Magnetocaloric effect in GdGeSi compounds measured by the acoustic detection technique: Influence of composition and sample treatment

A. O. Guimarães, M. E. Soffner, A. M. Mansanares, A. A. Coelho, A. Magnus G. Carvalho et al.

Additional information on J. Appl. Phys.

Magnetocaloric effect in GdGeSi compounds measured by the acoustic detection technique: Influence of composition and sample treatment

A. O. Guimarães,[1,a)] M. E. Soffner,[1] A. M. Mansanares,[1,b)] A. A. Coelho,[1] A. Magnus G. Carvalho,[2] M. J. M. Pires,[2] S. Gama,[3] and E. C. da Silva[4]

[1]*Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), CP 6165, 13083-970 Campinas, Sao Paulo, Brazil*
[2]*Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (INMETRO), 25250-020 Duque de Caxias, Rio de Janeiro, Brazil*
[3]*Departamento de Ciências Exatas e da Terra, Universidade Federal de São Paulo (UNIFESP), 09972-270 Diadema, Sao Paulo, Brazil*
[4]*Laboratório de Ciências Físicas, Universidade Estadual do Norte Fluminense Darcy Ribeiro, 28013-602 Campos dos Goytacazes, Rio de Janeiro, Brazil*

In this paper we explore the acoustic detection method applied to the investigation of the magnetocaloric effect in Gd and $Gd_5(Ge_{1-x}Si_x)_4$ compounds, in the temperature range from 230 to 360 K and for magnetic fields up to 20 kOe. Measurements were performed in as-cast materials, both for powder and pellet samples, and in tree samples with compositions around $Gd_5Ge_2Si_2$ that underwent different thermal treatments. Small differences were observed when comparing powder and pellet samples of Gd and $Gd_5(Ge_{1-x}Si_x)_4$ compounds with $0.500 < x \le 1.00$. For the alloys with composition around $Gd_5Ge_2Si_2$, which exhibit giant magnetostriction and coexistence of distinct phases, expressive changes were observed when comparing powder and pellet samples. Based on these cases, it is easy to see that the acoustic method can distinguish a second-order phase transition from a first-order magnetic-crystallographic one, and that it presents good sensitivity to detect spurious material phase in small quantities. © *2010 American Institute of Physics.*
[doi:10.1063/1.3357375]

I. INTRODUCTION

The magnetocaloric effect (MCE) is a promising choice for the construction of near room temperature refrigeration devices. In view of this, the search for magnetocaloric materials has been increasing in the recent past. The MCE is characterized in terms of the adiabatic temperature change (ΔT_S) in a solid due to an external magnetic field step, or by means of its isothermal entropy change (ΔS_T). It can be measured directly through the temperature rise of the sample or it can be calculated from magnetic or calorimetric measurements.[1,2]

Recently, a series of $Gd_5(Ge_{1-x}Si_x)_4$ alloys has been widely studied, specially after 1997, when large entropy changes in $Gd_5Si_2Ge_2$ were reported by Pecharsky and Gschneidner Jr.[3] Compositions in the range $0.24 \le x \le 0.50$ undergo a first order phase transition, in which a magnetic phase transition occurs simultaneously with a structural one, in a reversible way. The search for candidate materials increases and their use as magnetic active regenerators inevitably deals with mechanical processes, in order to get the proper form, as wires, thin plates, spheres, required by each specific machine.[4] Such processes may cause changes in the magnetocaloric properties of the materials since these properties are, in many cases, strictly related to the crystallographic structure. Thus, samples with the same composition

but different form, can present considerable changes in their MCE curves and, furthermore, care must be taken for comparing results obtained from magnetic, thermal, or combined methods.[5,6]

A suitable way for detecting temperature changes, due to the MCE, on a magnetic solid is the noncontact acoustic detection, in which a thermal wave is produced by the adiabatic application of a small modulated (ac) magnetic field and converted in an acoustic signal, thus detected by a microphone.[7,8] Recently we presented a simple method for the determination of the total MCE, meaning the effect caused by large magnetic field steps, based on the direct integration of the modulated temperature acoustically detected.[9] The key issue of the method is the continuous scanning of the static magnetic field, which is superimposed to the alternating one. This method can be used in both paramagnetic and ferromagnetic regions, as well as around the phase transition temperature, in which the maximum MCE occurs.

