrocaloric, elastocaloric, and multicaloric materials.

EXISTING MATERIAL-BASED FIGURES OF MERIT

Working within the physical limitations, many researchers have proposed optimization procedures or FOMs intended to guide material development. Using a simplified model of total entropy vs. temperature and magnetic field curves⁸ and the sum rule,²¹ Zverev *et al.*²⁹ claim that the optimum performance of a material is obtained when the isothermal entropy change, $\Delta S(T)_{\Delta H, T}$, curve has an aspect ratio given by the ratio of the Curie temperature, T_C , and the zero field heat capacity at that temperature, c_p ,

$$\frac{\text{width}}{\text{height}} \equiv \frac{\Delta T_w}{\Delta S_{\Delta H, T}^{\max}} = \frac{T_C}{c_p}, \quad (2)$$

where ΔT_w is defined loosely as the width of the $\Delta S(T)_{\Delta H, T}$ peak. For second order materials, this term does not have a firm definition; however, in first order materials, the width of the peak can be approximated by⁸

$$\Delta T_w \cong \Delta H \frac{\partial T_C}{\partial H}. \quad (3)$$

For the optimum aspect ratio, the argument is that ΔT_w is equal to the maximum adiabatic temperature change $\Delta T_{\Delta H, S}^{\max}$, which gives the value of the optimum adiabatic temperature change as

$$\Delta T_{\Delta H, S}^{\max}|_{\text{optimal}} = \left(\frac{M_0 T_C H}{c_p} \right)^{\frac{1}{2}}. \quad (4)$$

Sandeman extends this argument to estimate the maximum adiabatic temperature change for various values of the magnetic entropy change and compares the idealized curves with several real materials.³⁰ Ultimately, rather than proposing a single FOM, Ref. 30 concludes that economical materials with high values of both $\Delta S_{\Delta H, T}^{\max}$ and $\Delta T_{\Delta H, S}^{\max}$ will be necessary for successful devices.

Qian *et al.*³¹ propose comparing the latent heat of the phase change, L , with the energy required to change the temperature of the refrigerant by the desired lift temperature of the device, ΔT_{lift} . For magnetocaloric materials, this takes the form

$$\gamma_m = \frac{L}{c_p \Delta T_{\text{lift}}} = \frac{T_C \Delta S_{\Delta H, T}^{\max}}{c_p \Delta T_{\text{lift}}} \cong \frac{\Delta T_{\Delta H, S}^{\max}}{\Delta T_{\text{lift}}}. \quad (5)$$

The authors of Ref. 31 argue that the best material will have more energy available from the latent heat of the phase

change than what is required to change the temperature of the material, giving this figure a value greater than unity. It should be noted that this FOM aims to find materials suitable for a direct use of $\Delta T_{\Delta H, S}^{\max}$ rather than in a device employing regeneration. Qian *et al.* also highlighted the difficulty of defining a single FOM by proposing that this figure should serve to measure the magnitude of the effect, while another should serve to measure the efficiency of the effect. For this second figure, they refer to the study by Moya *et al.*³²

Moya *et al.* described the caloric efficiency for magnetocaloric, elastocaloric, and electrocaloric materials. For magnetocaloric materials, they compare the efficiencies for both electromagnets and permanent magnets. The efficiency, η , they define for magnetocaloric materials with permanent magnets generating the magnetic field is the ratio of the volume-normalized latent heat of the phase change to the volume-normalized energy of magnetizing the sample

$$\eta = \frac{\Delta S_{\Delta H, T}^{\max} T_C}{\mu_0 \int_0^H M dH}, \quad (6)$$

where μ_0 is the magnetic permeability of vacuum. This definition of the thermodynamic efficiency of the material does not require any information about the potential device it will be used in (i.e., temperature span). It is important to note that this efficiency is very much a property of the material. When constructing a device, the force (and hence the energy) needed to magnetize and demagnetize the sample will strongly depend on the geometry and the configuration of the device.^{33,34}

One of the challenges of using these metrics is that aside from the efficiency defined by Moya *et al.*, they rely on an accurate measure of the heat capacity to calculate the adiabatic temperature change. Non-adiabatic heat capacity measurements are known to have systematic errors based on commercially available analysis techniques.³⁵ Differential scanning calorimetry is also susceptible to systematic errors in the measurement of $\Delta S(T)_{\Delta H, T}$ based on the definition of the baseline.³⁶ Accurate measure of $\Delta S(T)_{\Delta H, T}$ using either method requires heat capacity measurements extending down to very low temperatures,³⁷ making data acquisition time-consuming. These challenges have resulted in highly specialized, one-of-a-kind equipment for gathering reliable heat capacity data using a semi-adiabatic technique that is not available commercially.³⁸ As a result, only a select few research groups are able to obtain reliable heat capacity data measured in the presence of magnetic field and extending to room temperature.

Equipment for measuring magnetization, on the other hand, is much more accessible, though it only results in the isothermal entropy change, $\Delta S(T)_{\Delta H, T}$. Although heat capacity measurements may provide more precise values of $\Delta S(T)_{\Delta H, T}$ at low temperatures, near ambient temperature, the precision of the two methods is comparable.⁴ Hence, the majority of potential magnetocaloric materials are characterized by only measuring magnetization, then calculating and reporting $\Delta S(T)_{\Delta H, T}$. This highlights a clear

need for a simple, yet meaningful FOM that does not require extensive characterization of a potential magnetocaloric material.

