APPLICATION NOTE

# Determination of the Magnetic Entropy Change from Magnetic Measurements:
## the Importance of the Measurement Protocol

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## 1. Introduction to magnetocaloric research

The search for energy-efficient technologies for developing new refrigerator appliances has made the magnetocaloric effect a field of current scientific interest.[1] The number of scientific publications on this topic is increasing exponentially in the recent years (Figure 1), which is proof of the high expectations that the scientific community is depositing on this field of research. Together with their increased energy efficiency, magnetic refrigerators are expected to have a more reduced environmental impact when compared with those based on the gas compression-expansion cycle, as they do not involve ozone-depleting or greenhouse effect related gases, and the lack of a large compressor in the refrigerator allows more reduced vibration and noise. Moreover, being a solid state refrigerator device, miniaturization will be possible, which brings a breadth of potential new applications like refrigeration of lab-on-a-chip reactors, for example.

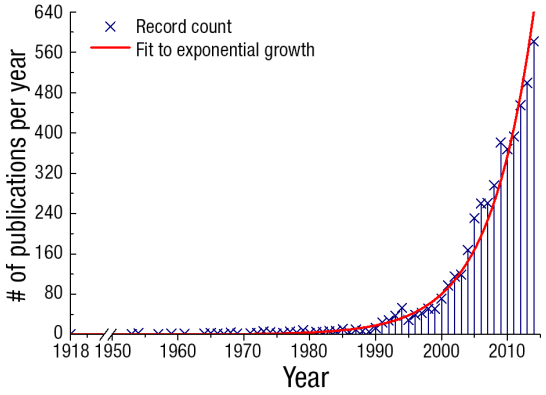



***Figure 1:*** *Time evolution of the number of publications on topics related to magnetic refrigeration, up to December 2014. Search terms for the bibliographic search: "magnetocaloric" or "magnetic refrigeration" or "magnetic entropy"*

The magnetocaloric effect is associated to a large change in magnetization close to the working temperature of the refrigerant material. Previously, magnetic refrigeration at low temperatures relied on paramagnetic salts, as their magnetization increases remarkably when approaching 0 K. However, for applications at temperatures close to room temperature, a different approach had to be found: the existence of a phase transition in the material close to the working temperature would produce the required abrupt change in magnetization. From the physical point of view, magnetic refrigerant materials can be classified by the type of phase transition that they undergo. It can be a second order magnetic phase transition, SOPT (like the ferro-paramagnetic transition of a ferromagnetic material at its Curie temperature), which is characterized by the lack of thermal and magnetic hysteresis, and in which the magnetization decreases continuously to zero. Pure gadolinium is a paradigmatic example of a magnetic refrigerant undergoing a phase transition of this kind. But phase transitions can also be of the first order type, FOPT, in which magnetization shows an abrupt change at the transition temperature, usually associated to a magneto-structural phase transition, giving rise to the giant magnetocaloric effect (GMCE), with $Gd_5Si_2Ge_2$ being the typical case of this kind of magnetic refrigerant materials.[2] However, although the large abrupt change in magnetization causes a correspondingly giant magnetic entropy change, this appears at the cost of thermal and magnetic hysteresis, which should be avoided in order to be able to apply these materials in refrigerator appliances.

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There are two important magnitudes (in addition to the adiabatic temperature change) which characterize the magnetocaloric effect: the magnetic entropy change, $\Delta S_M$, and the refrigerant capacity, *RC*, which is a measure of the amount of heat which can be transferred between the hot and cold reservoirs. While FOPTs exhibit a large (usually giant) $\Delta S_M$, it is usually extended over a narrow temperature range, which diminishes *RC*. These transitions also imply hysteretic losses and a slow time response, which would be detrimental for refrigerator design, although there are attempts to minimize these effects.[3] On the contrary, SOPT materials exhibit a broader $\Delta S_M$ peak of a smaller magnitude, but the width of the peak keeps *RC* comparable or larger than FOPT materials. Moreover, SOPTs have no thermal hysteresis and, in cases like soft magnetic amorphous alloys, magnetic hysteresis can also be negligible; the material does not break due to cycling the magnetic field (which might happen in the case of magnetostructural phase transitions due to the different volume of the phases before and after the transition) and electrical resistivity is larger than for crystalline materials, which diminishes eddy current losses.[4]

