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## Determination of the magnetocaloric entropy change by field sweep using a heat flux setup

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We report on a simple setup using a heat flux sensor adapted to a Quantum Design Physical Property Measurement System to determine the magnetocaloric entropy change ( $\Delta S$ ). The major differences for the existing setups are the simplicity of this assembly and the ease to obtain the isothermal entropy change either by a field sweep or a temperature sweep process. We discuss the use of these two processes applied to Gd and  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  samples. The results are compared to the temperature sweep measurements and they show the advantages of this setup and of the field sweep procedure. We found a significant reduction of  $\Delta S$  and on the refrigerating cooling power (RCP) at low field changes in a field sweep process when the sample is not driven to the same initial state for each temperature. We show that the field sweep process without any measuring protocol is the only correct way to experimentally determine  $\Delta S$  and RCP for a practical regenerative refrigerator.

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Traditionally the magnetocaloric parameters of a material, the isothermal entropy change and the adiabatic temperature change ( $\Delta T_{\text{ad}}$ ) are usually obtained by means of magnetization measurements with the aid of the Maxwell relation or by specific heat measurements. The isothermal magnetization curves  $M(H)$  are particularly more often used to determine  $\Delta S$  because experimentally they are more convenient to obtain. However, for materials presenting a first order magnetic transition (FOMT), hysteresis or field induced transitions introduce a magnetic history which can lead to unrealistic results.<sup>1</sup> In fact, most magnetocaloric effect (MCE) results obtained using isothermal magnetization data are not corroborated by the results coming from iso-field magnetization for a first order transition showing hysteresis and may be overestimated when compared to the entropy change calculated from specific heat measurements.<sup>2-4</sup> This is due to the different characteristics of each technique and procedures to be adopted before each isotherm measurement (or protocols) have been discussed to overcome this problem.<sup>5,6</sup> As a consequence of this scenario, the determination of the MCE potentials using heat flux methods emerge as an excellent alternative and among them, those using small Peltier units have proven to be very effective.<sup>7</sup> The main advantage of such calorimeter is its robustness and capacity to withstand relatively large mass samples, or single crystals showing high anisotropy, without problem. In relaxation calorimeters, the delicate sample holder can be damaged under strong magnetic fields since the sample might be subjected to very large torques. In fact, more recently Peltier element based setups have been used to determine the MCE potentials by different methods.<sup>7-10</sup> In essence, the idea is that the Peltier element is capable to determine the heat flux released or absorbed by the sample in a given process characterized by external parameters like magnetic field or temperature. From the results, it is quite simple to obtain the entropy change as function of temperature or magnetic field.

All the reported experimental setups use one or more heat flux sensors mounted in an appropriate configuration to fit a cryostat used in conjunction with a magnet. In this paper we report on the use of a simple setup adapted to a commercial PPMS. It provides a measuring platform with excellent capability to control or to vary temperature and magnetic field such that the adaptation of the original idea presented by Plackowski *et al.*<sup>7</sup> in this system opens up different possibilities to study the MCE. Besides the ease to determine the MCE properties of magnetic materials under strong magnetic fields, this setup allows one to determine the total heat evolved in a temperature or field sweep process. Despite any kind of measurement protocol, we believe that this is the real quantity of interest for magnetic refrigeration systems because it is a direct measure of the heat released or absorbed by the sample on each cycle of a practical regenerative refrigerator. However, it is also possible to follow the established protocols with this setup, allowing a comparison with other experimental results and with the theory. The simplicity of this setup and its ease to operate contrast with other more complex arrangements.<sup>8</sup>

In this letter, we present the results obtained for two materials: Gd, because it is a standard MCE material presenting a second order transition and  $\text{Gd}_5\text{Ge}_2\text{Si}_2$ , also a very important MCE material with a FOMT presenting hysteresis. We compare the results obtained from magnetization with those obtained by sweeping either the temperature or the magnetic field following two different measurement protocols. We also show the total heat per cycle for each case and discuss which experiment simulates better a real magnetic refrigerator.