Wood and Potter³⁹ outlined two such FOMs that describe the magnitude and efficiency of the magnetocaloric effect for a given material. They used refrigerant capacity as a measure of the magnitude of material performance. Unlike most metrics that focus on the work the refrigerant can do, the refrigerant capacity, Q , is the work done on the refrigerant that can reversibly move heat from one temperature to another

$$Q = \Delta S(T_{\text{cold}})_{\Delta H, T} \Delta T_{\text{lift}}, \quad (7)$$

where T_{cold} is the temperature on the cold side of the device. According to Ref. 39, optimal performance is achieved in a reversible thermodynamic cooling cycle, where the change in entropy at the hot temperature is equal to the change in entropy at the cold temperature. Wood and Potter illustrate that for a given $T_{\text{cold}} < T_C$, constraining the $\Delta S(T_{\text{cold}})_{\Delta H, T} = \Delta S(T_{\text{hot}})_{\Delta H, T}$ uniquely identifies an optimal hot side temperature T_{hot} also defining ΔT_{lift} . Additionally, for a given field and material, there is one value of T_{cold} that gives a maximum value of the refrigerant capacity, Q^{\max} . Although this quantity most rigorously applies to a material at uniform temperature as pointed out by Smith *et al.*,⁴⁰ it still identifies certain characteristics of materials that are desirable for a regenerative device.

To quantify the material efficiency, Wood and Potter then normalize the refrigerant capacity by the positive work done on the refrigerant by the magnetic field and call this the Coefficient of Refrigerant Performance (CRP),³⁹

$$CRP = \frac{\Delta S(T_{\text{cold}})_{\Delta H, T} \Delta T_{\text{lift}}}{\mu_0 V_m \int_0^H M(T_C, H) dH}, \quad (8)$$

where V_m is the volume of the refrigerant. This is a measure of the material efficiency (and not the device) again because the force needed to magnetize and demagnetize the material will strongly depend on the geometry and device configuration. The CRP is a description of how efficiently a material can convert magnetic energy into thermal energy.

Very similar to the refrigerant capacity is the Relative Cooling Power (RCP) defined as the product of $\Delta S_{\Delta H, T}^{\max}$ and the temperature range at which the value of the entropy change becomes half of the maximum, δ_{FWHM} , also known as the full width at half maximum (FWHM),⁵

$$RCP = \Delta S_{\Delta H, T}^{\max} \delta_{\text{FWHM}}. \quad (9)$$

All of the proposed FOMs aim to provide some indicator of which material properties will result in a device that performs well, so Niknia *et al.*⁴¹ propose using simulated device performance to select the most useful figure of merit. They use their one dimensional regenerator model to predict performance of a single layer of several known materials as

TABLE I. Comparison of existing figures of merit evaluated for a field change of 0 to 1 T for two canonical materials: LaFeSi²³ and Gd.^{44,45} Note: the calculation of RCP_{\max} relied on saturation magnetization, measured at 5 T.

	RCP_{\max} mJ cm ⁻³ (J kg ⁻¹)	RCP mJ cm ⁻³ (J kg ⁻¹)	Q^{\max} mJ cm ⁻³ (J kg ⁻¹)
Gd	2125 (269.00)	578 (73.21)	342 (43.27)
La(Fe _{0.88} Si _{0.12}) ₁₃	924 (128.31)	613 (85.12)	356 (49.39)

well as simulated materials based on the properties of MnFePAs. For a given material, they probe the space of operating conditions to identify the maximum exergetic cooling power.⁴² Ultimately, they find the FOM that best correlates with maximum exergetic cooling power provided by a single layer of material to be what they call RCP_{\max} ,

$$RCP_{\max} = \int_0^\infty \Delta S(T)_{\Delta H, T} dT \leq M_0 H. \quad (10)$$

It should be noted, however, that a device using multiple layers of LaFeSiH achieved an exergetic cooling power of 173 W T⁻¹L⁻¹ (Ref. 26), while an excellent device using a single layer of Gd achieved, *e.g.*, 85 W T⁻¹L⁻¹.⁴³ Table I shows that the values of the previously discussed FOMs are unable to capture the potential advantage of using multiple layers of material, *i.e.*, the values of the FOMs are comparable despite the disparity in device performance.

To capture this possible enhancement in performance from layering multiple materials, the FOM needs some flexibility to be able to objectively evaluate materials for either a single-layer or multiple-layer regenerator. A sensible strategy for providing this flexibility is to include the temperature span the material can or is intended to cover explicitly in the FOM. Here, we propose two strategies for deciding a reasonable temperature span over which to evaluate materials: (1) ΔT_{lift} characteristic of a single layer in a device; (2) ΔT_{lift} commensurate with ΔT_{ad} exhibited by the best first order materials known today in magnetic fields created with permanent magnets.

Following the first strategy, a 3 K temperature span typical for both demonstrated and simulated devices using first order materials will be used. The temperature span for a single-layer device could also be used; however, this span will depend on the ultimate application for the device (*e.g.*, air conditioning or freezing). A high value of the proposed FOM will highlight materials that can be most promising for applications over this range and therefore should be fully evaluated. Since this temperature range has been tuned to a certain class of materials, however, a low value of the FOM in this regime does not necessarily imply that a material cannot be suitable for other magnetocaloric applications. This temperature span is worth considering since materials with a small ΔT_w have the potential to achieve a higher $\Delta S_{\Delta H, T}^{\max}$ than those with a larger ΔT_w .

Following the second strategy, a 10 K temperature span will be used. This span is intended to address the challenges of initially assessing materials with a small ΔT_w , *i.e.*, where strict control over the T_C of each layer is required in order to

observe the full benefit of all the layers.²⁸ Materials with a slightly larger ΔT_w will be less sensitive to variability in the T_C for a single layer. This could simplify the manufacturing processes for synthesizing the materials and assembling regenerators, making these materials competitive, especially if they have an advantage in other material properties, such as heat capacity or thermal conductivity. As will be discussed below, the selection of 10 K temperature span also provides a correlation between the proposed FOM and the ΔT_{ad} for the best first-order phase transition magnetocaloric materials known today.

