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The maximum possible magnetocaloric ΔT effect

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The current boom of research activity in magnetocaloric materials science is fuelled by the expectation that new advanced refrigerants may be found whose ΔT will significantly surpass that of gadolinium (Gd) metal (2.6–2.9 K/T). Because of this expectation, the main effort in the field has been diverted from the important issues of refrigerator design to the routine characterization of magnetic materials. Estimating the maximum adiabatic temperature change that can be achieved in principle by applying a certain magnetic field, say 1 T, is a matter of priority. In this work the problem of maximum ΔT is approached from general principles. According to the most optimistic estimates, ΔT can never exceed ~ 18 K/T, the more realistic upper limit lying somewhere in high single figures. We therefore deem it most unlikely that a refrigerant much better than Gd, in respect of the ΔT value, will ever be found. © *2010 American Institute of Physics*. [doi:10.1063/1.3309769]

I. INTRODUCTION

The magnetocaloric effect (MCE) is generally recognized as the heating or cooling of magnetic solids in a varying dc magnetic field. It was discovered by Warburg[1] and, over the years, the nature and the behavior of MCE as a function of temperature and magnetic-field change were subjects of many experimental and theoretical studies. MCE fundamentals are well understood. Nevertheless, even today, advanced research of magnetothermal phenomena remains topical, both from the basic and practical perspectives. The fundamental significance of MCE arises from its intimate relationship with magnetism and the thermodynamics of solids. This relationship warrants further basic experimental and theoretical studies to bring about a more complete understanding of the thermal behavior of magnetic solids as functions of both temperature and magnetic-field change. The importance of MCE is easily appreciated from the fact that, for many years, it has been used successfully for reaching ultralow temperatures in a research environment.[2] Furthermore, recent technological advancements[3] strongly suggest that in the near future MCE may become the keystone for an energy-efficient and environmentally safe near-room-temperature solid-state refrigeration technology, provided all theoretical and practical aspects of continuous magnetic cooling are adequately solved.

The aim of our work is to demonstrate theoretically that a refrigerant significantly better than Gd will not be found. MCE in Gd reaches 3 K/T.

II. THEORETICAL CONSIDERATION

MCE consists in a release or absorption of heat by a solid experiencing a change of magnetic state (for example, magnetization or demagnetization by the external magnetic field H). We proceed from the well-known thermodynamic expression for the adiabatic temperature[21]

$$dT = -\frac{T}{C_B} \times \left(\frac{\partial M}{\partial T}\right)_B dB. \quad (1)$$

Under the conditions relevant to near-room-temperature refrigeration $(-T/C_B)$ depends rather little on magnetic field B, T remains close to 300 K, whereas by the Dulong–Petit law, C_B is approximately $3R$/mol or $3k_B$ per atom. For simplicity we shall regard $(-T/C_{B,p})$ as a constant. Since an upper bound for ΔT is sought, the neglect of the magnetic contribution to C_B is justified. An immediate conclusion can be drawn: the adiabatic temperature change is determined mainly by $(\partial M/\partial T)_B$. This partial derivative has the following properties: $(\partial M/\partial T)_B$ is a function of two variables, T and B; it has a large value in the vicinity of $T_C \approx 300$ K; and it is small far away from T_C. We now make a simplifying assumption regarding $(\partial M/\partial T)_B$, let it equal a (negative) constant ζ (independent of T or B) within a certain temperature interval around T_C and be nil outside this interval. The consequence of such a supposition is that the isothermal magnetic entropy change ΔS_m has the same shape as $(\partial M/\partial T)_B$, namely, it is constant within the same temperature interval about T_C and nil outside the interval. By the Maxwell relation this constant is just

$$(-\Delta S)_{max} = -\int_0^B \left(\frac{\partial M}{\partial T}\right)_B dB = -\zeta \times B. \quad (2)$$

However, our aim is the adiabatic ΔT rather than the isothermal ΔS_m. The fact is that during the process of magnetic *cooling* the temperature does not remain constant. The stronger the field, the higher the temperature. That is, the operating temperature in $\Delta S_m(T)$ plots moves not vertically but rather aslant.