A standard PPMS blind puck, consisting of a metal base with an electrical connector underneath, is used as a base for the Peltier element. In our case we used a 6 mm  $\times$  8 mm  $\times$  2.4 mm unit (Custom Thermoelectric, 03201-9G30-08RA) with 32 thermocouple pairs. A schematic of the setup is shown in Figure 1. A more detailed description about this assembly is available in the Quantum Design application

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note 1085–200. This arrangement is intended for heat capacity or magnetocaloric experiments and we have used it between 20 K and 320 K with magnetic fields up to 7 T.

The system was calibrated following the procedure described in Ref. 7, running the empty system and then running a  $m = 822.60$  mg of 99.999% pure copper fixed with a very thin layer of Apiezon N grease<sup>11</sup> for better thermal coupling. For all the temperature sweep experiments reported here we adopted a 0.5 K/min rate. With this procedure, the system effective heat capacity  $C_{\text{sys}}$  and the Peltier sensitivity, defined<sup>7</sup> as the quotient between the Seebeck coefficient ( $S_b$ ) and the thermal conductance ( $\kappa$ ) of the Peltier element,  $A = S_b/\kappa$ , were obtained as function of the temperature at several field values. At  $T = 300$  K and  $H = 0$ , we obtained  $C_{\text{sys}} = 97$  mJ/K and  $A = 0.35$  V/W, while at 30 K these quantities were found to be 7 mJ/K and 0.02 V/W, respectively. The major source of error is the Peltier voltage, typically  $\Delta V_P/V_P < 5\%$ . We verified the system calibration measuring the heat capacity of aluminum as function of the temperature obtaining the expected value within 5% error at 300 K.

The heat flux going through the Peltier element is given by<sup>8</sup>

$$\dot{Q} = T \frac{dS}{dt} = T \frac{\partial S}{\partial H} \dot{H} + T \frac{\partial S}{\partial T} \dot{T} = \frac{V_P(T, H)}{A(T)} \dot{T}, \quad (1)$$

where  $V_P(T, H)$  is the Peltier voltage. In an isofield temperature sweep, the heat associated to the sample is given by

$$\Delta Q_H(T) = \left( \frac{1}{\dot{T}} \right) \int_{T_0}^T \frac{V_P(T)}{A(T)} dT - \int_{T_0}^T C_{\text{sys}}(T) dT, \quad (2)$$

where  $\dot{T}$  is the constant heating rate and  $T_0$  is the initial temperature when  $\dot{T}$  is already stable at the desired value. The second term at the right refers to the heat absorbed by the addenda. The entropy of the material for a given field can be obtained by the usual relation  $\Delta S = \int \frac{\delta Q}{T}$ . On the other hand, a real isothermal field sweep is not possible with this simple setup because in this case, the Peltier voltage should be zero.<sup>12,13</sup> However, we can have an approximation of the isothermal path by making a discretization of the field change, integrating the heat flux in time until it decays back to zero. Providing these field increments cause small temperature deviations, the calculated total heat will be close to the real value for the isothermal regime. We obtained good results

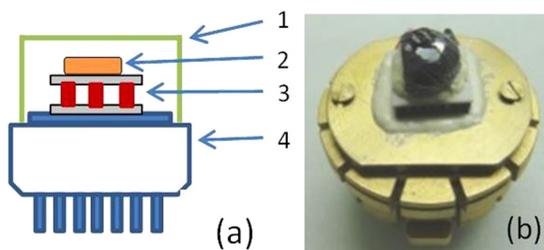


FIG. 1. (a) Schematic drawing of the Peltier element mounted on the PPM puck: 1—heat shield; 2—sample; 3—Peltier element; and 4—puck. (b) Picture of the actual puck with a  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  sample.

using field steps up to 0.25 T with  $\mu_0 \dot{H} = 150$  Oe/s rate where the heat for each step is

$$\Delta Q_i = \frac{1}{A(T)} \int_{t_0}^{t_1} V_P(t) dt, \quad (3)$$

and the total heat for the whole field change is given by the summation  $\Delta Q_{\text{Total}} = \sum \Delta Q_i$ . So, at a given temperature we can have the corresponding data for any field change up to the maximum field used.