To summarize, the questions addressed by the existing FOMs are, “how large is the caloric effect?” and “how efficiently does a given material convert the magnetic field work into heat?” As has become apparent, there is another question that needs to be addressed, that is, “how large is the caloric effect over a useful temperature range?” Ultimately, the full characterization of a material will be necessary to make any attempt at predicting its performance in a specific device. That being said, answering these questions will help guide research toward the most promising materials for further characterization.

A SIMPLE MATERIAL-BASED FIGURE OF MERIT

The Temperature averaged Entropy Change (TEC) is proposed as a simple, material-based FOM. It is calculated over a range of temperatures, ΔT_{lift} , that a material can reasonably support in response to a given field change ΔH when it forms either a single layer in a layered regenerator or constitutes the entire regenerator itself

$$TEC(\Delta T_{\text{lift}}) = \frac{1}{\Delta T_{\text{lift}}} \max_{T_{\text{mid}}} \left\{ \int_{T_{\text{mid}} - \frac{\Delta T_{\text{lift}}}{2}}^{T_{\text{mid}} + \frac{\Delta T_{\text{lift}}}{2}} \Delta S(T)_{\Delta H, T} dT \right\}. \quad (11)$$

The value of the temperature at the center of the average, T_{mid} , is chosen by sweeping over the available $\Delta S(T)_{\Delta H, T}$ data and selecting the value that maximizes $TEC(\Delta T_{\text{lift}})$ for the given ΔT_{lift} , similar to the evaluation of the maximum energy product of a permanent magnet.⁴⁶ Since $\Delta S(T)_{\Delta H, T}$ curves for first order materials are frequently asymmetric, the value of T_{mid} may lie to one side or the other of the T_C . Since the entropy change at the T_C is a maximum, however, it will always be contained within the integration bounds. Figure 1 shows how the integral average entropy change for a field change of 1 T behaves for three well-known, illustrative materials: a material with a high entropy change over a narrow temperature range, La(Fe_{0.88}Si_{0.12})₁₃,⁴⁷ a material with a high entropy change over a wide temperature range, FeRh,⁴⁸ and a material with a low entropy change over a very wide temperature range, Gd.^{44,45}

The entropy change curves in Fig. 1 are shifted in temperature by T_{mid} . Since Curie temperatures are often tunable,^{23,49–51} this shift facilitates the evaluation of materials with Curie temperatures that differ slightly from the target application and comparison of materials with slightly

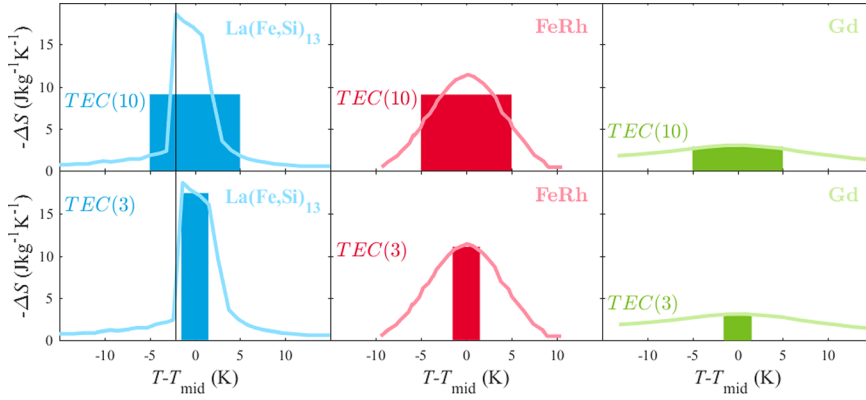


FIG. 1. Materials with a large entropy change over a narrow window are the most promising for layered regenerators, while materials with a wider temperature profile can be competitive if fewer layers or even a single layer is desired. The plotted values of $\Delta S(T)_{\Delta H=1T,T}$ are obtained by digitizing published data taken from Ref. 47 for $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$, Ref. 48 for FeRh, and Refs. 44 and 45 for Gd.

different Curie temperatures. When comparing materials with different Curie temperatures, however, care should be taken to ensure that the comparison is meaningful.⁵²

Since T_{mid} is determined numerically to maximize TEC , the values will change slightly for different values of ΔT_{lift} . For example, since the $\Delta S(T)_{\Delta H,T}$ for $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ falls faster on the low temperature side of the peak, shifting the integration window towards slightly higher temperatures maximizes the value of the integral average for a ΔT_{lift} of 10 K. This means that the $\Delta S(T)_{\Delta H,T}$ curve ends up further to the left in the plot showing $TEC(10)$ than in the plot showing $TEC(3)$, as illustrated by the vertical black lines in Fig. 1. At low fields, where first order materials are far from their saturation, this shift makes little difference in the value of the integral in Eq. (11). At higher fields, however, the magnetic entropy change curve widens out asymmetrically around the peak value. When this is the case, it becomes very important to allow the center of the integration range to vary from the peak entropy change temperature. This shift ensures that the integral average remains representative of the overall shape of the curve.

Figure 2 shows the field dependence of the $TEC(3)$, $TEC(10)$, RCP , and Q^{max} . For $TEC(3)$, the field dependence is very similar to that of the peak entropy change, for $TEC(10)$, the curves flatten out slightly, and in the limit of very high temperature lifts, the field dependence becomes linear in accordance with the sum rule. The RCP and Q^{max} show that all three materials exhibit a strong MCE; however, the $TEC(\Delta T_{\text{lift}})$ provides additional information. It shows that both $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and FeRh are more promising than Gd for temperature spans relevant to layered regenerators. The $TEC(3)$ shows that $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ is the most promising for a layered regenerator where each layer spans 3 K.

Although the magnetic field dependence is not the same for all materials, the values of TEC for several materials can be easily compared for a given field. Table II gives the values of $TEC(3)$, $TEC(10)$, RCP , and Q^{max} for several materials, all at $\mu_0\Delta H = 1$ T. The entries in the table are sorted by descending values of $TEC(3)$.