In fact, the ideal magnetocaloric material would be that which exhibits giant magnetocaloric effect like in FOPT but without the thermal hysteresis associated to it, its $\Delta S_M$ peak is extended over a large temperature range to enlarge *RC*, has no magnetic hysteresis, large resistivity, large thermal conductivity (to exchange heat easily with the heat transfer medium), good mechanical properties which ensures integrity of the materials while cycling, excellent corrosion resistance and non-toxic abundant and cheap constituent elements. At the moment, there is no single magnetocaloric material which fulfills all these requirements and designers have to find a trade-off between all of them, in combination with the refrigerator design. Even up to date, refrigerator prototypes are usually constructed initially with Gd as the refrigerant, and are modified at later stages to use FOPT materials as an alternative.

## 2. Background on data analysis

For the characterization of the magnetocaloric response of a material, three main parameters can be studied: the isothermal magnetic entropy change, $\Delta S_M$; the adiabatic temperature change, $\Delta T_{ad}$; and the refrigerant capacity, *RC*. $\Delta S_M$ can be calculated indirectly from the experimental magnetization curves by using Maxwell relation:

$$\Delta S_M = \mu_0 \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH \quad . \tag{1}$$

$\Delta T_{ad}$ can be either measured directly by recording the temperature change of the sample when submitted to a quick variation of magnetic field, or calculated from magnetization and heat capacity measurements:

$$\Delta T_{ad} = \mu_0 \int_0^H \frac{T}{C_H} \left( \frac{\partial M}{\partial T} \right)_H dH \quad . \tag{2}$$

*RC*, which is a measure of the energy that can be transferred between the hot and cold reservoirs, is defined as

$$RC(\Delta H) = \int_{T_{cold}}^{T_{hot}} \Delta S_M(T, \Delta H)\, dT \tag{3}$$

where ΔH is the difference between the minimum (usually 0) and maximum applied fields. The different definitions of *RC* appearing in the literature are the consequence of the different ways in which the integral is calculated. A schematic representation of the three broadly accepted definitions is presented in Figure 2: $RC_{FWHM}$ corresponds to taking the full width at half maximum of the peak ($\delta T_{FWHM}$) as the integration limits and approximating the integral as the peak value times that width ($RC_{\mathrm{FWHM}} = \Delta S_M^{pk} \delta T_{FWHM}$). $RC_{Area}$ corresponds to properly calculating the area under the peak within that $\delta T_{FWHM}$ temperature range. The third definition, proposed by Wood and Potter[5], $RC_{WP}$, corresponds to the area of the largest rectangle which can be inscribed into the $\Delta S_M(T)$ curve.

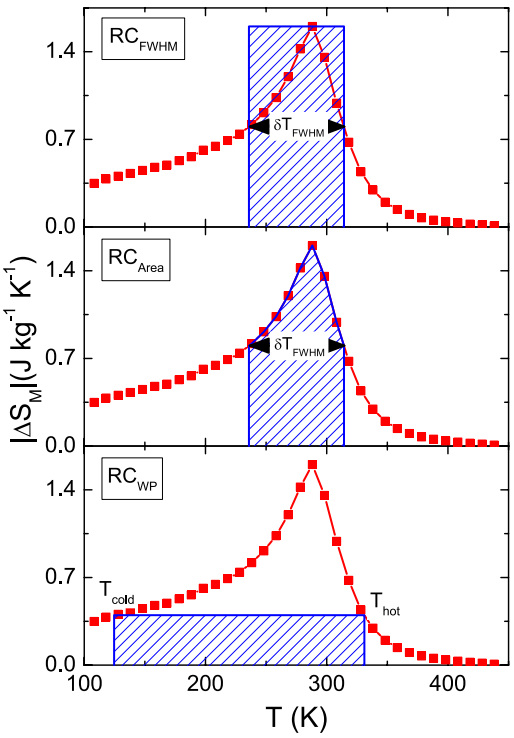



***Figure 2:*** *Different definitions of the refrigerant capacity.*

With the use of a magnetometer, $\Delta S_M$ and *RC* can be determined. They constitute a good first approximation to the potential performance of a material used as a magnetic refrigerator and it can be arguably claimed the most extended method of characterization of magnetocaloric materials. However, care has to be taken when using *RC* to gauge the potential performance of a material; it can be misleading in the cases that the magnetic entropy peak is small and too broad because a magnetocaloric material with a very small response in an unreasonably broad temperature range would not be applicable in a refrigerator device but can produce values of *RC* which are relatively large.