A Gd sample with 99.95% purity was cut in a parallelepiped shape weighing 621.38 mg. The  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  sample was prepared according to the literature<sup>14</sup> with  $m = 728.62$  mg. Unless otherwise noted, prior to each full field sweep the sample was heated up to 320 K and cooled down to the measuring temperature at zero field. This procedure is what we call “prepare the sample” which is the same protocol adopted for isothermal magnetization measurements.<sup>2</sup>

The temperature sweep results for Gd obtained at several fields are shown in Figure 2 where  $c_H$  was found using  $c_H = \frac{1}{m\dot{T}} \frac{V_P(T, H)}{A(T)}$ . The data were obtained after a zero field cooling (ZFC) process down to the measuring temperature and the maximum of the entropy change is in good agreement with the literature data.<sup>8</sup> In Figure 3, we show  $\Delta S$  obtained by sweeping the field in steps of 0.25 T as described above.

The  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  compound is very important in terms of the MCE because it presents a giant effect,<sup>15</sup> but because it is strongly dependent on the relative concentrations of Si and Ge,<sup>14</sup> a direct comparison of the experimental results available in the literature may not be conclusive.<sup>16,17</sup> Nevertheless, in Figure 4, we present the entropy change obtained by a temperature sweep at a constant field and the values and curve shape are consistent with the literature data obtained with a direct determination of the MCE.<sup>17</sup> We must consider that  $\Delta S$  shown in Fig. 4 is calculated by subtraction of the entropies  $S(T, H) - S(T, H = 0)$  and each entropy curve is obtained by integrating  $c_H/T$ . Therefore, unless the measurements are made starting well below the transition

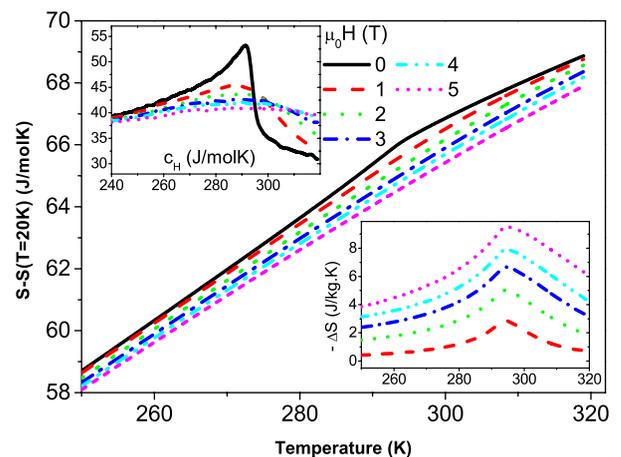


FIG. 2. Results obtained for a polycrystalline Gd sample: the entropy variation with temperature at magnetic fields up to 5 T, relative to  $S(T = 20\text{ K})$ , determined by the heat flux. The upper inset shows the specific heat while the lower inset shows the corresponding entropy change (MCE).

