ISSN 2176-5480

22nd International Congress of Mechanical Engineering (COBEM 2013)
November 3-7, 2013, Ribeirão Preto, SP, Brazil

DIRECT MEASUREMENT OF THE MAGNETOCALORIC EFFECT IN PROMISSOR MAGNETIC REFRIGERANTS

J. A. Lozano – jaime@polo.ufsc.br
M. S. Capovilla – matheus@polo.ufsc.br
J. R. Barbosa Jr. – jrb@polo.ufsc.br
POLO - Research Laboratories for Emerging Technologies in Cooling and Thermophysics
Department of Mechanical Engineering
Federal University of Santa Catarina (UFSC), Florianópolis, SC, 88040-900, Brazil.
Phone: + 55 48 3721-7970

L. Zhang – lian.zhang@basf.com
BASF Nederland B.V., Strijkviertel 67, 3454 PK De Meern, Netherlands

Abstract. *Magnetic refrigeration is an emerging cooling technology that employs the magnetocaloric effect. Due to its first-order magnetic phase transition at near room temperature and giant magnetocaloric effect, MnFe(P,As) is a promising solid refrigerant for active magnetic regenerators (AMRs). Since the operation (Curie) temperature of MnFe(P,As) can be tuned by changing its composition, multilayer regenerators can be designed for higher temperature spans. In this work, adiabatic temperature change was directly measured in a custom-built facility for a magnetic field change of 1.75 T between 250 and 350 K on 3 samples of MnFe(P,As) with Curie temperatures around room temperature. . The results showed a maximum adiabatic temperature change of 3.9 K. The full reversibility of the magnetocaloric effect in these samples was verified experimentally.*

Keywords: *magnetocaloric effect, adiabatic temperature change, direct measurement, active magnetic regenerator*

1. INTRODUCTION

Magnetic refrigeration is a cooling technology based on the magnetocaloric effect (MCE). The MCE is characterized by a temperature variation of the material when subjected to a changing magnetic field. Some magnetic materials exhibit a significant MCE at room temperature, such as gadolinium (Gd), La-based compounds ($La(Fe,Si)_{13}H$) (Fujita, Fujieda, Hasegawa et al., 2003) or manganese-based compounds MnFe(P,As) (Tegus, Brück, Buschow et al., 2002), which makes them potential candidates as refrigerants in active magnetic regenerators (AMR).

The MCE is usually quantified by both the isothermal entropy change, ΔS_M, and the adiabatic temperature change, ΔT_{ad}. Both properties are function of the temperature and the applied magnetic field. The isothermal entropy change is normally obtained indirectly from isofield or isothermal magnetization measurement using the Maxwell relation, or from isofield specific heat measurements. The adiabatic temperature change is normally obtained directly by measuring the temperature variation of a magnetocaloric material when a magnetic field is applied or removed. The indirect measurement requires complex and sophisticated equipment, in addition to quasi-static conditions in order to avoid deviation from thermodynamic equilibrium, and the use of theoretical relations in order to quantify the MCE. On the other hand, the direct measurement presents a more straightforward approach (Gschneidner and Percharsky, 2000).

The MCE is usually quantified by the isothermal entropy change, ΔS_M, or the adiabatic temperature change, ΔT_{ad}. Both properties are function of the temperature and the applied magnetic field. The isothermal entropy change can only be calculated via indirect measurements through isothermal magnetizations and the Maxwell relation or via isofield specific heat measurements. In contrast, the adiabatic temperature change can be obtained directly by measuring the temperature variation of a magnetocaloric material when a magnetic field is applied or removed. Therefore, our work is focus on the ΔT_{ad} which gives a more realistic notion of the MCE of a solid refrigerant for applications and numerical simulation, since it is the driving force for heat transfer between the solid and the fluid in magnetic regenerator (Trevizoli et al., 2011). Besides, it can be done by the use of conventional temperature measurement instruments, like thermocouples (Gschneidner and Percharsky, 2000).