In the present paper we explore the acoustic detection method in a different experimental setup applied to the investigation of Gd, which is the prototype material for magnetocaloric studies, and $Gd_5(Ge_{1-x}Si_x)_4$ compounds. Measurements were performed in as-cast materials, both for powder and pellet samples. Moreover, tree samples with compositions around $Gd_5Ge_2Si_2$, which underwent different thermal treatments, were also investigated. The aim here is to show the possibility of using the acoustic detection method to measure the MCE in samples with different forms and to

---

a)Present address: Laboratório de Ciências Físicas, Universidade Estadual do Norte Fluminense Darcy Ribeiro, 28013-602, Campos dos Goytacazes, RJ, Brazil.
b)Electronic mail: manoel@ifi.unicamp.br.

107, 073524-1

confirm the high sensitivity of the technique concerning the changes caused on the material's properties due to thermal treatment and mechanical process.

II. METHODOLOGY

The methodology we used is based on the photoacoustic technique principles, in which a thermal wave produced in a solid, by the absorption of a modulated light beam, is converted in an acoustic signal, being detected by a microphone.[10] For a fixed modulation frequency, the acoustic signal, S_{ac}, can be written as:

$$S_{ac} = G(T)F_{sys}\delta T \tag{1}$$

in which $G(T)$ is a temperature dependent factor carrying information about gas properties and F_{sys} depends on the electronics of the detection system. δT is the complex temperature oscillation at the sample surface, which depends on the light intensity and modulation frequency, besides the optical and thermal properties of the sample.

The acoustic measurement of the MCE is based on the same principles. However, the temperature oscillations are generated by an ac magnetic field, adiabatically applied, instead of the modulated light beam. Therefore, such magnetoacoustic (MA) signal can be written as in Eq. (1) in a way that an appropriate calibration procedure provides the temperature rise values from the microphone response. The calibration is done in two steps: first we have determined the temperature dependence of the cell, $G(T)$, using an electrical resistance inside the acoustic cell as the heat source (Joule effect); the further step was to determine the F_{sys} factor by comparing the measured normalized signal to the calculated MCE values (δT_S) for a reference sample. The adiabatic temperature rise can be expressed by combining one of the fundamental Maxwell's relations with an appropriate TdS equation,[11] as:

$$\delta T_S = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H \delta H. \tag{2}$$

Therefore, the temperature oscillation can be calculated for a reference sample provided the heat capacity, C_H, and magnetization, M, of the sample are known as function of the magnetic field, H, and temperature.

As mentioned before, the interest concerning magnetocaloric materials involves the adiabatic temperature variation ΔT_S due to large magnetic field steps. In this way, we propose a simple method to determine the total MCE from the sum of several δT_S quantities acoustically detected. From the experimental curves of δT_S versus H, a finite temperature variation ΔT can be found, as follows:

$$\Delta T = \int_0^H \delta T_S = \frac{1}{\delta H}\int_0^H \delta T_S dH. \tag{3}$$

It is important to observe that the acoustically detected temperature oscillation, δT_S, is indeed adiabatic since the modulation period (of the order of milliseconds) is very small when compared to the typical thermal diffusion time (of the order of hundreds of milliseconds). However, the integration path in Eq. (3) is along an isothermal magnetic field

scan, which causes ΔT to deviate from ΔT_S. Such a deviation is estimated as of a few percent, as discussed in Ref. 9.

III. MATERIALS

The samples we have studied were polycrystalline Gd (reference sample for calibration), $Gd_{5.09}Ge_{2.03}Si_{1.88}$ and $Gd_5(Ge_{1-x}Si_x)_4$ ($x=0.500$, 0.625, 0.750, 0.875, and 1.00). These compounds were prepared by arc melting of the constituent elements under inert atmosphere, with the lost of material being negligible. The purity of the constituents were 99.9% for gadolinium, 99.9999% for silicon and germanium. The Gd powder sample used for calibration was obtained by filing the material, while the other samples were prepared by hand grinding the bulk materials. The samples were typically grains smaller than 50 μm. The pellets, with approximately 3 mm length, were prepared by uniaxially pressing the powder samples using a hardened tool steel die (2.3 mm in diameter) where the material was compacted under pressure around 600 MPa. For measurements with pellets, a Gd bulk sample with similar form was used for calibration purposes.