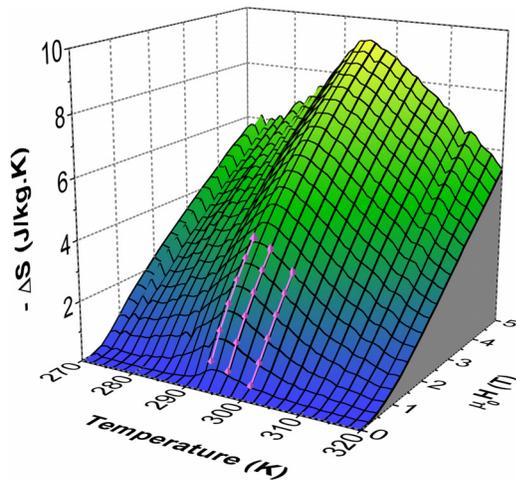


FIG. 3. The entropy change for Gd at several temperatures obtained by sweeping the field in steps of 0.25 T to simulate an isothermal path. The full symbols are data taken from Ref. 8.

temperature, there can be a shift on the curves towards lower  $-\Delta S$  values.

Although our results are comparable with the literature, it will be interesting to compare the results obtained by the different methods for the same sample. Figure 5 shows  $\Delta S$  obtained by isofield magnetization and also by the temperature and field sweep methods using the heat flux technique. As a general rule we found that the values obtained from magnetization and temperature sweep agree quite well. The field sweep (after preparing the sample) shows a  $\Delta S_{\max}$  slightly enhanced and shifted from the ferromagnetic (FM)  $\rightarrow$  paramagnetic (PM) down to the PM  $\rightarrow$  FM transition temperature, related to the thermal hysteresis of the compound. The curve for the not-prepared case, however, is limited to the common region between the temperature sweep and field sweep curves, delimited by the thermal hysteresis.

In Figure 6, we show the transition temperature obtained for our sample by measuring the magnetization as function of the temperature. The black line represents the transition occurring in a field heating process and the orange line represents the transition in a field cooling process, showing the thermal hysteresis. We assume that the transition lines have an arbitrary width where different phases coexists.<sup>2,18</sup> We

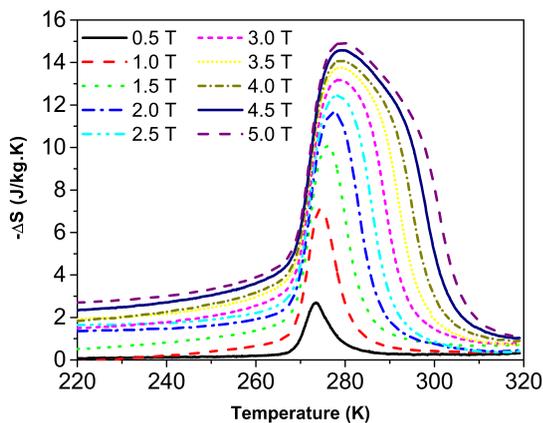


FIG. 4. The  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  entropy change for several values of  $\Delta H$  obtained by sweeping the temperature at 0.5 K/min after a ZFC process. In this calculation the integrals started at  $T = 20$  K.

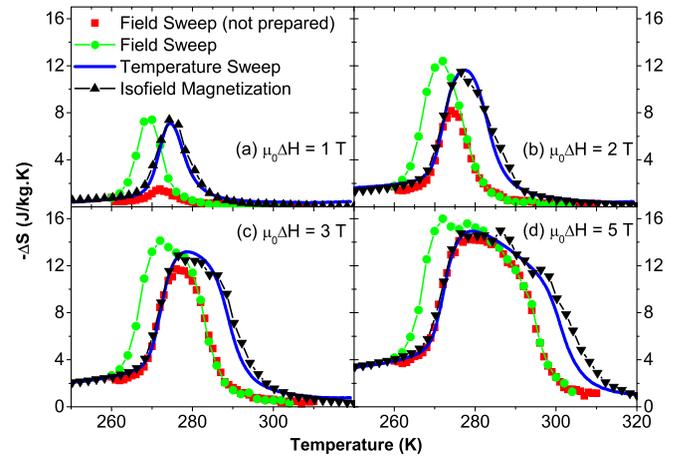


FIG. 5. Entropy change for a 1, 2, 3, and 5 T field change obtained by isofield magnetization and by the heat flux method using field and temperature sweep.