Manganese-based materials are one of the most promising solid refrigerants for applications near room-temperature. It presents a first order phase transition at its Curie temperature (T_C). This temperature can be tuned by varying the phosphorus (P) and arsenic (As) ratio in its composition (Brück, 2007). This ability makes possible to build a multi-layer AMR making these materials become more interesting for magnetic refrigeration applications. The multi-layer regenerator is an interesting solution to the narrow range of temperature where the MCE is observed in single-layer regenerators. For instance, while the Gd, which is considered as benchmark material, have its T_C around 293 K (Bahl

ISSN 2176-5480

and Nielsen, 2009), the MnFe(P,As) compounds can have their T_C tuned within a range from 150 to 350K (Brück, 2007). Another advantage in the use of Mn-based materials is it raw materials low cost, in comparison to the rare-earth-based compounds.

Different methods and apparatus for direct measurement of the ΔT_{ad} have been reported in literature, where the main difference among them is how the magnetic field is generated. Some of them make use of an electromagnet (Zhang et al., 2000; Canepa et al., 2005), others superconductor coils (Benford and Brown, 1981; Gopal et al., 1997; Gschneidner and Percharsky, 2000; Rosca et al., 2010) and, most recently, permanent magnet assemblies (Huang et al., 2005; Trevizoli et al., 2009, 2011; Madireddi et al., 2009; Bahl and Nielsen, 2009; Khovaylo et al., 2010). In this work, samples of MnFe(P,As) with different Curie temperatures of 282, 292 and 313 K were characterized via direct measurement of the ΔT_{ad} in an improved custom-built facility originally described in Trevizoli *et al.* (2011).

2. EXPERIMENTAL WORK

For our measurement, the magnetic field is provided by a Nd-Fe-B Halbach permanent magnet assembly with a volume of uniform magnetic flux density of 1.75 T. The magnetic field was measured by a LakeShore® 425 model gaussmeter and a transversal gaussmeter probe model HMMT-6J04-VF, with an uncertainty of ±1 % of experimental value. A pneumatic actuator with a nylon arm is used to place the sample in and out of the magnetic field with a rapid change of magnetic field of the order of milliseconds. More details of this set up can be found in Trevizoli *et al.* (2011).

The apparatus is placed inside of a temperature chamber, which was especially constructed to shelter it, as shown in Fig. 1. To control the temperature inside the chamber, a copper coil was used, where a mixture of water and ethylene-glycol (1:1 in volume) flowed from a Quimmis® ultra thermostatic temperature-controller bath. In addition, two Peltier modules fed by a PS 6000 ICEL® direct current source were employed to improve the heating and cooling rates of the sample. Aluminum blocks, heat exchangers and fans are employed to absorb and extract the heat from and to the thermoelectric modules. To insulate the chamber, 100 mm of polystyrene foam was employed. The temperature inside the 0.0286m³ chamber can be controlled between the range of 250 and 350 K and maintained within ±0.05 K.

Figure 1. Direct measurement of the adiabatic temperature change apparatus.

The samples were shaped into two rectangular prisms and between them a copper-constantan 0.13 mm (0.005 in) diameter OMEGA® thermocouple (T-type) was carefully placed to enable the characterization of the temperature change. This kind of thermocouple was especially chosen because it presents the greatest homogeneity of the component wires among thermocouples, which reduces errors due to temperature gradient in a magnetic field (Green and Schroeder, 1988). The thermocouple was placed in a way that the temperature measured was at the center of the face of the sample. To improve thermal contact, a thin layer of a high-density polysynthetic silver thermal compound (Artic Silver 5®) – with thermal conductance over 350 kW/(m·K) – was placed within the two prisms. And the samples were thermally insulated with a 5 mm layer of expanded polystyrene.

A T-type OMEGA® thermocouple built-in a copper cylinder to improve its temperature stability was placed inside the chamber in order to monitor the ambient temperature. Both thermocouples, ambient and sample, were calibrated between 278 and 308K, following the process described in Trevizoli *et al* (2009).

When the sample stabilizes in the desired temperature within ±0.05 K the solenoid valve activates the pneumatic actuator placing the sample inside the magnet, causing an instantaneous change of the magnetic field in the sample from 0 to 1.75 T, i.e. the *magnetization* process. The sample stays in the magnetic field for a few seconds before the solenoid valve is closed and the sample is moved out of the magnetic field, i.e. the *demagnetization* process. Fig. 2 shows a typical measurement which consists in a curve with the 3 steps of the measurement: stabilizing the temperature before (de)magnetization, the (de)magnetization process (with thermocouple interference) and after (de)magnetization. This

ISSN 2176-5480

measurement procedure is repeated five times for each desired temperature to guarantee reproducibility and decrease experimental uncertainty, which, according to Trevizoli *et al.* (2010), is calculated as ±0.20 K.