## 3. Measuring protocols: the importance of hysteresis

For applying Eq. 1 and Eq. 3 and subsequently determining $\Delta S_M$ and *RC*, we would need either the isothermal magnetization curves measured at different temperatures, i.e., a set of curves of the type $M(H, T=\text{constant})$, or the temperature dependent magnetization curves measured at different values of applied field, i.e., curves $M(H=\text{constant}, T)$. There is no doubt that stabilizing the magnetic field at different values (or sweeping it continuously) is much faster than stabilizing the temperature at different setpoints or sweeping it at a ramp rate that the sample is able to follow. Therefore, if we only take into account the time required for performing the measurement, the isothermal magnetization curves would be the method of choice. However, in this section we will see that, depending on the type of phase transition that the material experiences, this might not be the optimal choice for the characterization of a sample, as there is the possibility of experiencing huge artifacts that will give us a completely wrong idea of the characteristics of the material.

### 3.1. Second order phase transition materials

As indicated above, the most straightforward classification of magnetocaloric materials is according to the order of the phase transition that they undergo: either second order (continuous) phase transitions (SOPT), like Gd or transition metal based amorphous alloys, or first order magneto-structural phase transition (FOPT) like the giant magnetocaloric materials $Gd_5Si_2Ge_2$[2] and $La(FeSi)_{13}$.[6]

In second order phase transition materials, there is no coexistence of phases during the transition and the order parameter gradually decreases to zero as the transition temperature is approached. The most typical example is the ferro-paramagnetic transition of a ferromagnetic material, in which magnetization (the order parameter) decreases to zero as the Curie temperature is approached from below. There is no thermal hysteresis associated to this kind of transition.

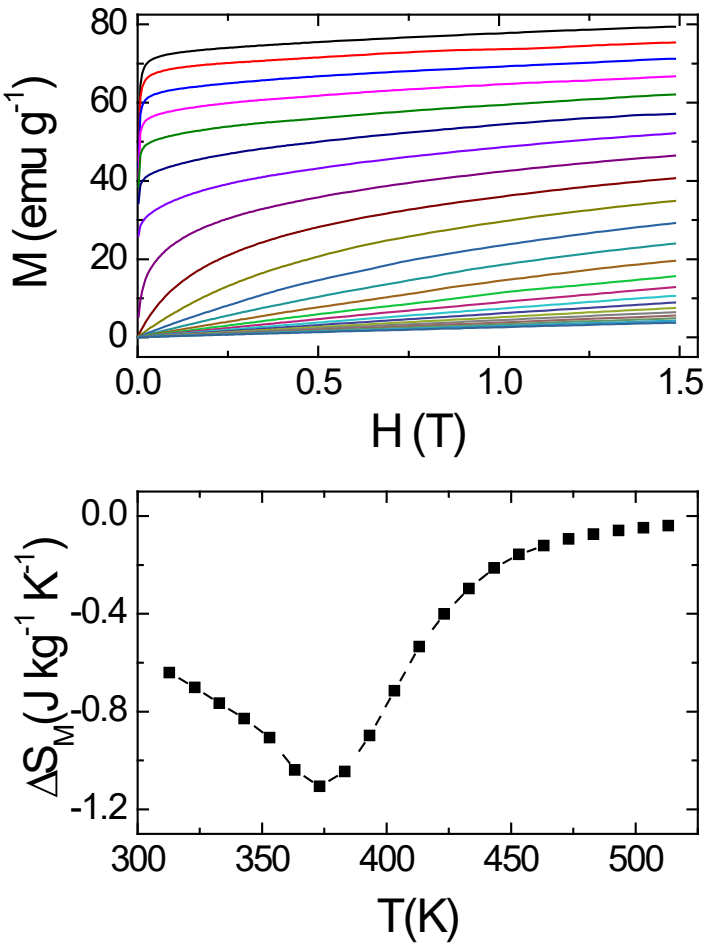



***Figure 3:*** *Upper panel: magnetization curves for a typical Fe-based soft magnetic amorphous alloy measured around its Curie temperature. Lower panel: corresponding magnetic entropy change curve.*