took both prepared and not prepared procedures for a 2 T field sweep as an example. On the left, the green dotted lines correspond to the “prepared” experiment such that coming from 320 K to any temperature below 265 K drives the sample into the FM state, regardless of the field. Following this protocol, as one comes from 320 K and approaches temperatures slightly higher than 265 K, part of the sample remains on the PM state, and the remaining goes through the PM to FM transition (orange line) triggered by the field sweep. Maintaining this routine, as the temperature is increased, that part of the sample still in the PM state will go through the transition which is irreversible below  $T = 272$  K. This results in a maximum in  $\Delta S$  with an upper limit around 277 K. On the other hand, for the “not-prepared” case (red dashed lines on the right), the sample remains in the FM state for any temperature below  $T \sim 272$  K. Above this temperature up to  $T \sim 277$  K, the sample will suffer a PM  $\rightarrow$  FM transition in the same way as in the prepared experiment, and the effect ceases at the same temperature for both processes. Also, for

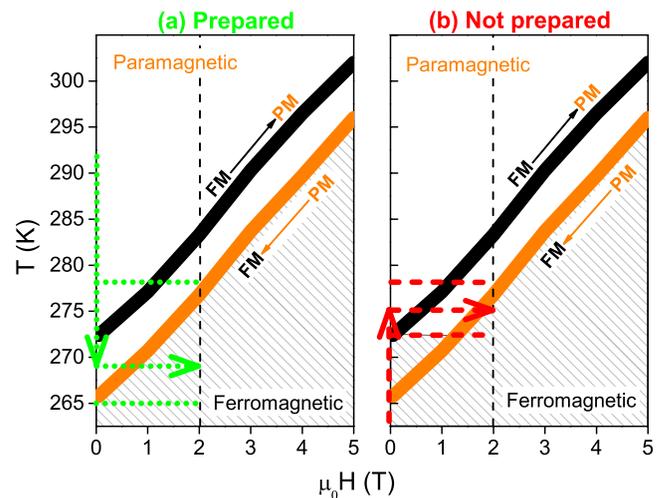


FIG. 6.  $T$  vs.  $H$  diagram showing the magnetic phase transition borders for  $\text{Gd}_5\text{Ge}_2\text{Si}_2$  obtained by magnetization. The orange line represents the transition from the paramagnetic to the ferromagnetic state, while the black line is the inverse. The left panel shows the prepared field sweep process (green dotted lines) while the right panel shows the warming up not-prepared field sweep process (red dashed lines).

the warming up “not-prepared” case, the FM  $\rightarrow$  PM transition (black line) rules the MCE as well as in a temperature sweep process such that both  $\Delta S$  curves start at the same temperature. This scenario explains why the “not prepared” field sweep experiment shows the  $\Delta S$  curve restricted to the common area between the temperature sweep and prepared field sweep experiments (see Figure 5), which leads to a smaller total heat for each cycle, especially when using low magnetic fields.

In fact, in each cycle of a real regenerative refrigerator the temperature of the magnetocaloric material should be sequentially reduced and consequently, there is no possibility to prepare the sample to the same initial state for each temperature. Also, the practical process to introduce the sample to a steady magnetic field region is equivalent to a field sweep process. Therefore, we believe that the field sweep procedure without preparing the sample is more adequate to estimate the MCE potential of a material when it presents a first order transition with hysteresis. The results of Fig. 7 clearly show a reduction on either  $\Delta S_{\max}$  and on the useful temperature range, especially at lower magnetic fields, when no protocol is adopted.

Using the definition of relative cooling power,  $RCP = \Delta S_{\max} * \Delta T_{full\ width-half\ max}$ , which gives the sample effective refrigerant capacity, we summarize the results obtained in Fig. 8. We can see a very good agreement between the temperature sweep and the field sweep RCP, but there is a significant difference for the “not-prepared” field sweep values, especially at lower field changes. The results for a sequential experiment (not-prepared) which is similar to the cycles of a magnetic regenerative refrigerator are significantly smaller than the usual calculations,<sup>13,19</sup> especially at the low field side.