Both the RCP and Q^{max} tend to overestimate the merit of materials with a very broad magnetocaloric response but small entropy change.^{40,52} This is illustrated in Table II for

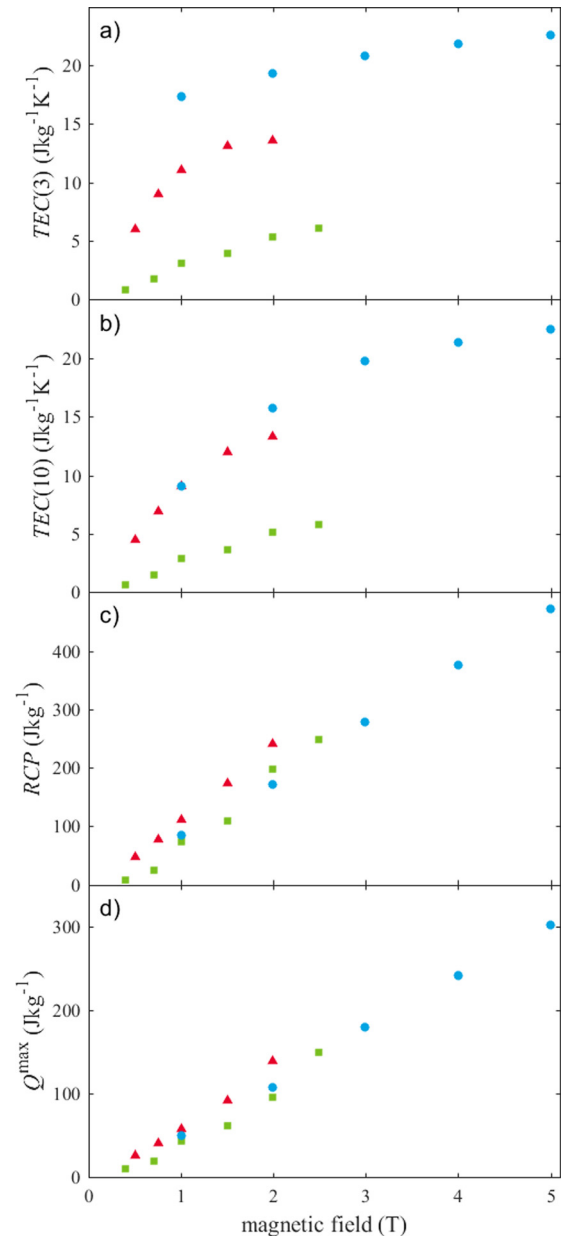


FIG. 2. Magnetic field dependence of the Temperature averaged Entropy Change at (a) 3 K and (b) 10 K temperature lifts, (c) Relative Cooling Power, and (d) maximum refrigerant capacity for $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ (●),⁴⁷ FeRh (▲),⁴⁸ and Gd (■).^{44,45}

TABLE II. Temperature averaged Entropy Change for a ΔT_{lif} of 3 and 10 K compared with the Relative Cooling Power and maximum refrigerant capacity for a magnetic field change of 1 T.

Material	$TEC(3) \text{ mJ cm}^{-3} \text{ K}^{-1}$ ($\text{J kg}^{-1} \text{ K}^{-1}$)	$TEC(10) \text{ mJ cm}^{-3} \text{ K}^{-1}$ ($\text{J kg}^{-1} \text{ K}^{-1}$)	$RCP \text{ mJ cm}^{-3}$ (J kg^{-1})	$Q^{\text{max}} \text{ mJ cm}^{-3}$ (J kg^{-1})	References
Gd ₅ Si _{0.5} Ge _{3.5}	158 (19.96)	86.9 (11.00)	810 (102.6)	405 (51.27)	53
La(Fe _{0.88} Si _{0.12}) ₁₃	125 (17.36)	65.6 (9.11)	613 (85.12)	356 (49.39)	47
Ni _{49.26} Mn _{36.08} In _{14.66} (multicaloric, combined)	121 (15.13)	52.6 (6.58)	470 (58.77)	241 (30.11)	54
FeRh	109 (11.09)	89.0 (9.08)	1092 (111.44)	565 (57.61)	48
LaFe _{11.66} Mn _{0.14} Si _{1.2} H _{1.65}	82.9 (12.19)	39.1 (5.75)	332 (48.89)	176 (25.85)	49
Gd ₅ Si ₂ Ge ₂	75.3 (9.91)	52.4 (6.89)	547 (71.99)	274 (36.00)	55
MnFe _{0.95} P _{0.595} B _{0.075} Si _{0.33}	54.9 (9.15)	36.3 (6.05)	354 (59.02)	178 (29.60)	51
Gd	24.1 (3.05)	23.0 (2.91)	578 (73.21)	342 (43.27)	44
LaFe ₁₁ Co _{0.8} Si _{1.2}	23.6 (3.37)	22.7 (3.24)	574 (81.94)	290 (41.47)	50
La _{0.813} K _{0.16} Mn _{0.987} O ₃	8.34 (1.49)	8.23 (1.47)	435 (77.62)	298 (53.28)	56

La_{0.813}K_{0.16}Mn_{0.987}O₃. Even though the maximum entropy change is only about $1.5 \text{ J kg}^{-1} \text{ K}^{-1}$, the values of the RCP and Q^{max} are both higher than those of gadolinium and even LaFe_{11.66}Mn_{0.14}Si_{1.2}H_{1.65}. This material is not expected to be useful, as properly reflected by $TEC(3)$ and $TEC(10)$, since the small entropy change coupled with large molar heat capacity will likely be washed out by irreversible losses even at moderate temperature spans in any actual device. Similar caution should be used when comparing materials at higher values of ΔT_{lif} . Considering the ΔT_{lif} of 10 K, many of the materials given in the table do not have a useful response over such a wide window, so they may not perform well individually at this value of ΔT_{lif} .