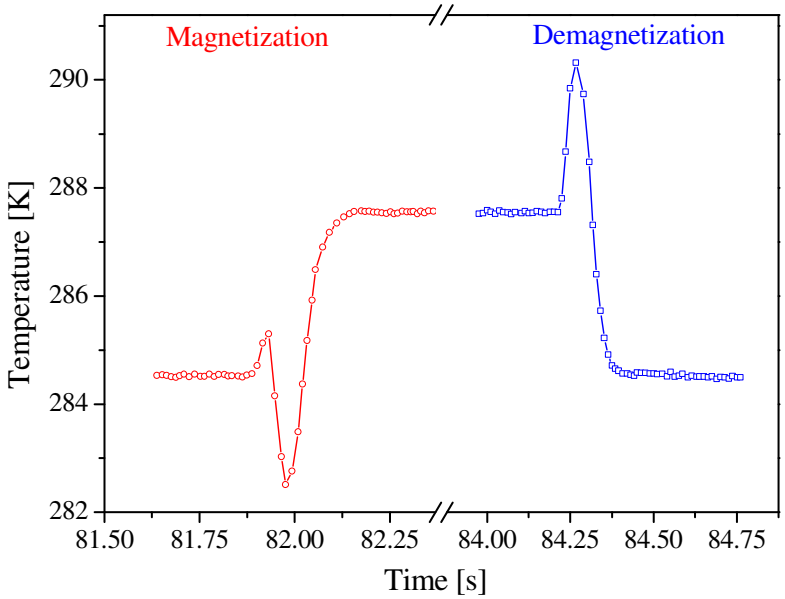


Figure 2. Typical experimental measurement procedure of the temperature variation while magnetization and demagnetization of a magnetocaloric sample.

The adiabatic temperature change is taken as the difference between the average plateau temperatures of the sample when it is out and in the magnetic field. The temperature spikes are due to magnetic induction of the thermocouple when it is moving in the field. They are excluded from the averaging.

The demagnetization factor, N_D, of a sample is calculated according to its geometrical shape. For prism shaped bodies the demagnetization factor is calculated according to Aharoni (1998). The N_D is responsible for reducing the intensity of internal magnetic field, H_{int}, in comparison with the applied magnetic field and it is calculated as (Bahl and Nielsen, 2009; Smith *et al.*, 2010):

$$H_{\text{int}} = H_{\text{app}} - N_{\text{D}}M \tag{1}$$

where H_{app} corresponds to the applied magnetic field. In this case, $\mu_0 H_{app} = 1.75$ T and μ_0 is the permeability of free space.

In this work three samples of MnFe(P,As) synthesized via high-energy ball milling plus sintering and homogenization heat treatment with Curie temperatures of 282, 292 and 313 K have been measured. Table 1 shows the specification of the samples.

Table 1. Specification of the samples.

Samples	T_C [K]	x-axis [mm]	y-axis [mm]	z-axis [mm]	N_D
Mn-1	282	6.5	3.2	4.7	0.458
Mn-2	292	6.7	2.0	5.0	0.579
Mn-3	313	6.0	2.0	4.7	0.558

The adiabatic temperature change as a function of the temperature was obtained for all the samples while magnetization and demagnetization in order to verify the reversibility of the MCE in these samples, as proposed by Bahl and Nielsen (2009). Additionally, the samples were tested while heating and cooling to check their thermal hysteresis.

3. RESULTS AND DISCUTION

When performing the first measurement in the sample Mn-1 an interesting result was found, as shown in Fig. 3. The sample was initially cooled down to 275 K and then the sample was heated while the magnetization and demagnetization were carried out until 304 K. However, when the experiments were performed while cooling the sample, it was observed an increase in the magnetocaloric effect. A reproducible curve was only observed since the

ISSN 2176-5480

second heating cycle of the sample. Therefore, a pre-training-cycle was accomplished in the other samples in order to remove the effect. After having eliminated the training effect in sample Mn-1, a maximum adiabatic temperature change of 3.9 K was attained at a peak temperature (considered as T_C) of 290 K when applied a magnetic field of 1.75 T. The results are summarized for all the samples in Table 2.