In this case, there is no difference in the results when applying Eq. 1 to isothermal magnetization curves or to isofield ones. Likewise, there should be no difference if the measurements are taken starting from zero field up to the maximum field, or when field is decreased to zero from its maximum value. The only precaution that has to be taken into account in this case is that the magnetocaloric material should not exhibit a large magnetic hysteresis, which will produce a difference in the magnetizing and demagnetizing results. Hysteretic materials would not be suitable for repeated magnetization/demagnetization cycles that should be performed in a magnetic refrigerator because the heat released due to hysteretic losses would be detrimental for the capability of the material to behave as a magnetic refrigerant. If the material is fully saturated at the maximum applied field, the discrepancies between magnetizing and demagnetizing magnetic entropy change curves is minimized. Strictly speaking, the magnetization and demagnetization curves will produce $\Delta S_M$ curves with different sign. Materials with a direct MCE will have a negative $\Delta S_M^{pk}$ when magnetized, being positive when demagnetized. Conversely, inverse MCE materials will

have a positive $\Delta S_M^{pk}$ when magnetized and negative when demagnetized. However, for the purpose of comparison, this application note will always use negative $\Delta S_M^{pk}$ for direct MCE materials and positive $\Delta S_M^{pk}$ for inverse MCE, which corresponds to the sign upon magnetization, even if section 3.2 will present some protocols which imply measuring upon removing the field. Whichever is the case, the hysteretic losses should be subtracted from the calculated *RC* in order to calculate the actual refrigerant capacity of the material.[7]

Therefore, for second order phase transition materials, the optimal procedure to perform the magnetocaloric characterization of a sample would be to measure the isothermal magnetization curves at different temperatures around the Curie temperature and subsequently applying Eq. 1 to those data. An example of the magnetization curves and of the kind of $\Delta S_M$ curve found in this case for a typical Fe-based amorphous alloy is shown in Figure 3.

### 3.2. First order phase transition materials

The situation is completely different for first order phase transition material due to the coexistence of phases during the transition. This means that the application of Eq. 1 to isothermal magnetization curves gives unphysical magnetic entropy change spikes unless the sample is properly prepared before each measurement.[8,9] As an example, Figure 4 shows the magnetic entropy change curve of a $La(Fe,Si)_{13}$ type sample for which the measurement protocol resembled that used in section 3.1. The large magnetic entropy change peak, which would be different if the sample is either measured with increasing or decreasing magnetic field, is not associated to the intrinsic properties of the sample but to a wrong application of Maxwell relation.

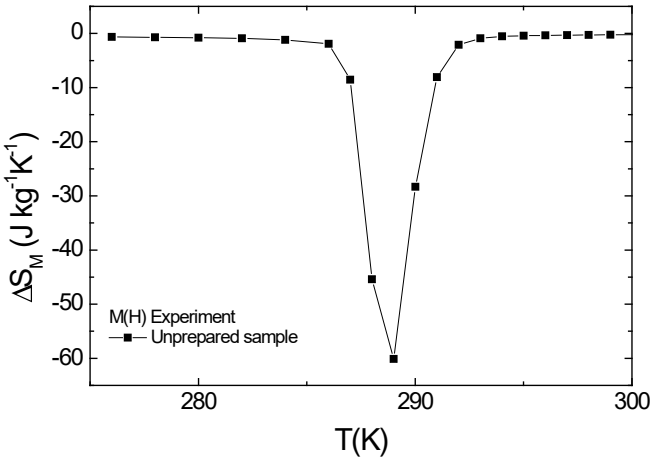



***Figure 4:*** *Magnetic entropy change curve corresponding to a $La(FeSi)_{13}$ type sample measured using isothermal magnetization curves from low to high temperatures without erasing the memory of the sample in between measurements.*

In order to avoid these spurious results, two different approaches can be followed: either measuring isofield magnetization curves or preparing the sample to be in a single phase state before each isothermal measurement.