The $Gd_5(Ge_{1-x}Si_x)_4$ alloys have been widely investigated as a promising option for near room temperature refrigeration systems. Compositions with $x > 0.50$ undergo a purely magnetic (ferromagnetic to paramagnetic) second order phase transition, while compositions in the range $0.24 \leq x \leq 0.50$ present a simultaneous magnetic and structural (orthorhombic to monoclinic) first order phase transition.[12,13] It is common the formation of other phases besides the one with the nominal stoichiometry. For samples prepared with nominal stoichiometries around 5:2:2, two phase transitions occurring in temperatures relatively close to each other have been reported in several works.[3,14,15] Usually, one of the phase transitions is of first order type and the other is of second order type, and different thermal treatments can be done in order to seek for the desired phase purity. In this way, in addition to the as-cast samples, we investigated also two $Gd_5Ge_2Si_2$ powder samples which underwent different thermal treatments. For simplicity, in the text these samples are referred as annealed $Gd_5Ge_2Si_2$ sample 1 (1650 °C/48 h) and annealed $Gd_5Ge_2Si_2$ sample 2 (1300 °C/2 h+900 °C/1 week, provided by V. K. Pecharsky).

IV. EXPERIMENTAL SETUP

The experimental apparatus we have used was adapted in a commercial Varian E-12 electron spin resonance spectrometer. The dc magnetic field scan is provided by the electromagnet and the alternating magnetic field, parallel to the static one, is produced by the coils of a microwave rectangular cavity. The acoustic cell consists of a cylindrical glass tube with 2.4 mm diameter and 45 cm length, having a closed bottom end where the sample is held, and an open top end sealed by a Teflon holder with a Senheiser microphone. The microphone signal is analyzed by a lock-in amplifier (Stanford SR830). The temperature control is achieved by means of a cooled/heated N_2 gas flow and the temperature is measured by a type K thermocouple. In order to determine the temperature dependence of the cell, a constant power
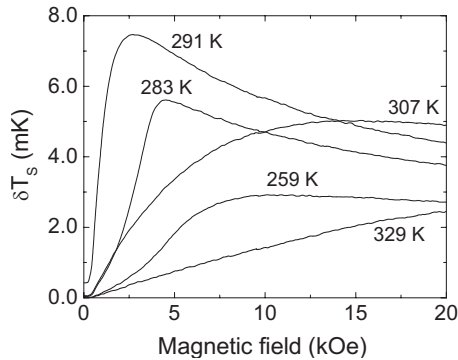
FIG. 1. Modulated MCE, δT_S, for the Gd powder sample as a function of the dc magnetic field, for some representative temperatures.

heat source was provided by a ~ 10 Ω resistance (coil) placed in the microphone holder. Modulated current of a few milliampere was delivered by a controlled current source.

Measurements were performed scanning the dc magnetic field from 0 to 20 kOe with data recording every 15 Oe. The alternating magnetic field was 36 Oe peak-to-peak with a modulation frequency of 270 Hz. At this frequency, the adiabatic condition is fulfilled and a good signal/noise ratio is ensured since it is close to one of the acoustic resonances of the cell. Temperature was controlled within 0.1 K in the 230–360 K range.

V. RESULTS AND DISCUSSION

Gadolinium was chosen as the reference material for the calibration procedure. The measured MA signal amplitude was properly normalized by the temperature response of the cell, G(T). The normalized signal was thus fitted, using minimum square method, to the calculated adiabatic temperature rise, δT_S, for Gd in the temperature range from 290 to 325 K, for three values of the dc magnetic field (2, 3, and 4 kOe). For the calculated δT_S, the values of $(\partial M / \partial T)_H$ used in Eq. (2) were obtained from magnetization measurements performed in a Quantum Design® SQUID magnetometer. Moreover, a single value of the specific heat, (280 ± 20) J/kg K, was used for the entire temperature range (paramagnetic region) and for the three magnetic fields chosen for the calibration. This value was obtained from literature data[1,16–18] and confirmed by thermal diffusivity measurements of the reference sample, at zero magnetic field, using the photoacoustic technique. The data fitting allows one to determine the constant F_{sys}, which is used to transform every measured MA signal amplitude into modulated MCE, δT_S.

