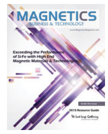

Magnetocaloric Measurements: From Energy Efficient Refrigeration to A Tool for the Study of Phase Transitions

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In the past 20 years, there has been a surge in research on the magnetocaloric response of materials, due mainly to the possibility of applying this effect for magnetic refrigeration close to room temperature. But in addition to the studies of magnetocaloric materials for increasing the energy efficiency of temperature control systems, the magnetocaloric effect can be used to gain fundamental insight into the characteristics of magnetic phase transitions. This article will discuss magnetometry measurements of relevant magnetocaloric materials and the resultant analysis and procedures proposed to characterize the phase transition using purely magnetic measurements.

The magnetocaloric effect (MCE) is the reversible change in temperature of a magnetic material with the application or removal of a magnetic field. Magnetic refrigeration based on the MCE is more efficient than the process based on compression/expansion of gasses, and since no refrigerant gasses are used it is environmentally friendly in that there are no concerns about ozone depletion or greenhouse effect.[1-4]

To characterize a magnetocaloric material (MCM) one needs to measure the adiabatic temperature change, ΔT_{ad}, when the material is adiabatically magnetized/demagnetized, or one can measure the magnetic entropy change, ΔS_M:

$$\Delta S_M = \mu_0 \int_0^{H_{max}} \left(\frac{\partial M}{\partial T} \right)_H dH \qquad (1)$$

where μ_o is the magnetic permeability of vacuum and H_{max} is the maximum applied field. Another important magnitude of a magnetic refrigerant material is its refrigerant capacity, *RC*, which is the amount of heat that can be transferred between the cold and hot reservoirs, at temperatures T_{cold} and T_{hot}, respectively, and is expressed as:

$$RC(H) = \int_{T_{cold}}^{T_{hot}} \Delta S_M(T,H)\, dT, \qquad (2)$$

From equation (1) it is clear that the largest MCE occurs at temperatures where the magnetization is changing most abruptly. For practical magnetic refrigeration this needs to occur close to room temperature, hence MCMs with phase transitions (abrupt changes in *M*) near room temperature are desirable. Therefore, there is an intrinsic connection between the characterization of MCMs and the study of their phase transitions, which might be of first-order type (FOPT) or second-order type (SOPT). And while the largest magnetocaloric response is associated to FOPT materials, it is also at the expense of larger thermal and magnetic hysteresis and usually smaller narrower peak than for SOPT MCMs, which usually relates to a lower *RC*.

Magnetocaloric Effect Measurements

Direct Measurements - In principle, the simplest method for characterizing a MCM is to measure $\Delta T_{ad}(H)$ by adiabatically isolating a sample and measuring its temperature change with a sensor as the magnetic field is varied. This technique is appropriate when the thermal mass of the sample is much larger than the thermal mass of the addenda (i.e., sample holder plus temperature sensor). However, as it requires a good adiabatic isolation, it has to be performed in dedicated experimental setups. Standard versions of this technique would not be appropriate for measuring small samples, like thin films, small amount of powders, nanostructured materials, etc. For these types of samples other methods are needed.

Indirect Measurements - Indirect measurements are much simpler to perform and only rely on experimental devices that are readily available commercially, such as magnetometers and calorimeters. Magnetometry is the most common technique that is used to measure the temperature- and field-dependent magnetization curves to calculate ΔS_M using equation (1). One reason being that magnetometry, unlike calorimetry, is a contactless measurement, thus it can easily measure materials in any form (e.g., powders, solids, thin films, etc.). Magnetometry measurements are most commonly performed using either vibrating sample magnetometers (VSM) or superconducting quantum interference device magnetometers (SQUID).

Magnetic Measurement Techniques

Magnetometry techniques can be broadly classified into two categories: inductive and force based. In this article we will focus on two most commonly employed inductive techniques: vibrating sample magnetometry (VSM) and superconducting quantum interference device magnetometry (SQUID).