Let us set $B=1$ T. Then the area under the $\Delta S_m(T)$ curve (known as the relative cooling power, RCP) equals the magnetization change ΔM. It is known from general principles that magnetization can vary between 0 and $10\mu_B$/atom at the most. Thus, it is impossible to have a ΔM (or an RCP)

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greater than $10\mu_B$/atom. Since the area under the $\Delta S_m(T)$ curve is limited, it is essential for the curve to be shaped so that the RCP is not wasted. There are two obvious extreme cases.

(1) A broad but low peak in $\Delta S_m(T)$. It is possible to arrange things so that the operating temperature never leaves the temperature interval where $(\partial M/\partial T)_B \equiv \zeta = \text{const} \neq 0$. Then, by Eqs. (1) and (2),

$$\Delta T = -\left(\frac{T}{C_B}\right) \times \zeta \times B = -\left(\frac{T}{C_B}\right) \times \Delta S_{\max}. \tag{3}$$

That is, up to a constant factor the value of ΔT is determined by the height of the ΔS_m peak, which in this particular case is rather low.[4–8]

(2) A high but narrow peak in $\Delta S_m(T)$. Let the starting temperature point lie within the interval where $(\partial M/\partial T)_B \equiv \zeta$. As the applied magnetic field varies, the temperature moves rapidly toward the edge of the interval. There $(\partial M/\partial T)_B$ vanishes and, by Eq. (1), no further temperature change can occur. The maximum possible ΔT is thus equal to the width of the ΔS_m peak. Therefore, materials with narrow ΔS_m peaks cannot be good refrigerants. Many such examples are known.[9–12]

The optimum performance[13–18] is achieved when the peak's aspect ratio satisfies the following condition:

$$\frac{(\text{width})}{(\text{height})} = \frac{T}{C_B} \tag{4}$$

or

$$(\text{width})^2 = \frac{T}{C_B} \times (\text{RCP}), \tag{5}$$

where $(\text{width}) = \Delta T_{\max}$. Hence

$$\Delta T_{\max} = \sqrt{\frac{T}{C_B} \times (\text{RCP})}. \tag{6}$$

Assuming for definiteness that $B=1$ T, we finally get

$$\Delta T_{\max} = \sqrt{T \times \frac{\Delta M}{C_B} \times (1\ \text{T})}, \tag{7}$$

where $T \approx 300$ K.

Since it is known that no elemental solid can compete with Gd metal, it is sensible to consider a hypothetical binary compound. Let its molecule consist of two atoms, one of them endowed with a maximum possible magnetic moment, $10\mu_B$ (Ho), the other one nonmagnetic. Thus, $\Delta M = 10\mu_B$/molecule. By the Dulong–Petit law, $C_B = 6k_B$/molecule. (More complex structures are hardly advantageous since they have higher C_B.) Taking into account that $T \approx 300$ K, $\mu_B = 9.27 \times 10^{-24}$ J/T, and $k_B = 1.38 \times 10^{-23}$ J/K from Eq. (7) one can obtain

$$\Delta T_{\max} \approx 18\ \text{K}, \tag{8}$$

for this highly special hypothetical refrigerant.

This result should be regarded as a strong inequality,

$$\Delta T \ll 18\ \text{K}. \tag{9}$$

Any deviation from the assumptions made (nonoptimal ΔS_m peak aspect ratio, dilution with nonmagnetic atoms, using $3d$ elements instead of rare earths, taking account of the magnetic contribution to C_B, etc.) will inevitably reduce the above optimistic estimate.

III. CONCLUSION

We have estimated the upper bound of the adiabatic temperature change. The estimate has been obtained from general thermodynamic considerations and applies equally to refrigerants undergoing first- or second-order phase transitions. The result, Eq. (8), should be regarded as a strong inequality,

$$\Delta T \ll 18\ \text{K}.$$

Thus, as far as ΔT is concerned, refrigerants outperforming Gd by a factor of 2 to 3 are not impossible, but rather improbable. One such material does exist, it is FeRh with $\Delta T = 6.5$ K/T.[9–12] It is, however, unsuitable for applications due to the prohibitively high cost of rhodium. The quantity ΔT considered herein refers to a single-stage refrigeration cycle and is a property of the refrigerant material rather than of the cooling device. The latter can be multistage, with much wider temperature spans. Still, the best material for each individual stage is Gd metal, perhaps doped with another heavy rare earth. This conclusion is limited to near-room-temperature refrigeration; for low temperatures refrigerants significantly better than Gd are known.[19,20]

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