Ni_{49.26}Mn_{36.08}In_{14.66} exhibits both magnetocaloric and elastocaloric effects. Fitting the entropy change data for the elastocaloric and magnetocaloric effects for Ni_{49.26}Mn_{36.08}In_{14.66} with an asymmetric Lorentzian peak⁵⁷ allows the two effects to be accounted for together. Combining the applied fields for multicaloric materials like this could increase the TEC significantly. Although the two effects are generally not expected to be additive, this optimistic estimate illustrates the possible advantages of applying multiple fields to the same material, especially if a magnetostructural transition cannot be completed by a limited single field, but adding a second one completes the transformation.

Although the TEC specifically excludes the requirement of direct or indirect measurement of the ΔT_{ad} , the choice of ΔT_{lif} around 10 K clearly correlates with $\Delta T(T)_{\Delta H, S}^{\text{max}}$ for the best magnetocaloric materials known today. The analysis of the relationship between $\Delta S(T)_{\Delta H, T}$ and $\Delta T(T)_{\Delta H, S}^{\text{max}}$ by Pecharsky *et al.*⁸ and later by Sandeman³⁰ shows that for materials with moderate dependence of Curie temperature on applied magnetic field, $\partial T_C / \partial H$, the $\Delta T(T)_{\Delta H, S}^{\text{max}}$ is approximately equal to ΔT_w , while for materials with larger $\partial T_C / \partial H$, the $\Delta T(T)_{\Delta H, S}^{\text{max}}$ is less than the ΔT_w . The best known materials that exhibit the giant magnetocaloric effect have values of $\partial T_C / \partial H$ around $4\text{--}6 \text{ K T}^{-1}$,³⁰ and at fields achievable using permanent magnets, $\mu_0 H \leq 2 \text{ T}$, the experimentally measured $\Delta T(T)_{\Delta H, S}^{\text{max}}$ for the best materials known today is around $6\text{--}8 \text{ K}$.⁵⁸ Setting the ΔT_{lif} at 10 K will capture the entire width of the $\Delta S(T)_{\Delta H, T}$ curve for these materials. For materials with comparable $\Delta S_{\Delta H, T}^{\text{max}}$, the TEC increases with increasing ΔT_w , which will in turn correspond to larger values of $\Delta T(T)_{\Delta H, S}^{\text{max}}$. At the same time, by constraining ΔT_{lif} at 10 K for fields of 2 T and below, we avoid overestimating of $\Delta T(T)_{\Delta H, S}^{\text{max}}$ from the peak width for materials with very high $\partial T_C / \partial H$ (such as FeRh where $\partial T_C / \partial H = -8.5 \text{ K T}^{-1}$).⁴⁸ Figure 3 shows the correlation between $TEC(10)$ and $\Delta T(T)_{\Delta H, S}^{\text{max}}$ for the current pool of highest-performing magnetocaloric materials. It immediately follows

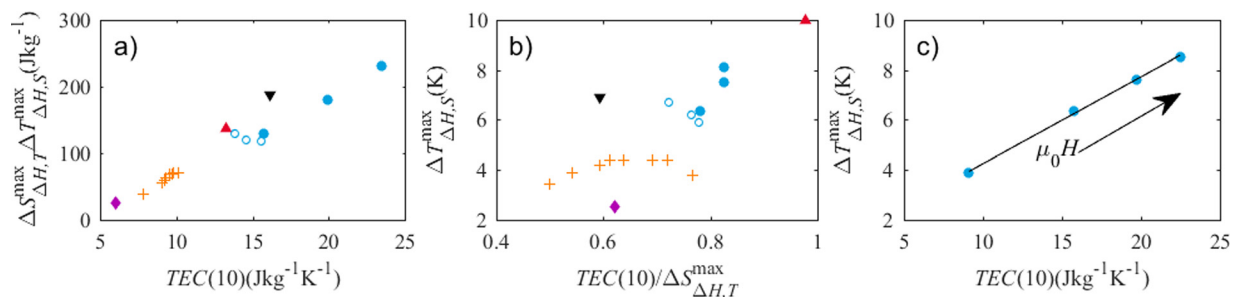


FIG. 3. (a) Values of the entropy change averaged over a lift temperature of 10 K correlate most strongly with the product of the maximum entropy change and the maximum adiabatic temperature change. (b) Strong correlation still exists between the adiabatic temperature change and the entropy change averaged over 10 K normalized by the maximum entropy change. (c) Linear regression of the entropy change averaged over 10 K and the adiabatic temperature change for a single material under different applied field changes. Values shown are for FeRh (▲),⁴⁸ Gd₅Si₂Ge₂ (▼),⁵⁵ La(Fe_xSi_{1-x})₁₃ (●),⁴⁷ La(Fe_{0.88}Si_{0.12})₁₃H_x (○),²³ LaFe_xMn_ySi_zH_{1.65} (+),⁴⁹ MnFe_{0.95}P_{0.595}B_{0.075}Si_{0.33} (◆).⁵¹

that $TEC(10)$ provides the much needed, predictive FOM based on a single measured or calculated isothermal entropy change dataset.

DISCUSSION

Despite significant effort to distill the response of magnetocaloric materials down to a single parameter, the simple truth of the matter is that these materials are complex. It should be telling that the nondimensionalization of Sarlah and Poredos⁵⁹ resulted in no fewer than five dimensionless parameters, the majority of which are temperature dependent, field dependent, or both. In any attempt to compare magnetocaloric materials with each other, let alone other refrigerants, their temperature- and magnetic field-dependent properties must be considered while also keeping in mind other important parameters such as thermal conductivity, corrosion resistance, and mechanical properties. As discussed previously, even allowing for two parameters can leave room for misinterpretation.