#### 3.2.1. Temperature dependent magnetization curves

The measuring protocol can consist of setting different values of the field and, for each of them, measuring *M(T)* for increasing and decreasing temperature ramps. Depending on the temperature span of the measuring interval, it would be advisable to stabilize the temperature at each measuring point, or to ramp the temperature continuously at a low heating/cooling rate. In the first case, which would be appropriate for narrow intervals, the influence of the inherent temperature lag between sample and sensor would be minimized. However, for broad temperature spans, the measuring time using this procedure would be too long, due to the time required for stabilizing the temperature, and it is preferable to ramp the temperature continuously. As an example, Figure 5 shows in solid symbols the magnetic entropy change curves obtained for the same sample measured in Figure 4. The difference between heating and cooling curves is due to the intrinsic thermal hysteresis of the material. It is worth noting that the artifacts mentioned previously were as much as 100% of the actual magnetic entropy change of the sample.

The main drawback of this measuring protocol is that each *M(T)* curve will take a relatively long measuring time, which limits the number of applied fields (number of curves) which can be used and this can affect the accuracy of the magnetic entropy change curves.

#### 3.2.2. Isothermal magnetization curves

As the spurious spikes are due to the coexistence of phases during the phase transition, an alternative procedure to measuring isofield magnetization curves is to prepare the state of the sample to have it in a well-defined situation before each isothermal magnetization curve is measured. This can be done by either heating up the material well above the transition temperature in zero applied field in between each *M(H)* curve and subsequently cooling the material to the desired temperature for measuring the curves with increasing field, or by cooling the material well below the transition temperature in a large magnetic field (large enough to drive the field induced transition) and subsequently heating the sample to the desired setpoint for measuring the demagnetization curve. As an example, Figure 5 shows in hollow symbols the results obtained for the same sample using these two protocols. For the sake of comparison, and as indicated above, the sign of all the $\Delta S_M$ curves has been kept negative.

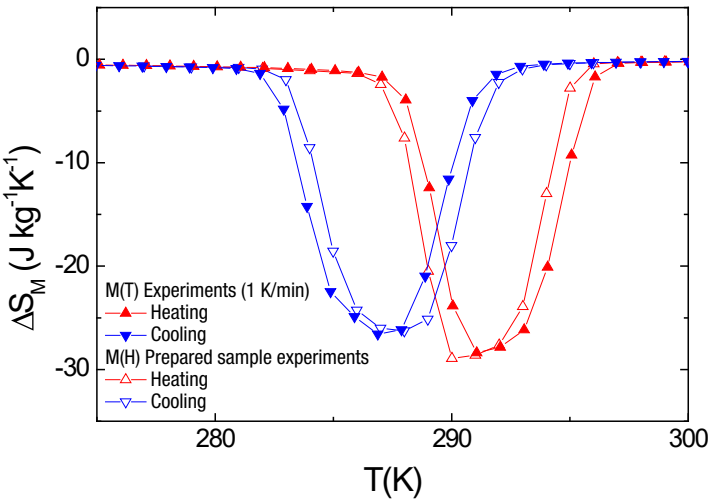



***Figure 5:*** *Magnetic entropy change curves calculated using different protocols: a) performing thermomagnetic M(T) curves measured at different fields upon cooling or heating and b) isothermal magnetization curves in which the sample memory is erased between isotherms. Note the criterion of signs described in the text of section 3.1.*

The advantages of this method are twofold: on the one hand, although we need to allocate time for the temperature sweep in between *M(H)* curves, this can be done at a larger ramp rate than the *M(T)* curves described in section 3.2.1; on the other hand, a larger number of magnetic fields can be measured and this would improve the resolution of the results.

The differences between the results obtained from the protocols of sections 3.2.1 and 3.2.2 are due to the abovementioned small thermal lag of the sample if the temperature is swept continuously.

As a summary, the steps which should be followed for the three measurement protocols indicated in this section are shown in Table I. Note that the reset field during cooling or heating protocols should be changed in the case that the transition is shifted to lower temperatures upon the application of a magnetic field.