Vibrating Sample Magnetometry (VSM) - In this method, originally developed by Foner,[5] a magnetic material is vibrated within a uniform magnetic field, *H*, inducing an electric current in suitably placed sensing coils. The resulting voltage induced in the sensing coils is proportional to the magnetic moment of the sample. The magnetic field may be generated by an electromagnet, or a superconducting magnet. Variable temperatures from cryogenic to high temperatures (<4 K to 1,273 K) may be achieved using cryostats and furnace assemblies, respectively.

Commercial VSM systems are available that provide measurements to field strengths of ~3 T (30,000 Oe) using conventional electromagnets,[6,7] as well as systems employing superconducting magnets to produce fields to 16 T.[8,9] When used with electromagnets, one can make very small step changes in field (i.e., ~1 mOe) and the measurement is very fast. When used with superconducting magnets, higher field strengths are possible; however, this limits the field setting resolution, and the measurement speed is inherently slower due to the speed at which the magnetic field can be varied in superconducting magnets. The ultimate noise floor of commercially available VSMs is 10^{-7} emu. This is sufficient sensitivity for many magnetic materials.

SQUID Magnetometry - Quantum mechanical effects in conjunction with superconducting detection coil circuitry are used in SQUID-based magnetometers to measure the magnetic properties of materials. Theoretically, SQUIDs are capable of achieving sensitivities of 10^{-12} emu, but practically, they are limited to sensitivities of 10^{-8} emu, because the SQUID also picks up environmental noise. As in a VSM, SQUIDs may be used to perform measurements from low to high temperatures (<2 K to 1,000 K), and to field strengths of 7 T employing superconducting magnets.[8,9] Like the superconducting magnet based VSM systems, the measurement is inherently slow due to the speed at which the magnetic field can be varied in superconducting magnets.

Magnetocaloric Materials

As Gd has a large magnetic moment (7.6μ_B) with a Curie temperature close to room temperature, it has been considered the benchmark material for magnetic refrigeration since the first prototype developed by Brown.[10] The largest impact on magnetic refrigeration research in recent years was the discovery of the giant magnetocaloric effect (GMCE) in $Gd_5(SiGe)_4$ at the end of the 20th century,[12] which appears in materials with a FOPT. Subsequently, the discovery of GMCE in other materials, such as $La(FeSi)_{13}$ and its hydrides,[12,13] and MnFePAs,[14] make this field of research bloom, with an evolution, which can be followed in recent reviews.[4] But in addition to the search for appropriate materials for magnetic refrigeration, magnetocaloric characterization can be used to gain information about the characteristics of phase transitions, like the determination of critical exponents in cases that the standard procedures do not work, or to unequivocally determine the order of the phase transition from purely magnetic measurements.[15] In SOPT materials, the field dependence of the magnetocaloric response is directly related to the critical exponents of the transition, allowing us to extract them in a non-iterative way, with good agreement with conventional techniques, or even in cases where these techniques are not applicable due to the mix of phases.[16]

Measurement Results

In order to characterize the magnetocaloric response of a sample using magnetic measurements, its temperature and field dependent magnetization curves have to be recorded. If the sample exhibits a SOPT, such as Gd, the fastest procedure is to record isothermal magnetization curves at different temperatures in the environment of the Curie temperature, ideally with larger temperature resolution close to the transition, and with enough field resolution to be able to properly define the shape of the curves. Once these set of data is acquired, equation (1) should be applied. This implies the processing of typically ~50 isotherms with ~70 field values each in the case of measurements up to 1.5 T. The manual processing of all these data takes a fair amount of work and is prone to errors, unless a processing software is used. This is especially true if the field dependence of the magnetocaloric response has to be calculated, as all the operations have to be performed for each of the fields.

