Photoacoustic based technique for measuring the magnetocaloric effect

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Abstract. This paper presents a method for detecting the magnetocaloric effect (MCE), based on the acoustic detection. Small temperature oscillations, due to the application of a modulated magnetic field, are detected by a microphone in a closed cell. The continuous scanning of a superimposed dc magnetic field allows, by numerical calculation, the determination of large temperature variations caused by magnetic field steps from zero to tens of kOe. Measurements were performed in Gd and Gd₅(SiₓGe₁₋ₓ)₄ compounds. The obtained results show the efficiency of the technique, which is suitable for the investigation of materials undergoing both purely magnetic phase transitions and magnetic-crystallographic first order ones.

1. Introduction

The magnetocaloric effect (MCE) is a promising option for the construction of near room temperature refrigeration devices. In the recent past, the search for new magnetocaloric materials has been increasing and also it is the need for characterizing them. The MCE is characterized in terms of the adiabatic temperature change ($\Delta T_s$) of a solid due to an external magnetic field step, or by means of its isothermal entropy change ($\Delta S_T$). It can be measured directly though the temperature rise of the sample or it can be calculated from magnetic or calorimetric measurements [1].

A suitable way for measuring temperature changes, due to the MCE, on a magnetic solid is the non-contact acoustic detection. It was already reported by Glorieux et al. to obtain the critical exponents of Gd [2]. This technique is based on the photoacoustic detection principles, with the thermal wave being produced by the adiabatic application of a modulated (ac) magnetic field (tens of Oe) superimposed to a static (dc) one. Rather than focusing on the effects of small temperature oscillations $\delta T_s$, the technological interest in magnetocaloric materials involves large temperature variations $\Delta T_s$ caused by large magnetic field steps from zero to tens of kOe.

This work reports a simple method for the total MCE determination based on the direct integration of the modulated temperature acoustically detected. The key issue of the method is the continuous scanning of the static magnetic field, from zero to 20 kOe. This method may be used in both paramagnetic and ferromagnetic regions, as well as around the transition temperature, in which the
maximum MCE occurs. Furthermore, after the calibration procedure, no additional data is required. We investigated Gd and Gd₅(SiₓGe₁₋ₓ)₄ samples with different compositions.

2. Methodology

The photoacoustic technique is based on the detection of acoustic waves produced in a closed cell using a microphone. For solid samples, the absorption of intensity modulated light heats up the sample and the temperature oscillations δT are related to the microphone signal Sₘᵢᶜ, for a fixed modulation frequency, in the following way:

\[ S_{\text{mic}} = G(T) F_{\text{sys}} \delta T \]

in which \( G(T) \) is a temperature dependent factor carrying information about gas properties, \( F_{\text{sys}} \) depends on the electronics of the detection system, and \( \delta T \) is the complex temperature oscillation at the sample surface.

The acoustic measurement of the MCE is based on the same principles, with the temperature oscillations being generated by an ac magnetic field, 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. For this purpose, 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 \( F_{\text{sys}} \) factor by comparing the measured normalized signal to the calculated MCE values (\( \delta T_S \)) for a reference sample. This temperature rise can be expressed, combining one of the fundamental Maxwell’s relations with an appropriate T dS equation [1], as

\[ \delta T_S = -\frac{T}{C_H} \left( \frac{\partial M}{\partial T} \right)_H \delta H \]

In the above equation \( M \) is the total magnetization and \( C_H \) is the heat capacity of the sample. Therefore, the temperature oscillation can be calculated for a reference sample provided \( C_H \) and \( M \) are known as function of \( H \) and \( T \).

However, as mentioned in the introduction, the interest concerning magnetocaloric materials involves the adiabatic temperature variation due to larger magnetic field steps (kOe), which could be reached by integrating Eq. 1. In this sense, we present here a simple way to determine the total MCE, \( \Delta T \), from the sum of several \( \delta T_S \) quantities acoustically detected, by means of the numerical area under the experimental curves of \( \delta T_S \) vs. \( H \) divided by \( \delta H \).

3. Materials

A prototype material for room temperature range refrigeration is the lanthanide gadolinium, which orders magnetically at 290 K. Recently, a series of Gd₅(SiₓGe₁₋ₓ)₄ alloys has been widely investigated, mainly after the discovery of the so called giant MCE in Gd₅Si₂Ge₂. Compositions in the range 0.24 < x < 0.5 present a simultaneous magnetic-crystallographic first order transition.