**Table I: Steps to be followed for the different measuring protocols. In the case of FOPT, the cooling and heating protocols are defined for a case in which the transition is shifted to higher temperatures upon the application of the field.**

| 2nd order phase transition | 1st order phase transition | | |
|---|---|---|---|
| | *M(T)* curves | *M(H)* curves | |
| | | Cooling protocol | Heating protocol |
| 1. Set measuring temperature ($T_{meas}$) | 1. Set measuring field ($H_{meas}$) | 1. Heat well above the transition in zero field | 1. Cool well below the transition in $H_{max}$ field |
| 2. Measure *M(H)* curve | 2. Measure *M(T)* (either heating or cooling) | 2. Set measuring temperature ($T_{meas}$) | 2. Set measuring temperature ($T_{meas}$) |
| 3. Repeat from step 1 with a different $T_{meas}$ value | 3. Repeat from step 1 with a different $H_{meas}$ value | 3. Measure *M(H)* curve from 0 to $H_{max}$ | 3. Measure *M(H)* curve from $H_{max}$ to 0 |
| | | 4. Repeat from step 1 with a different $T_{meas}$ value | 4. Repeat from step 1 with a different $T_{meas}$ value |

## 4. Field dependence of the magnetocaloric effect of second order phase transitions

### 4.1. Extrapolations to higher fields

When trying to optimize materials' properties, it is of the utmost importance to be able to compare results measured in different experimental conditions. Although the simplest and most usual approach to compare the performance of different materials is to quote $\Delta S_M^{pk}/H_{max}$ for each alloy (which means to make linear extrapolations and interpolations of $\Delta S_M^{pk}$), this gives rise to errors of the order of 30% in making the comparison when changing the maximum field from 1.5 T to 5 T. That is why in the recent years there has been an increasing number of papers focusing on the field dependence of the magnetocaloric effect. The appropriate solution to the problem of comparing results measured at different laboratories for different maximum applied fields, in the case of second order phase transition materials, is to use power laws of the form $\Delta S_M^{pk} \propto H^n$,[10,11] with a relation between $n$ and the critical exponents of the alloy given by $n=1+1/\delta(1-1/\beta)$, where $\beta$ and $\delta$ are the critical exponents of the transition. In fact, the field dependence of the magnetocaloric effect has been proposed as an alternative procedure to determine these critical exponents.[12]

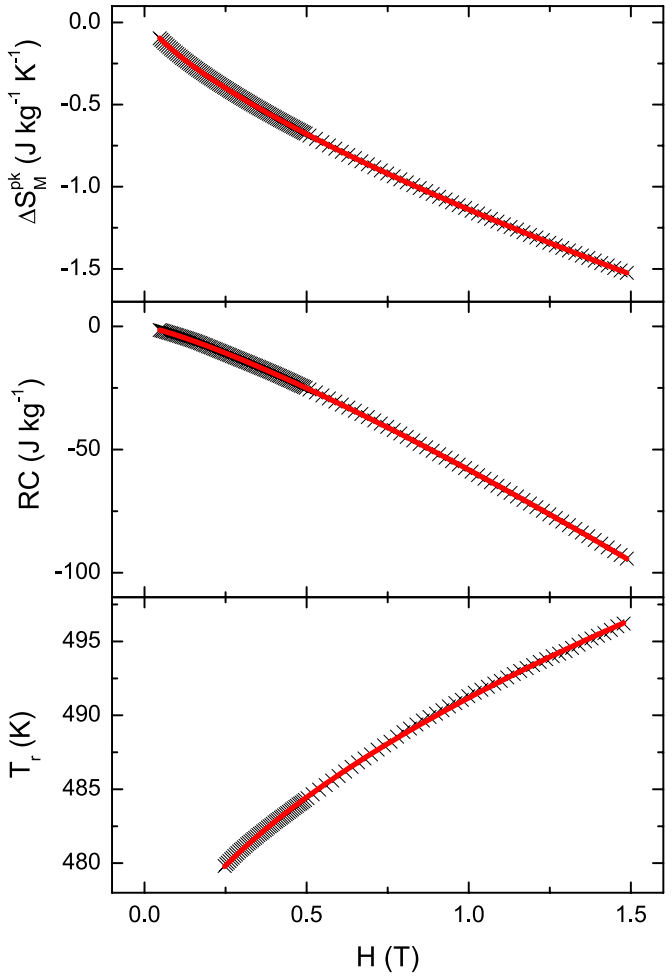



***Figure 6:*** *Field dependence of the peak magnetic entropy change, refrigerant capacity and temperature at which the magnetic entropy change is 50% of the peak (i.e., reference temperature) for a typical iron-based soft magnetic amorphous alloy. Crosses are experimental points; lines are power-law fits to the data. The table indicates the relationship between these field dependences and the critical exponents of the material.*