In the case of FOPT, there has been some controversy about the applicability of Maxwell relations for the extraction of ΔS_M. However, the current understanding is that equation (1) is applicable in the case that the proper measuring protocol is followed, which "erases" the memory of the material in between isothermal measurements, or uses isofield instead of isothermal measurements.[17]

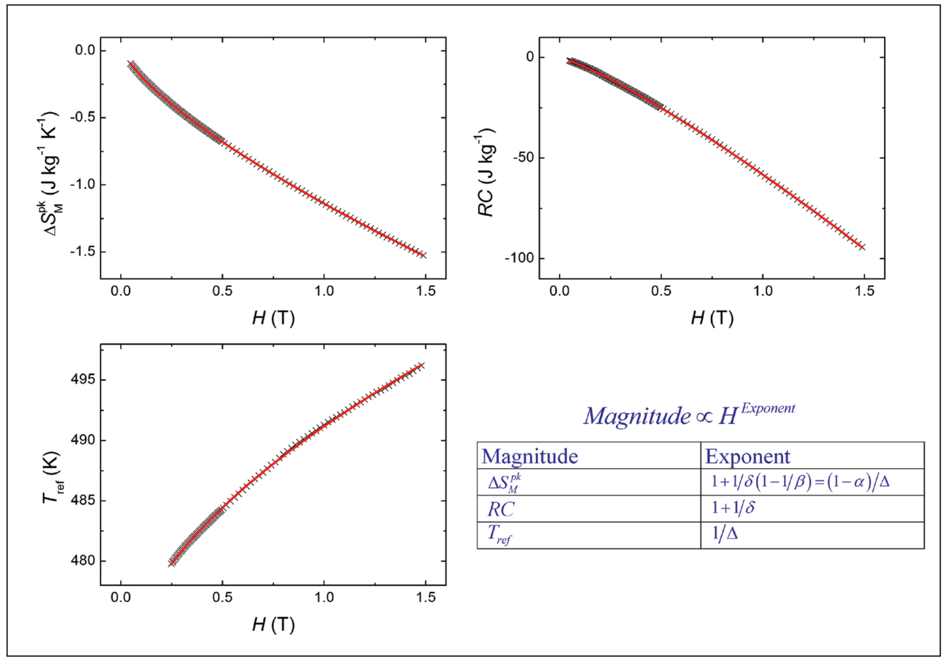

Figure 1. Field dependence of the peak magnetic entropy change, refrigerant capacity and temperature at which the magnetic entropy change is 50 percent of the peak (reference temperature) for a typical iron-based soft magnetic amorphous alloy. Crosses are experimental points; lines are power-law fits to the data. The table indicates the relationship between these field dependences and the critical exponents of the material.