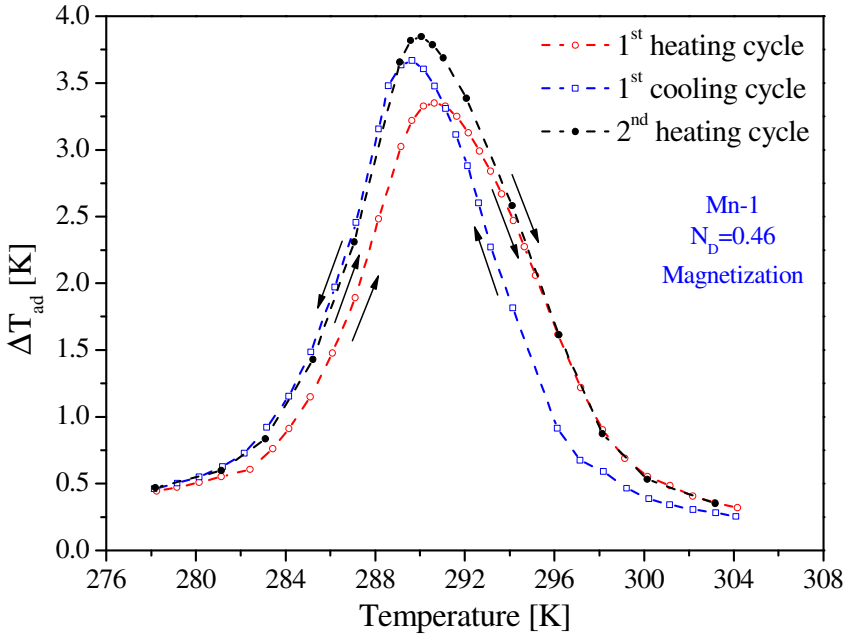
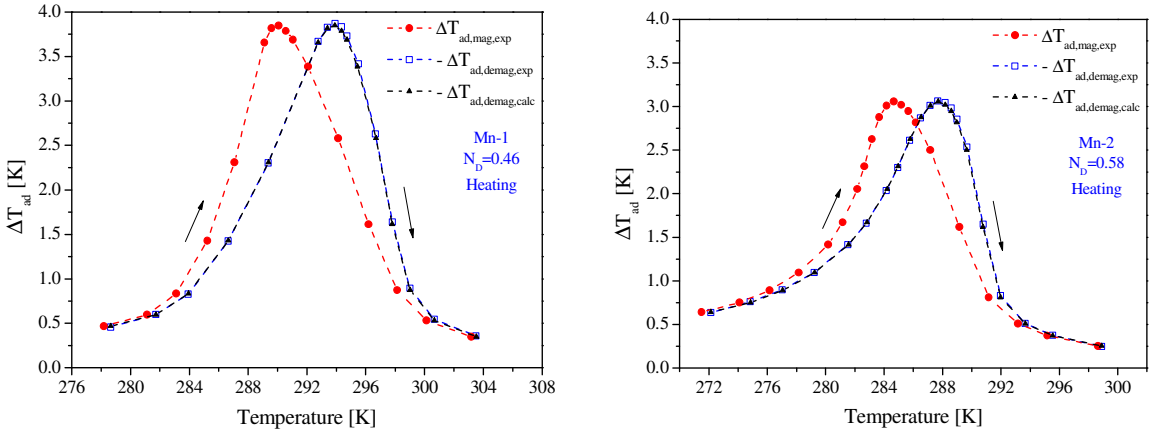


Figure 3. Adiabatic temperature change for sample Mn-1 with an unusual effect at its first thermal cycles while magnetization.