One important material property that will affect the value of the TEC is hysteresis, *i.e.*, the dependence of MCE on the magnetic field and temperature history. The TEC can be estimated with a single set of isofield (heating or cooling) or isothermal (magnetization or demagnetization) magnetization measurements and used as a guide to determine whether a material merits the effort of full characterization (including hysteresis). With a complementary magnetization dataset, the energy lost to hysteresis can be calculated from, *e.g.*, the area between the magnetization and demagnetization curves;^{60,61} however, the relationship between this energy loss and the impact on the MCE is not clear. More directly, Guillou *et al.*⁶² show that if the change in transition temperature due to hysteresis is larger than the change in transition temperature due to the changing magnetic field, then the material will not exhibit a cyclable ΔT_{ad} . Heat capacity measurements, the challenges of which have been discussed above, can be used to parameterize more detailed material models.⁶³ These models can provide hysteresis-corrected $\Delta S(T)_{\Delta H,T}$,⁶⁴ which can be used to calculate hysteresis-corrected TEC . Through this progression, the TEC can provide a useful comparison between materials at each level of characterization.

As detailed above, the TEC provides a quantity that is easy to calculate with a minimum amount of information available for any given caloric material, including elastocaloric and electrocaloric materials, without any modifications (a given, fixed change of stress/strain or electric field still applies). By restricting the temperature range being considered, the potential superiority (or inferiority) of one material compared with another can be solidly established. The most sensible way to apply this restriction is by considering the proposed end use of the material. The value of ΔT_{lift} can be tailored to the proposed application of the material. Since each material has a unique temperature profile, different applications may very well favor different materials.

CONCLUSION

The temperature averaged entropy change over 10 K is suggested as a simple, easy-to-evaluate figure of merit based

solely on the field-induced isothermal entropy change data commonly available and reported for caloric materials. This figure provides the benefit of quickly rejecting materials that exhibit overly broad $\Delta S(T)_{\Delta H,T}$ with low absolute entropy changes that is lacking in other FOMs, such as RCP and Q^{\max} , and is applicable for early assessment of the potential of all known types of caloric materials, regardless of the nature of the driving field. Most importantly, the suggested temperature averaged entropy change can be easily extended to gauge utility of multicaloric materials, *i.e.*, those that respond to more than a single field trigger. Restricting the temperature range of consideration by using existing prototypes and modeling as a practical guide clarifies and strengthens the argument of which materials should be considered for further characterization, development, and scale-up. This metric can provide an early indicator for which materials hold the most promise for application in layered devices for magnetocaloric cooling around room temperature. Given the relative ease with which magnetization data can be measured compared with heat capacity, this metric can help in identifying materials that merit further study.

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¹P. Debye, "Einige bemerkungen zur magnetisierung bei tiefer temperatur," *Ann. Phys.* **386**, 1154 (1926).

²W. F. Giauque, "A thermodynamic treatment of certain magnetic effects. A proposed method of producing temperatures considerably below 1° absolute," *J. Am. Chem. Soc.* **49**, 1864 (1927).

³W. F. Giauque and D. P. MacDougall, "Attainment of temperatures below 1° absolute by demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$," *Phys. Rev.* **43**, 768 (1933).

⁴V. K. Pecharsky and K. A. Gschneidner, Jr., "Magnetocaloric effect from indirect measurements: Magnetization and heat capacity," *J. Appl. Phys.* **86**, 565 (1999).

⁵K. A. Gschneidner, Jr. and V. K. Pecharsky, "Magnetocaloric materials," *Annu. Rev. Mater. Sci.* **30**, 387 (2000).

⁶K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, "Recent developments in magnetocaloric materials," *Rep. Prog. Phys.* **68**, 1479 (2005).

⁷H. Oesterreicher and F. T. Parker, "Magnetic cooling near Curie temperatures above 300 K," *J. Appl. Phys.* **55**, 4334 (1984).

⁸V. K. Pecharsky, K. A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, "Thermodynamics of the magnetocaloric effect," *Phys. Rev. B* **64**, 144406 (2001).

⁹A. Kitanovski, J. Tušek, U. Tomc, U. Plaznik, M. Ozbolt, and A. Poredoš, *Magnetocaloric Energy Conversion* (Springer International, Cham, Switzerland, 2015).

¹⁰J. Tušek, A. Kitanovski, and A. Poredoš, "Geometrical optimization of packed-bed and parallel-plate active magnetic regenerators," *Int. J. Refrig.* **36**, 1456 (2013).

¹¹T. Tsukagoshi, K. Matsumoto, T. Hashimoto, T. Kuriyama, and H. Nakagome, "Optimum structure of multilayer regenerator with magnetic materials," *Cryogenics* **37**, 11 (1997).

¹²C. Zimm, A. Boeder, J. Chell, A. Sternberg, A. Fujita, S. Fujieda, and K. Fukamichi, "Design and performance of a permanent-magnet rotary refrigerator," *Int. J. Refrig.* **29**, 1302 (2006).