The samples we have studied were pure Gd (reference sample for calibration) and some Gd₅(SiₓGe₁₋ₓ)₄ compounds, which were arc melted three times in Ar atmosphere. Commercial 99.9 wt % Gd and electronic grade Si and Ge were used. The resulting powder samples were prepared with grains smaller than 50 µm. Besides the as-prepared sample, for x=0.5, we used also a sample which underwent a thermal treatment (1650°C/48h), seeking for the desired phase purity. It is common, however, the formation of other phases than the one with the nominal stoichiometry, with phase transitions occurring in temperatures relatively close to each other. Usually one of the transitions is of first order type and the other is of second order type [3].
4. Experimental aspects

The experimental apparatus we have used was adapted in a commercial Varian E-12 electron spin resonance (ESR) spectrometer. The dc magnetic field scan is provided by the electromagnet and the alternating field, parallel to the static one, is produced by coils in a resonance rectangular cavity. The acoustic cell consists in a 2.4 mm in diameter tube with 45 cm length connected to 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\textsubscript{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 heat source was provided by a 10 \textohm resistance placed in the microphone holder.

Measurements were performed scanning the dc magnetic field from 0 to 20 kOe. The ac magnetic field was 36 Oe peak-to-peak with a modulation frequency of 270 Hz, which is not far from one of the acoustic resonances of the cell, ensuring a good signal/noise ratio, and fulfilling the adiabatic condition. Temperature was controlled with accuracy of 0.1 K in the 230 – 360 K interval.

5. Results and discussion

Gadolinium was chosen as the reference material for the calibration procedure. Its specific heat data was taken from literature [1] and magnetization measurements were performed in a commercial SQUID magnetometer (Quantum Design\textsuperscript{®}). The temperature dependence of the cell was adjusted by a polynomial function. Comparison between the experimental normalized data and the simulated curves was done for the Gd in the paramagnetic temperature range, at dc fields of 1, 2 and 3 kOe. Thus, it was obtained a function of the temperature that allows one to convert the MA signal in $\delta T_S$ values, for any investigated sample.

Figure 1. Modulated MCE, $\delta T_S$, for Gd as a function of the (a) dc magnetic field and (b) temperature. (c) Total MCE, $\Delta T$, for Gd (black circles) and Gd\textsubscript{x}(Si\textsubscript{1-x}Ge\textsubscript{x})\textsubscript{4} compounds (open symbols) measured by acoustic detection. Results of a conventional direct measurement are also shown for Gd (gray circles).

Figure 1a shows the modulated MCE for the Gd sample as function of the dc magnetic field for some representative temperatures. The maximum MCE values are for temperatures around the Curie point and it peaks at magnetic fields of a few kOe. In the ferromagnetic temperature range the MCE saturates for fields higher than 10 kOe and for the paramagnetic region it shows a smooth rising in increasing the magnetic field. Another way to look at these data is presented in figure 1b, where $\delta T_S$ is plotted as function of the temperature, for some representative dc field values. The curves get wider in increasing the magnetic field, with their peaks getting reduced values and shifted to higher temperatures, as a consequence of the displacement of the transition temperature. The shape of the curves is mainly governed by \((\partial M / \partial T)_{H}\) \cite{2}.

The numerical integration previously described was performed based on the $\delta T_S$ vs. $H$ curves and the results are plotted in Fig. 1c, for a zero to 20 kOe field step. The black circles represent the total MCE ($\Delta T$) for Gd, determined from the acoustically detected effect. In addition, the temperature rise
in a 1 g Gd bulk sample, located in the PPMS (Quantum Design) inner chamber, was measured by a Cernox temperature sensor (gray circles in Fig. 1c). 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. Figure 1c also shows the total MCE for Gd₁₋ₓ(SiₓGe₁₋ₓ)₄ compounds with 0.5 ≤ x ≤ 1, 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 of the unitary cell volume [4].

Figure 2a presents δTₛ as function of the temperature for several dc magnetic fields for the thermally treated GdₓSi₂Ge₂ sample. The shape of the curves clearly reveals the occurrence of two phase transitions. The MCE has a maximum around 300 K, at low magnetic fields and gets wider when increasing the magnetic field, similar to the behavior observed in figure 1b, which is typical for a second order phase transition. Concerning the expected first order phase transition, around 270 K, δTₛ is not significant for magnetic fields lower than 2 kOe, although the magnetization undergoes abrupt changes. This is due to the influence of the specific heat, which peaks around the transition temperature, thus suppressing the temperature variations of the sample. Increasing the magnetic field, the signal becomes prominent, with the maximum MCE shifted to higher temperatures. The total MCE is plotted in figure 2b. The main shape of the curves is in agreement with results in literature for multiphase materials [5]. It is important to emphasize the good sensitivity of the technique, which is able to detect spurious material phase in very small quantities. Figure 2c shows magnetization curves at low magnetic fields. The second order phase transition, around 300 K, is evidenced in the insert.

In conclusion, it was shown that the acoustic detection is a suitable technique to measure the MCE, with no restriction in view of the nature of the phase transitions, and it is applicable to investigate the effect in low magnetic fields. Moreover, the advantage of the non-contact approach, with the air as the transducer, allows the MCE detection for low mass samples. The errors in the acoustic MCE measurements are about 15-20%, of the same order of those of conventional methods.

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