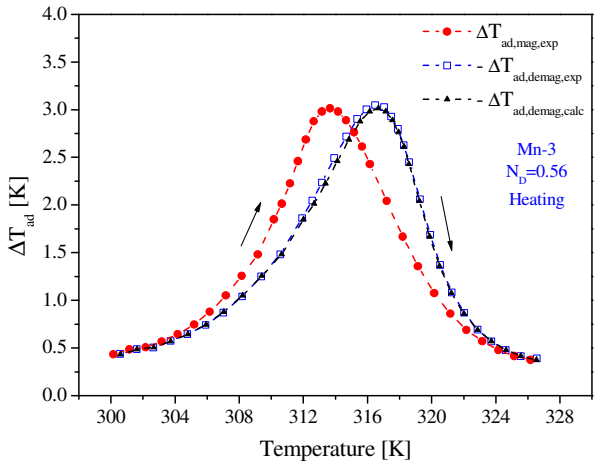
Table 2. Adiabatic temperature change and peak temperature (~ T_C) while magnetization and heating cycle of the samples when submitted to an applied magnetic field of 1.75 T.

Samples	ΔT_{ad} [K]	~ T_C [K]	N_D
Mn-1	3.9	290.0	0.46
Mn-2	3.1	284.7	0.58
Mn-3	3.0	313.7	0.56

The reversibility of the MCE of the samples was verified, as shown in Fig. 4 that when the sample is demagnetized it cools down the same amount as it heats up while it is magnetized. Thus, if the measurement is considered adiabatic, it suggests that the field-induced phase transition is fully reversible within the accuracy of the measurement. A theoretical demagnetization curve was calculated as proposed by Nielsen et al. (2010) and it was overlapped over the experimental curve, as shown in Fig. 4 (as solid triangles).



ISSN 2176-5480



(c)

Figure 4. Direct measurement of the adiabatic temperature change for samples (a) Mn-1, (b) Mn-2 and (c) Mn-3 as a function of temperature while magnetization and demagnetization with an applied magnetic field of 1.75 T.

The greater adiabatic temperature change of Mn-1 may be partially due to the lower demagnetization shape factor than that of Mn-2 and Mn-3. In order to calculate the actual internal field, the magnetization as a function of temperature and magnetic field should be measured, but that is out of the scope of this work.

Since Mn-based compounds undergo a first-order transition, a thermal hysteresis is expected to occur around the transition temperature. The thermal hysteresis is, in principle, an undesirable effect for the application of these materials in AMR devices and a more detailed study of this effect in these compounds is presented by von Moos *et al.* (2013). As shown in Fig. 5., the Mn-4 sample was subjected to two thermal cycles; first heating up and other cooling down. A thermal hysteresis of about ~0.6 K was observed in the sample Mn-4 while the magnetization measurements.

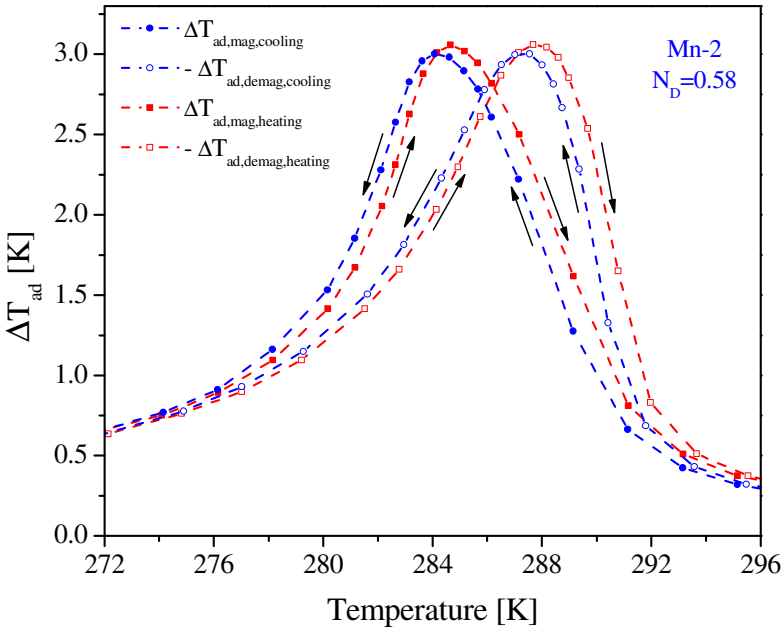


Figure 5. Thermal hysteresis study for sample Mn-4.

One of the main advantages of manganese-based compounds is its capability to tune its T_C, which enables to build a multi-layer active regenerator, allowing to reach higher temperature spans in the application. The results obtained in this work have showed how the magnetocaloric effect can be overlapped by employing different compositions of MnFe(P,As) compounds, as summarized in Fig. 6.