- ¹³M.-A. Richard, A. M. Rowe, and R. Chahine, "Magnetic refrigeration: Single and multimaterial active magnetic regenerator experiments," *J. Appl. Phys.* **95**, 2146 (2004).
- ¹⁴J. Tušek, A. Kitanovski, U. Tomc, C. Favero, and A. Poredoš, "Experimental comparison of multi-layered La-Fe-Co-Si and single-layered Gd active magnetic regenerators for use in a room-temperature magnetic refrigerator," *Int. J. Refrig.* **37**, 117 (2014).
- ¹⁵K. Engelbrecht and C. R. H. Bahl, "Evaluating the effect of magnetocaloric properties on magnetic refrigeration performance," *J. Appl. Phys.* **108**, 123918 (2010).
- ¹⁶M. A. Benedict, S. A. Sherif, M. Schroeder, and D. G. Beers, "The impact of magnetocaloric properties on refrigeration performance and machine design," *Int. J. Refrig.* **74**, 576 (2017).
- ¹⁷D. Eriksen, K. Engelbrecht, C. R. H. Bahl, R. Bjørk, K. K. Nielsen, A. R. Insinga, and N. Pryds, "Design and experimental tests of a rotary active magnetic regenerator prototype," *Int. J. Refrig.* **58**, 14 (2015).
- ¹⁸D. Eriksen, K. Engelbrecht, C. R. Haffenden Bahl, and R. Bjørk, "Exploring the efficiency potential for an active magnetic regenerator," *Sci. Technol. Built Environ.* **22**, 527 (2016).
- ¹⁹P. L. Dulong and A.-T. Petit, "Recherches sur quelques points importants de la theorie de la chaleur," *Ann. Chim. Phys.* **10**, 395 (1819).
- ²⁰C. Kittel, *Introduction to Solid State Physics* (Wiley, 2005).
- ²¹L. H. Bennett, R. D. McMichael, L. J. Swartzendruber, R. D. Shull, and R. E. Watson, "Monte Carlo and mean-field calculations of the magnetocaloric effect of ferromagnetically interacting clusters," *J. Magn. Magn. Mater.* **104**, 1094 (1992).
- ²²V. K. Pecharsky and K. A. Gschneidner, Jr., "Giant magnetocaloric effect in Gd₅(Si₂Ge₂)," *Phys. Rev. Lett.* **78**, 4494 (1997).
- ²³A. Fujita, S. Fujieda, Y. Hasegawa, and K. Fukamichi, "Itinerant-electron metamagnetic transition and large magnetocaloric effects in La(Fe_xSi_{1-x})₁₃ compounds and their hydrides," *Phys. Rev. B* **67**, 104416 (2003).
- ²⁴O. Tegus, E. Brück, K. H. J. Buschow, and F. R. De Boer, "Transition-metal-based magnetic refrigerants for room-temperature applications," *Nature* **415**, 150 (2002).
- ²⁵A. Rowe and A. Tura, "Experimental investigation of a three-material layered active magnetic regenerator," *Int. J. Refrig.* **29**, 1286 (2006).
- ²⁶S. Jacobs, J. Auringer, A. Boeder, J. Chell, L. Komorowski, J. Leonard, S. Russek, and C. Zimm, "The performance of a large-scale rotary magnetic refrigerator," *Int. J. Refrig.* **37**, 84 (2014).
- ²⁷M. A. Benedict, S. A. Sherif, M. Schroeder, and D. G. Beers, "Experimental impact of magnet and regenerator design on the refrigeration performance of first-order magnetocaloric materials," *Int. J. Refrig.* **74**, 190 (2017).
- ²⁸T. Lei, K. K. Nielsen, K. Engelbrecht, C. R. H. Bahl, H. N. Bez, and C. T. Veje, "Sensitivity study of multi-layer active magnetic regenerators using first order magnetocaloric material La (Fe, Mn, Si) 13Hy," *J. Appl. Phys.* **118**, 014903 (2015).
- ²⁹V. I. Zverev, A. M. Tishin, and M. D. Kuz'min, "The maximum possible magnetocaloric ΔT effect," *J. Appl. Phys.* **107**, 043907 (2010).
- ³⁰K. G. Sandeman, "Magnetocaloric materials: The search for new systems," *Scr. Mater.* **67**, 566 (2012).
- ³¹S. Qian, D. Nasuta, A. Rhoads, Y. Wang, Y. Geng, Y. Hwang, R. Radermacher, and I. Takeuchi, "Not-in-kind cooling technologies: A quantitative comparison of refrigerants and system performance," *Int. J. Refrig.* **62**, 177 (2016).
- ³²X. Moya, E. Defay, V. Heine, and N. D. Mathur, "Too cool to work," *Nat. Phys.* **11**, 202 (2015).
- ³³N. Bianchi and S. Bolognani, "Design techniques for reducing the cogging torque in surface-mounted PM motors," *IEEE Trans. Ind. Appl.* **38**, 1259 (2002).
- ³⁴A. R. Insinga, C. Bahl, R. Bjørk, and A. Smith, *Optimising Magnetostatic Assemblies* (Department of Energy Conversion and Storage, Technical University of Denmark, 2016).
- ³⁵V. Hardy, Y. Bréard, and C. Martin, "Derivation of the heat capacity anomaly at a first-order transition by using a semi-adiabatic relaxation technique," *J. Phys.: Condens. Matter* **21**, 075403 (2009).
- ³⁶J. Marcos, F. Casanova, X. Batlle, A. Labarta, A. Planes, and L. Mañosa, "A high-sensitivity differential scanning calorimeter with magnetic field for magnetostructural transitions," *Rev. Sci. Instrum.* **74**, 4768 (2003).
- ³⁷L. M. Moreno-Ramírez, J. S. Blázquez, J. Y. Law, V. Franco, and A. Conde, "Optimal temperature range for determining magnetocaloric magnitudes from heat capacity," *J. Phys. D: Appl. Phys.* **49**, 495001 (2016).
- ³⁸V. K. Pecharsky, J. O. Moorman, and K. A. Gschneidner, Jr., "A 3–350 K fast automatic small sample calorimeter," *Rev. Sci. Instrum.* **68**, 4196 (1997).