It is commonly accepted that the isothermal magnetization measurements can provide unrealistic  $\Delta S$  results (the appearing of a peak) if the proper protocol is not followed.<sup>1</sup> In fact, the heat flux technique with a field sweep, which is similar to the isothermal magnetization, shows no evidence of the questionable peak. Furthermore, it is the only way to estimate the entropy change or RCP without preparing the sample, which is closer to a real condition found in practical systems.

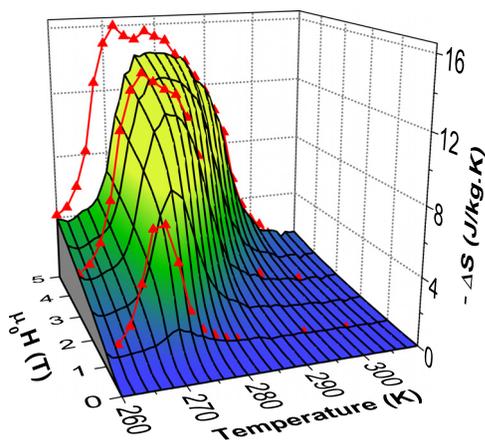


FIG. 7. The entropy change for a not-prepared  $Gd_5Ge_2Si_2$  obtained by field sweep, starting at 260 K. The red triangles are the results using the “prepared” protocol for a  $\mu_0\Delta H$  of 1, 3, and 5 T.

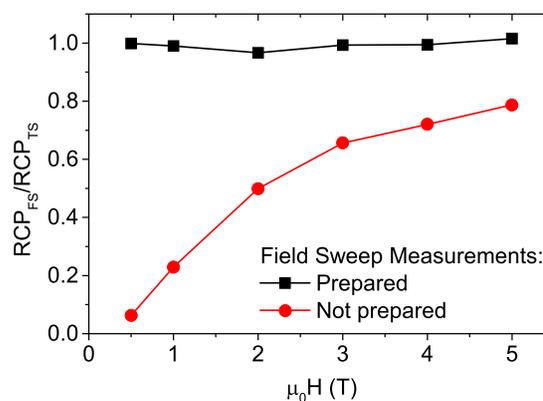


FIG. 8. The relative cooling power for the field sweep processes ( $RCP_{FS}$ ) normalized by the  $RCP_{TS}$ , obtained from the temperature sweep data, as function of the magnetic field.

In conclusion, this study reports on the adaptation of a heat flux setup to a commercial QD-PPMS in order to obtain the specific heat and the entropy change. This very simple setup allied to the versatility and robustness of the PPMS allows the investigation of different aspects of the MCE, contrasting with the use of specific and more complex instrumentation to obtain a direct measurement of the entropy change. We discussed a temperature sweep and a field sweep process and for this last case, we presented a way to get a good approximation of the isothermal entropy change and the results obtained for a Gd sample (representing second order materials) are in good agreement with the literature data. We also studied  $Gd_5Ge_2Si_2$  as one of the most relevant materials for the MCE presenting a first order transition. Using the same sample to compare the different methods, we found equivalence between the results coming from the iso-field magnetization and the heat flux temperature sweep, as expected. However, the field sweep experiment shows a strong dependence on the adopted protocol. Following the usual protocol, we obtain comparable  $\Delta S_{\max}$  and RCP but the maximum of the curve is dislocated to lower temperatures due to the hysteresis. More importantly, if the sample is not prepared, the sequential field sweep process shows a reduced value for both  $\Delta S_{\max}$  and RCP compared to the values coming from magnetization or temperature sweep. It is also interesting because it requires to measure only around the transition, which are the temperatures of interest. We believe the field sweep process is the only correct way to experimentally determine the entropy change and RCP for a practical regenerative refrigerator.

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