ISSN 2176-5480

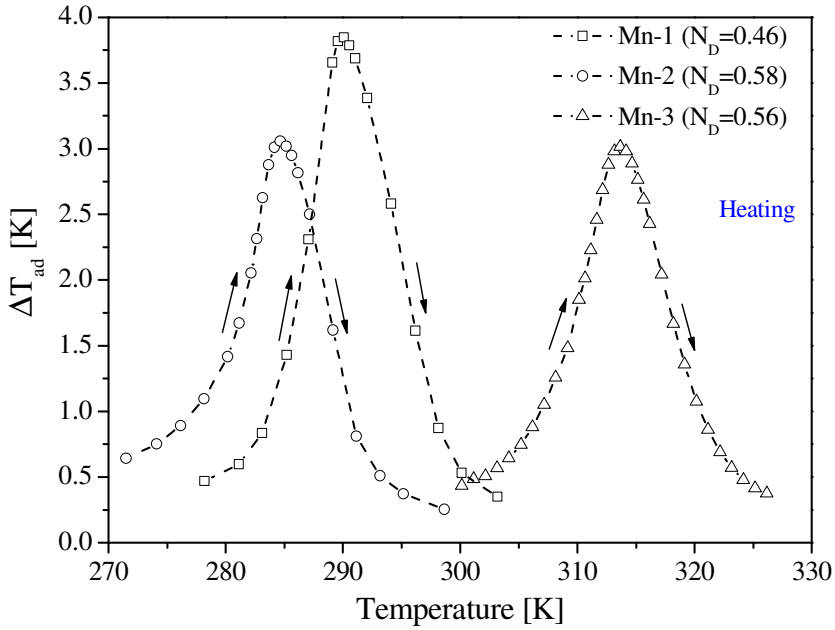


Figure 6. Adiabatic temperature change of three MnFe(P,As) samples with different compositions when submitted under an applied magnetic field of 1.75 T.

Fig. 6 shows that samples with demagnetization factor around 0.5, which decreases considerable the internal magnetic field, attains temperature changes above 1.7 K/T. The difference in the magnitude of the magnetocaloric effect in these samples is due to the different demagnetization factor of the samples measured on this work.

4. CONCLUSIONS

In this work 3 samples of the magnetic refrigerant MnFe(P,As) have been characterized through direct measurements of the adiabatic temperature change. A maximum temperature change of 3.9 K for an applied magnetic field change from 0 to 1.75 T. A *training* effect was found on these samples which display a lower adiabatic temperature change upon the first measurement thermal cycle. Direct measurement procedure which involves both thermal and field cycle has shown a thermal hysteresis of about 0.6 K for all three samples. The advantage to tune the Curie temperature together with the low cost of the raw materials and the synthesis make the MnFe(P,As) compounds promising room-temperature magnetic refrigerants.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge the support of CNPq through Grant No. 573581/2008-8 (National Institute of Science and Technology in Cooling and Thermophysics).

6. REFERENCES

Aharoni, A., 1998. *Demagnetizing factors for rectangular ferromagnetic prisms*. Journal of Applied Physics, v. 83, p. 3432–3434.

Bahl, C.R.H., and Nielsen, K.K., 2009. *The effect of desmagnetization on the magnetocaloric properties of gadolinium*. J. Appl. Phys., v. 105, p. 13916.

Benford, S.M. and Brown, G.V., 1981. *T-S diagram for gadolinium near the curie temperature*. Journal of Applied Physics, v. 52, p. 2110–2112.

Brück, E., 2007. *Magnetocaloric refrigeration at ambient temperature*. In: Buschow, K.H.J. Handbook of Magnetic Materials. Elsevier Science & Technology Books, v. 17, p. 235-291.

Canepa, F., Cirafici, S., Napoletano, M., Ciccarelli, C. and Belfortini, C., 2005. *Direct measurement of the magnetocaloric effect of microstructured gd eutectic compounds using a new fast automatic device*. Solid State Communications, v. 133, p. 241–244.

Fujita, A., Fujieda, S., Hasegawa, Y., Fukamichi, K., 2003. *Itinerant-electron metamagnetic transition and large magnetocaloric effects in La(FexSi1-x)13 compounds and their hydrades.* Phys. Rev. B., v. 67, p. 104416.