Figure 1 shows δT_S for the Gd powder sample, as function of the dc magnetic field, for some representative temperatures. The curves are similar to those previously reported in Refs. 9 and 19, with the maximum MCE values found around the Curie temperatures, peaking at magnetic fields of a few kilo-oersted. In the ferromagnetic temperature range the MCE saturates for magnetic fields higher than 10 kOe, and for the paramagnetic region it shows a smooth rising when increasing the magnetic field. It can be noticed that the shape of the curves is mainly governed by $(\partial M / \partial T)_H$, as expected when dealing with a second order phase transition,
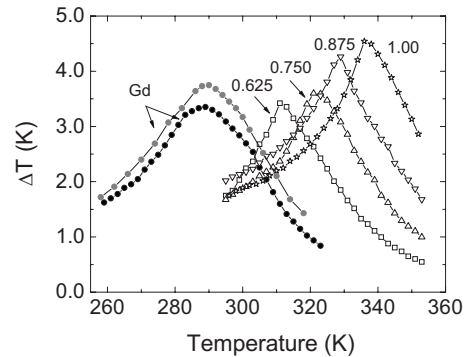

FIG. 2. Total MCE, ΔT, vs temperature for Gd (black circles) and for as-cast $Gd_5(Ge_{1-x}Si_x)_4$ powder samples (open symbols, $x=0.625$, 0.750, 0.875, and 1.00) measured using acoustic detection for 20 kOe magnetic field step. Results of a conventional measurement are also shown for Gd (gray circles).

which was also reported in Refs. 7 and 20. This characteristic behavior was also observed for all as-cast powder $Gd_5(Ge_{1-x}Si_x)_4$ samples with $x \geq 0.500$.

The numerical integration presented in Eq. (3) was performed based on the δT_S versus H curves and the results for the total MCE, ΔT, are plotted in Fig. 2 for Gd (black circles), for 20 kOe magnetic field step. In addition, the temperature rise in a 1.0 g bulk Gd sample, positioned in the inner chamber of a Quantum Design® PPMS, was conventionally measured by a Cernox sensor as a function of the temperature for the same 20 kOe magnetic field step, and it is also shown in Fig. 2 (gray circles). The results obtained by the acoustic detection are in good agreement with the conventionally measured MCE and with data reported in literature for Gd, concerning both the shape and the magnitude of the curves.[18,21]

Figure 2 also presents the total MCE, ΔT, for $Gd_5(Ge_{1-x}Si_x)_4$ powder compounds with $0.500 < x \leq 1.00$ (open symbols), which present orthorhombic structure and undergo a purely magnetic second order phase transition. The temperatures of the peaks, as well as their magnitudes, increase with Si concentration as expected, due to the reduction in the unitary cell volume.[12] The results for Gd_5Si_4 agree with data reported in Ref. 22 concerning the shape of the curves.

Figure 3 presents δT_S as function of the temperature for several dc magnetic fields for the annealed $Gd_5Ge_2Si_2$
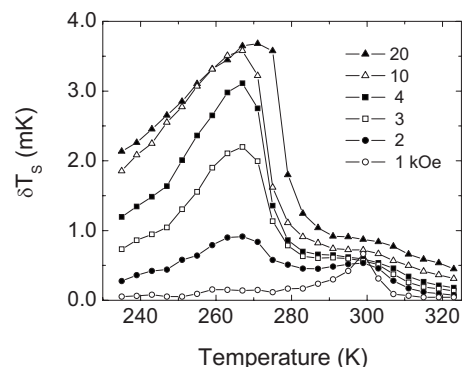