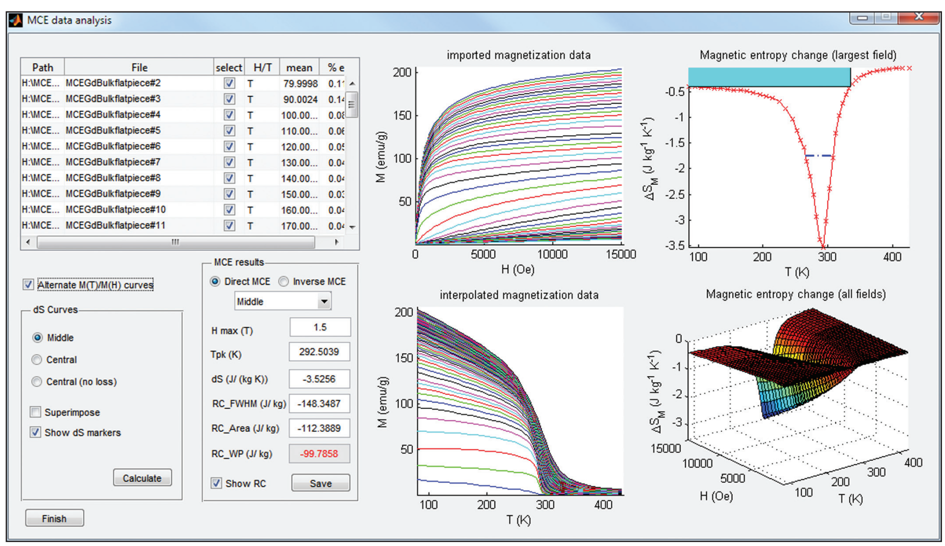

Figure 2. Screenshot of the software for the analysis of the magnetocaloric effect[18], applied to a bulk Gd sample of 2 mg. The two left figures show the isothermal (measured)[19] and isofield (calculated) magnetization curves; the two figures on the right show the magnetic entropy change for the maximum applied field and the field dependence of ΔS_M in the whole field and temperature range. Characteristic parameters are given on the table.

MCE analysis software[18] has been developed for the calculation of the relevant magnetocaloric parameters which can be extracted from magnetization curves (ΔS_M and *RC*, the latter calculated using the different accepted definitions) as a function of the maximum applied field. Both isothermal and isofield curves can be processed, to accommodate for the different measuring protocols. The analysis of the exponents of the power laws of these magnitudes in SOPT materials can also be used to extract the values of critical exponents.

Summary

In addition to being a hot topic due to the search for magnetic refrigerant materials close to room temperatures, magnetocaloric characterization is a useful technique for determining the nature of magnetic phase transitions and can be used to calculate critical exponents without performing iterative methods. Data acquisition can be done in readily available magnetometers and new software for processing the extensive amount of data needed for the complete characterization of magnetocaloric effect materials.

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Victorino Franco obtained his PhD in Physics from Sevilla University (Spain) in 1999, where he is now a Professor at the Condensed Matter Physics Department. His research interest is focused on magnetic materials for energy applications, including soft magnetic materials and magnetocaloric materials.

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References

1. *K. A. Gschneidner Jr. and V. K. Pecharsky, Annual Review of Materials Science 30, 387 (2000).*
2. *E. Bruck, Journal of Physics D-Applied Physics 38, R381 (2005).*
3. *O. Gutfleisch, M. A. Willard, E. Bruck, C. H. Chen, S. G. Sankar, and J. P. Liu, Advanced Materials 23, 821 (2011).*
4. *V. Franco, J. S. Blázquez, B. Ingale, and A. Conde, Annual Review of Materials Research 42, 305 (2012).*
5. *S. Foner, Review of Scientific Instruments 30, 548 (1959).*
6. *Lake Shore Cryotronics, USA.*
7. *Microsense, USA.*
8. *Quantum Design, USA.*
9. *Cryogenic Limited, UK.*
10. *G. V. Brown, Journal of Applied Physics 47, 3673 (1976).*
11. *V. K. Pecharsky and K. A. Gschneidner Jr., Physical Review Letters 78, 4494 (1997).*
12. *F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Cheng, G. H. Rao, and X. X. Zhang, Applied Physics Letters 78, 3675 (2001).*
13. *A. Fujita, S. Fujieda, Y. Hasegawa, and K. Fukamichi, Physical Review B 67, 104416 (2003).*
14. *O. Tegus, E. Bruck, K. H. J. Buschow, and F. R. de Boer, Nature 415, 150 (2002).*
15. *V. Franco and A. Conde, International Journal of Refrigeration-Revue Internationale Du Froid 33, 465 (2010).*
16. *V. Franco, A. Conde, V. Provenzano, and R. D. Shull, Journal of Magnetism and Magnetic Materials 322, 218 (2010).*
17. *L. Tocado, E. Palacios, and R. Burriel, Journal of Applied Physics 105, 093918 (2009).*
18. *MCE analysis software developed by V. Franco (Sevilla University) and Lake Shore Cryotronics.*
19. *Isothermal measurements were performed using a Lake Shore Cryotronics Model 7407 VSM.*

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