Gopal, B.R., Chahine, R. and Bose, T.K., 1997. *A sample translatory type insert for automated magnetocaloric effect measurements.* Review Scientific Instruments, v. 68, No. 4, p. 1818–1822.

ISSN 2176-5480

Green, G. and Schroeder, E., 1988. *A finite element model of an experimental magnetocaloric refrigerator*. In Proceedings of International Cryocooler Conference. Monterey, CA, USA, pp. 69-80.

Gschneidner, K.A. and Pecharsky, V.K., 2000. *The influence of magnetic field on the thermal properties of solids*. Materials Science and Engineering, v. 287, No. 2, p. 301–310.

Gschneidner, K.A. Jr and Pecharsky, V.K., 2000. *Magnetocaloric materials*. Ann. Rev. Mater. Sci., Vol. 30, pp. 387-429.

Huang, J.H., Qiu, J.F., Liu, J.R., Jin, P.Y., Xu, L.Z. and Zhang, J.X., 2005. *A direct measurement set-up for the magnetocaloric effect*. In Proceedings in First International Conference on Magnetic Refrigeration at Room Temperature. Montreux, Switzerland.

Khovaylo, V.V., Skokov, K.P., Gutfleisch, O., Miki, H., Kainuma, R. and Kanomata, T., 2010. *Reversibility and irreversibility of magnetocaloric effect in a metamagnetic shape memory alloy under cyclic action of a magnetic field*. Applied Physics Letters, v. 97, No. 052503.

Madireddi, S., Zhang, M., Pecharsky, V.K. and Jr., K.A.G., 2009. *Magnetocaloric effect of Gd5Si2Ge2 and its characteristics under different operating conditions*. In Proceedings in 3rd International Conference on Magnetic Refrigeration at Room Temperature. Ames, IA, USA.

Nielsen, K.K., Bahl, C.R.H. and Smith, A., 2010. *Constraints on the adiabatic temperature change in magnetocaloric materials*. Physical Review B, Vol. 81, 5, p. 054423.

Rosca, M., Zawilski, B., Plaindoux, P., Lyard, L., Marcus, J., Fruchart, D. and Miraglia, S., 2010. *Direct measurements of magnetocaloric parameters*. In Proceedings in 4th International Conference on Magnetic Refrigeration at Room Temperature. Baotou, China.

Smith, A., Nielsen, K.K., Christensen, D.V., Bahl, C.R.H., Bjørk, R., Hattel, J., 2010. *The demagnetizing field of a nonuniform rectangular prism.* Journal of Applied Physics, v. 107, p. 103910(1-8)

Tegus, O., Brück, E., Buschow, K.H.J., De Boer, F.R., 2002. *Transition-metal-based magnetic refrigerants for room temperature applications.* Nature, v. 415, 6868, p. 150-152.

Trevizoli, P.V., Barbosa, J.R., Oliveira, P.A., and Ferreira, R.T.S., 2010. *The reversibility of the magnetocaloric effect and its consequences for the active magnetic regenerator refrigeration cycle*. In Proceedings of ENCIT 2010. Uberlandia, MG, Brazil.

Trevizoli, P.V., Barbosa, J.R., Oliveira, P.A., Prata, A.T. and Ferreira, R.T.S., 2009. *Direct measurements of the magnetocaloric effect of gadolinium samples at near room temperature*. In Proceedings of COBEM 2009. Gramado, RS, Brazil.

Trevizoli, P.V., Barbosa Jr, J.R., Oliveira, P.A., Canesin, F.C. and Ferreira, R.T.S., 2012. *Assessment of demagnetization phenomena in the performance of an active magnetic regenerator*. International Journal of Refrigeration, v. 35, 4, p. 1043-1054.

von Moos, L., Nielsen, K.K., Engelbrecht, K. and Bahl, C.R.H., 2013, *Experimental investigation of the effect of thermal hysteresis in 1st-order material MnFe(P,As) applied in an AMR device*. International Journal of Refrigeration, in Press.

Zhang, Y.X., Liu, Z.G., Zhang, H.H. and Xu, X.N., 2000. *Direct measurement of thermal behaviour of magnetocaloric effects in perovskite-type la sr ca mno 0.75 x 0.25yx 3*. Materials Letters, v. 45, p. 91–94.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.