FIG. 3. Modulated MCE, δT_S, vs temperature for annealed $Gd_5Ge_2Si_2$ sample 1 (1650 °C/48 h) measured with different dc magnetic fields, from 1 to 20 kOe.
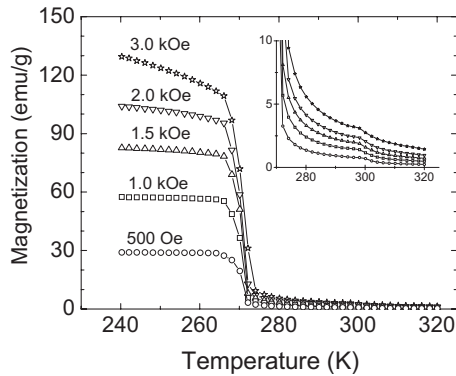
FIG. 4. Magnetization as a function of the temperature for the annealed $Gd_5Ge_2Si_2$ sample 1 for several magnetic fields. The inset shows details around the second order phase transition temperature.

FIG. 6. Total MCE, ΔT, vs temperature for Gd (black circles) and for the as-cast $Gd_5(Ge_{1-x}Si_x)_4$ pellet samples (open symbols, $x=0.625$, 0.750, 0.875, and 1.00) measured using acoustic detection for 20 kOe magnetic field step.

sample 1. The shape of the curves clearly reveals the occurrence of two phase transitions, associated to distinct compositions in the sample. At low magnetic fields the MCE has a maximum around 300 K, and it gets wider when increasing the magnetic field, similar to the behavior observed for Gd, which is actually typical for second order phase transition. Concerning the expected first order phase transition, around 270 K, δT_S is not significant for magnetic fields below 2 kOe, although the magnetization undergoes abrupt changes (see Fig. 4). This is due to the influence of the specific heat, which peaks close to the phase transition temperature, thus suppressing the temperature oscillations of the sample. Increasing the magnetic field, the signal becomes prominent, with the maximum MCE slightly shifted to higher temperatures. It is important to stress how sensitive the technique is, enabling the detection of spurious phase in the material, in very small quantities, which undergoes second order phase transition. Magnetization curves of the annealed $Gd_5Ge_2Si_2$ sample 1, for low magnetic fields, are shown in the Fig. 4, and the occurrence of the second order phase transition, around 300 K, is revealed in the inset.

The total MCE, ΔT, as function of temperature, for the three samples with stoichiometries around 5:2:2 is plotted in Fig. 5, for 20 kOe magnetic field step. The shape of the curves is in agreement with results reported in the literature for such multiphase materials.[23] The curves show the same behavior in the ferromagnetic range, while above the first
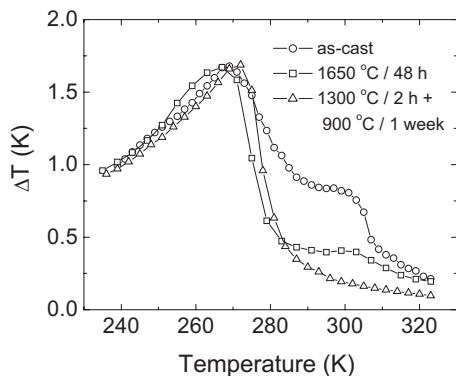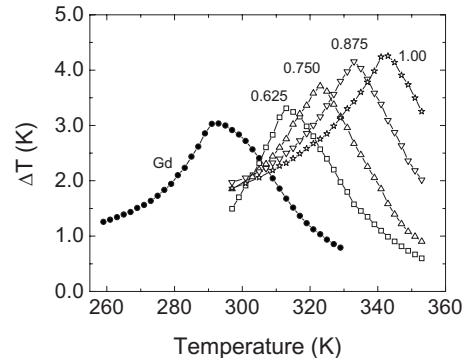
order phase transition (270 K) the shape of each one strictly depends on the fraction of monoclinic phase present in the sample. It is clear that the temperature peak related to the second order phase transition for the annealed sample 1, around 300 K, is much less pronounced than for the as-cast $Gd_{5.09}Ge_{2.03}Si_{1.88}$ sample, and it is completely absent for the annealed sample 2. Indeed, the second order phase transition is much more evident in the magnetization curves of the as-cast $Gd_{5.09}Ge_{2.03}Si_{1.88}$ sample[24] than we can see in Fig. 4 for the annealed sample 1. Again we notice, by means of the ΔT curves, the sensitivity of the technique in detecting small amounts of spurious phase undergoing second order phase transitions in multiphase materials.