- ³⁹M. E. Wood and W. H. Potter, "General analysis of magnetic refrigeration and its optimization using a new concept: Maximization of refrigerant capacity," *Cryogenics* **25**, 667 (1985).
- ⁴⁰A. Smith, C. R. H. Bahl, R. Bjørk, K. Engelbrecht, K. K. Nielsen, and N. Pryds, "Materials challenges for high performance magnetocaloric refrigeration devices," *Adv. Energy Mater.* **2**, 1288 (2012).
- ⁴¹I. Niknia, P. V. Trevizoli, T. V. Christiaan, P. Govindappa, R. Teyber, and A. Rowe, "Material screening metrics and optimal performance of an active magnetic regenerator," *J. Appl. Phys.* **121**, 064902 (2017).
- ⁴²A. Rowe, "Configuration and performance analysis of magnetic refrigerators," *Int. J. Refrig.* **34**, 168 (2011).
- ⁴³A. Tura and A. Rowe, "Permanent magnet magnetic refrigerator design and experimental characterization," *Int. J. Refrig.* **34**, 628 (2011).
- ⁴⁴S. Y. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner *et al.*, "Magnetic phase transitions and the magnetothermal properties of gadolinium," *Phys. Rev. B* **57**, 3478 (1998).
- ⁴⁵A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Applications* (CRC Press, 2016).
- ⁴⁶D. Jiles, *Introduction to Magnetism and Magnetic Materials* (CRC Press, 2015).
- ⁴⁷S. Fujieda, A. Fujita, and K. Fukamichi, "Large magnetocaloric effect in La (Fe_xSi_{1-x})₁₃ itinerant-electron metamagnetic compounds," *Appl. Phys. Lett.* **81**, 1276 (2002).
- ⁴⁸A. Chirkova, K. P. Skokov, L. Schultz, N. V. Baranov, O. Gutfleisch, and T. G. Woodcock, "Giant adiabatic temperature change in FeRh alloys evidenced by direct measurements under cyclic conditions," *Acta Mater.* **106**, 15 (2016).
- ⁴⁹V. Basso, M. Küpferling, C. Curcio, C. Bennati, A. Barzca, M. Katter, M. Bratko, E. Lovell, J. Turcaud, and L. F. Cohen, "Specific heat and entropy change at the first order phase transition of La (Fe-Mn-Si) 13-H compounds," *J. Appl. Phys.* **118**, 053907 (2015).
- ⁵⁰A. Yan, K.-H. Müller, and O. Gutfleisch, "Magnetocaloric effect in LaFe_{11.8-x}Co_xSi_{1.2} melt-spun ribbons," *J. Alloys Compd.* **450**, 18 (2008).
- ⁵¹F. Guillou, G. Porcari, H. Yibole, N. van Dijk, and E. Brück, "Taming the first-order transition in giant magnetocaloric materials," *Adv. Mater.* **26**, 2671 (2014).
- ⁵²V. K. Pecharsky and K. A. Gschneidner, Jr., "Some common misconceptions concerning magnetic refrigerant materials," *J. Appl. Phys.* **90**, 4614 (2001).
- ⁵³Y. Mudryk, "R5T4 compounds-unique multifunctional intermetallics for basic research and applications," *Mater. Matters* **11**, 120 (2016).
- ⁵⁴L. Mañosa, D. González Alonso, A. Planes, E. Bonot, M. Barrio, J. L. Tamarit, S. Aksoy, and M. Acet, "Giant solid-state barocaloric effect in the Ni-Mn-In magnetic shape-memory alloy," *Nat. Mater.* **9**, 478 (2010).
- ⁵⁵A. O. Pecharsky, K. A. Gschneidner, Jr., and V. K. Pecharsky, "The giant magnetocaloric effect of optimally prepared Gd₅Si₂Ge₂," *J. Appl. Phys.* **93**, 4722 (2003).
- ⁵⁶W. Zhong, W. Chen, W. P. Ding, N. Zhang, A. Hu, Y. W. Du, and Q. J. Yan, "Synthesis, structure and magnetic entropy change of polycrystalline La_{1-x}K_xMnO_{3+δ}," *J. Magn. Magn. Mater.* **195**, 112 (1999).
- ⁵⁷M. A. Benedict, S. A. Sherif, D. G. Beers, and M. Schroeder, "A new model of first-order magnetocaloric materials with experimental validation," *Int. J. Refrig.* **70**, 138 (2016).
- ⁵⁸J. Liu, T. Gottschall, K. P. Skokov, J. D. Moore, and O. Gutfleisch, "Giant magnetocaloric effect driven by structural transitions," *Nat. Mater.* **11**, 620 (2012).
- ⁵⁹A. Sarlah and A. Poredos, "Dimensionless numerical model for simulation of active magnetic regenerator refrigerator," *Int. J. Refrig.* **33**, 1061 (2010).
- ⁶⁰V. Provenzano, A. J. Shapiro, and R. D. Shull, "Reduction of hysteresis losses in the magnetic refrigerant Gd₅Ge₂Si₂ by the addition of iron," *Nature* **429**, 853 (2004).
- ⁶¹S. Stadler, M. Khan, J. Mitchell, N. Ali, A. M. Gomes, I. Dubenko, A. Y. Takeuchi, and A. P. Guimarães, "Magnetocaloric properties of Ni₂Mn_{1-x}Cu_xGa," *Appl. Phys. Lett.* **88**, 192511 (2006).
- ⁶²F. Guillou, H. Yibole, G. Porcari, L. Zhang, N. H. Van Dijk, and E. Brück, "Magnetocaloric effect, cyclability and coefficient of refrigerant performance in the MnFe (P, Si, B) system," *J. Appl. Phys.* **116**, 063903 (2014).
- ⁶³M. LoBue, V. Basso, C. P. Sasso, and G. Bertotti, "Entropy and entropy production in magnetic systems with hysteresis," *J. Appl. Phys.* **97**, 10E513 (2005).
- ⁶⁴L. von Moos, C. R. H. Bahl, K. K. Nielsen, and K. Engelbrecht, "The influence of hysteresis on the determination of the magnetocaloric effect in Gd₅Si₂Ge₂," *J. Phys. D: Appl. Phys.* **48**, 025005 (2014).