Measurements of the modulated MCE, scanning the dc magnetic field, were performed for the pellet samples, and the total MCE, ΔT, as a function of the temperature, was determined. Figure 6 shows the results for Gd (solid symbols) and $Gd_5(Ge_{1-x}Si_x)_4$ compounds with $0.500 < x \leq 1.00$ (open symbols), for 20 kOe magnetic field step. The δT_S versus H curves (not shown) present the same behavior observed in Fig. 1, typical for second order phase transitions, having the maximum MCE values around the Curie temperatures and peaking at magnetic fields of a few kOe. In an overall view, there are not significant changes, for these samples with respect to the corresponding powder ones, both in δT_S and ΔT values. But carefully comparing Figs. 2 and 6, we notice that ΔT curves are somewhat wider for pellet samples, with the transition temperature slightly shifted to higher temperatures. Such effects were already reported in Ref. 5, and for that case they were related to modification in exchanges interactions of the alloy, although it is not clear how it exactly happens. In the case of $Gd_5(Ge_{1-x}Si_x)_4$ samples investigated here, it is believed that the differences between the results of powder and pellet come from changes in the phase composition and from magnetostriction effects. The size of the particles in both types of samples is large enough to prevent significant alteration in the exchange interactions.[25] Indeed, we can suppose that most of the particles are multidomain (single- or poly-) crystals, and also that the compression/fragmentation leads to distinct range of temperature for phase transition by involving distinct strain fields and phase nucleation process.[25,26]
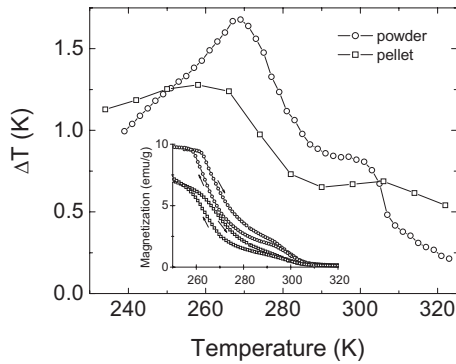

FIG. 5. Total MCE, ΔT, vs temperature for the as-cast $Gd_{5.09}Ge_{2.03}Si_{1.88}$ powder sample and the annealed $Gd_5Ge_2Si_2$ ones (sample 1 and sample 2), for 20 kOe magnetic field step.

FIG. 7. Total MCE, ΔT, vs temperature for the as-cast $Gd_{5.09}Ge_{2.03}Si_{1.88}$ powder (same result presented in Fig. 5) and pellet samples, for 20 kOe magnetic field step. The inset shows magnetization curves for both samples at 200 Oe.

The compounds with composition around 5:2:2, however, undergo expressive changes on their magnetocaloric properties caused by the pressure exerted on the pellets during the preparation. Figure 7 shows ΔT as a function of the temperature for $Gd_{5.09}Ge_{2.03}Si_{1.88}$, in powder and pellet samples. For these compositions the distinction between powder and pellet samples are magnified since such alloys are known to exhibit giant magnetostriction and the coexistence of distinct phases is common. Two phase transitions can be seen for both samples, and it is clear how wider such transitions became for the pellet one, which is also confirmed by magnetization measurements in the inset of Fig. 7. The hysteresis on the magnetization curves indicates that the first order transition, around 270 K, is kept. Nevertheless, some more drastic changes were observed for the as-cast $Gd_5Ge_2Si_2$ compound, shown in Fig. 8. For the powder sample, ΔT is typically governed by the second order phase transition, around 300 K, which is also revealed in the magnetization curves, in the inset of Fig. 8. The magnetization shows, in addition, a less pronounced first order transition, around 270 K, which does not clearly manifest itself in terms of a temperature rise, when compared with the second order phase transition. However, for the pellet sample, one can see that besides the purely magnetic phase transition, the ΔT curve undoubtedly exhibits also the magnetic-crystallographic first order transition around 270 K. It is clear from the magnetization data that the second order phase
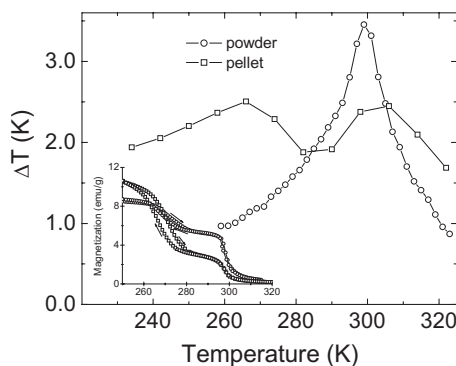
transition got wider, while the first order one became sharper, and that an expressive alteration in the phase composition took place due to the compression process. The first order character of the phase transition around 270 K is also evidenced by δT_S curves (not shown), similar to those in Fig. 3, in which the MCE is suppressed at low magnetic fields by the influence of the heat capacity.

The uncertainties involved in this technique, estimated in 15%–20% for powder samples,[9] can be equally assumed when dealing with pellets. Although the signal to noise ratio is greater for pellets, the variations on the sample's volume is greater as well. It is worth pointing out that such changes are reflected in the gas volume in the cell, which is a source of errors since the modulation frequency used is not far from an acoustic resonance of the cell. Besides these contributions, the uncertainties in the specific heat value used for calibration is common to both powder and pellet samples.

VI. CONCLUSIONS

The results presented in this paper show the potentiality of using the acoustic detection technique to measure the MCE in different sets of samples. The experimental setup combines photothermal typical devices with a commercial ESR spectrometer and allows one to investigate both powder and pellet magnetocaloric materials. The measurements are reproducible, with an appropriate calibration procedure leading to temperature rise values, δT_S, in the sample. The continuous scanning of the dc magnetic field, from zero up to 20 kOe, permits the ΔT determination based on a numerical integration. Results for Gd are in agreement with literature and with a conventional direct measurement. More than quantifying the MCE, by means of ΔT, the acoustic detection method revealed to be highly sensitive concerning the changes caused on the material's properties due to thermal treatments and mechanical processes.

For the $Gd_5(Ge_{1-x}Si_x)_4$ compounds with $0.500 < x \leq 1.00$, the total MCE, ΔT, was evaluated and the results for powder samples are very similar to those for pellet ones, presenting some small differences related to changes in their phase composition and magnetostriction effects. The δT_S curves show the same main behavior observed for Gd, which is actually typical for materials undergoing a purely magnetic second-order phase transition. Concerning the alloys with composition around 5:2:2, however, some expressive changes were observed, when comparing powder and pellet samples. For these alloys, which exhibit giant magnetostriction and coexistence of distinct phases, an alteration in the phase composition took place during the compression process related to the pellet preparation. Such changes are clearly reveled by ΔT as well as δT_S, allowing one to distinguish a second-order phase transition from a magnetic-crystallographic first-order one, in which the influence of the specific heat is pronounced. Furthermore, based on the measurements with powder samples that underwent different thermal treatments, it is worth to emphasize the good sensitivity of the technique, being able to detect spurious material phase in small quantities.

FIG. 8. Total MCE, ΔT, vs temperature for the as-cast $Gd_5Ge_2Si_2$ powder and pellet samples, for 20 kOe magnetic field step. The inset shows magnetization curves for both samples at 200 Oe.

The uncertainties involving the acoustic detection include different sources of errors. Deviations smaller than 2% are caused mainly by noise and the reproducibility of the overall experimental conditions. Changes in the gas volume in the cell, due to the sample's volume, produce variations in the measured signal, which was properly evaluated by varying the amount of sample. The last important source of error remains in the uncertainty in the specific heat value used for calibration, which is of 7% in our case. Thus, considering these sources, the errors in the acoustically detected MCE measurements are estimated in 15%–20%, of the same order of those in conventional methods.

ACKNOWLEDGMENTS

[1] V. K. Pecharsky and K. A. Gschneidner, Jr., J. Appl. Phys. **86**, 565 (1999).
[2] M. Foldeaki, W. Schnelle, E. Gmelin, P. Benard, B. Koszegi, A. Giguere, R. Chahine, and T. K. Bose, J. Appl. Phys. **82**, 309 (1997).
[3] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[4] A. M. Tishin and Y. I. Spichkin, *The MCE and its Applications* (Institute of Physics, Bristol, Philadelphia, 2003).
[5] M. Foldeaki, R. Chahine, B. R. Gopal, T. K. Bose, X. Y. Liu, and J. A. Barclay, J. Appl. Phys. **83**, 2727 (1998).
[6] P. V. Trevizoli, C. S. Alves, M. A. B. Mendes, A. Magnus, G. Carvalho, S. Gama, J. Magn. Magn. Mater. **320**, 1582 (2008).
[7] C. Glorieux, J. Caerels, and J. Thoen, J. Appl. Phys. **80**, 3412 (1996).
[8] B. R. Gopal, R. Chahine, and T. K. Bose, Rev. Sci. Instrum. **68**, 1818 (1997).
[9] A. O. Guimarães, M. E. Soffner, A. M. Mansanares, A. A. Coelho, A. Magnus, G. Carvalho, M. J. M. Pires, S. Gama, and E. C. da Silva, Phys. Rev. B **80**, 134406 (2009).
[10] M. V. Marquezini, N. Cella, A. M. Mansanares, H. Vargas, and L. C. M. Miranda, Meas. Sci. Technol. **2**, 396 (1991).
[11] V. K. Pecharsky and K. A. Gschneidner, Jr., J. Magn. Magn. Mater. **200**, 44 (1999).
[12] V. K. Pecharsky and K. A. Gschneidner, Jr., Adv. Mater. **13**, 683 (2001).
[13] A. M. G. Carvalho, C. S. Alves, A. Campos, A. A. Coelho, S. Gama, F. C. G. Gandra, P. J. von Ranke, and N. A. Oliveira, J. Appl. Phys. **97**, 10M320 (2005).
[14] A. O. Pecharsky, K. A. Gschneidner, Jr., and V. K. Pecharsky, J. Magn. Magn. Mater. **267**, 60 (2003).
[15] S. Gama, C. S. Alves, A. A. Coelho, C. A. Ribeiro, A. I. C. Persiano, and D. Silva, J. Magn. Magn. Mater. **272–276**, 848 (2004).
[16] C. Glorieux, J. Thoen, G. Bednarz, M. A. White, and D. J. W. Geldart, Phys. Rev. B **52**, 12770 (1995).
[17] G. Bednarz, D. J. W. Geldart, and M. A. White, Phys. Rev. B **47**, 14247 (1993).
[18] S. Yu. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **57**, 3478 (1998).
[19] A. O. Guimarães, A. M. Mansanares, A. Magnus, G. Carvalho, A. A. Coelho, S. Gama, M. J. M. Pires, and E. C. da Silva, J. Phys.: Conf. Ser. (in press).
[20] W. Otowski, C. Glorieux, R. Hofman, and J. Thoen, Thermochim. Acta **218**, 123 (1993).
[21] B. R. Gopal, R. Chahine, M. Földeàki, and T. K. Bose, Rev. Sci. Instrum. **66**, 232 (1995).
[22] K. A. Gschneidner, Jr., V. K. Pecharsky, A. O. Pecharsky, and C. B. Zimm, Mater. Sci. Forum **315–317**, 69 (1999).
[23] A. Giguère, M. Foldeaki, B. R. Gopal, R. Chahine, T. K. Bose, A. Frydman, and J. A. Barclay, Phys. Rev. Lett. **83**, 2262 (1999).
[24] M. J. M. Pires, A. M. G. Carvalho, S. Gama, E. C. da Silva, A. A. Coelho, and A. M. Mansanares, Phys. Rev. B **72**, 224435 (2005).
[25] R. C. O'Handley, *Modern Magnetic Materials: Principles and Applications*, (Wiley, New York, 2000), Chap 8.
[26] J. D. Moore, G. K. Perkins, Y. Bugoslavsky, M. K. Chattopadhyay, S. B. Roy, P. Chaddah, V. K. Pecharsky, K. A. Gschneidner, Jr., and L. F. Cohen, Appl. Phys. Lett. **88**, 072501 (2006).