Figure 6 shows an example of the field dependence of the different magnetocaloric parameters in an extended field range. The good quality of the fits allows us to use these power laws to extrapolate the experimental values to fields which are much higher than those available in the actual experimental device that we could be using. However, care has to be taken when extrapolating to very large fields (typically well above 15 T), as scaling laws might start to fail, increasing the error margin of the extrapolations. The relationship between the exponent of the power law for the different magnetocaloric parameters and the critical exponents of the material is indicated in Table II.

**Table II: Exponents controlling the field dependence of different magnitudes related to the magnetocaloric effect (*magnitude* $\propto H^{exponent}$). The critical exponents employed have their usual meanings.**

| Magnitude | Exponent |
|---|---|
| $T_r$ | $1/\Delta$ |
| $T_{pk}$–$T_c$ (not mean field) | $1/\Delta$ |
| $T_{pk}$–$T_c$ (mean field) | 0 |
| $\Delta S_M$ $(T=T_c)$ | $1+1/\delta(1-1/\beta)=(1-\alpha)/\Delta$ |
| $\Delta S_M^{pk}$ | $1+1/\delta(1-1/\beta)=(1-\alpha)/\Delta$ |
| $RC_{Area}$ or $RC_{FWHM}$ | $1+1/\delta$ |

### 4.2. Extrapolations in temperature: universal curve

As second order phase transitions follow scaling laws, if the magnetic entropy change or the adiabatic temperature change are plotted versus the appropriate axis, a universal curve for the magnetocaloric response can be found.[10,13] Even if the analytical expression of the equation of state is not known for a certain material, a phenomenological procedure has been proposed that allows us to construct the universal curve by using the experimental data without the need of introducing any model.[10,11] Its construction was based on the assumption that, if such universal curve exists, equivalent points of the different $\Delta S_M(T)$ curves measured up to different maximum applied fields should collapse onto the same point of the universal curve. Therefore, the key is to identify which are the equivalent points of the different curves for different fields. As there is no doubt that the peaks (which in the mean field case coincide at $T_C$) should be in equivalent conditions, we can assume that points which are at a certain level with respect to the peak are also equivalent one to the others (if this hypothesis was not correct, then we would not be able to construct the universal curve). The temperatures of these points will be denoted as reference temperatures $T_r$, and their identification constitutes the first step of the procedure. They fulfill that $\Delta S_M(T_r)=\varepsilon\ \Delta S_M^{pk}$, with a factor $\varepsilon$ smaller than 1 and which value is arbitrarily chosen for each of the curves (preferably close or higher than ½), not affecting the procedure. The second step is the normalization of the curves with respect to their maximum. Finally, the temperature axis is rescaled in such a way that the reference temperatures are all at $\theta=1$ by using

$$\theta = \frac{T - T_C}{T_r - T_C} \qquad (4)$$

By imposing the position of two points of each of the curves (those at $T_c$ and at $T_r$), which implies three free parameters, the whole curve collapses in a single universal curve.

By constructing this universal curve, it is possible to make extrapolations of experimental results of alloys with similar values of the critical exponents to temperatures which were not available in the laboratory. As an example, results for $Fe_{91-x}Mo_8Cu_1B_x$ (x=15, 17, 20) amorphous alloys are presented in Figure 7.[14] This universal curve was applied to the x=17 and x=20 alloys. The x=15 alloy, due to the small number of experimental points below $T_C$, was not included in this universal curve to avoid the need of using reference temperatures too close to $T_C$. However, assuming that this alloy also follows the scaling behavior, its temperature dependence can be extrapolated below room temperature by the following procedure: 1) calculating the $\Delta S_M / \Delta S_M^{pk}$ ratio for the first experimental point; 2) obtaining the corresponding $\theta$ value from the universal curve; 3) calculating the reference temperature from Eq. (4) and 4) performing the inverse transformation of the master curve with the adequate values of $T_C$, reference temperatures and $\Delta S_M^{pk}$ for this alloy. Figure 7 shows the extrapolated data for the x=15 alloy together with the experimental values for all the studied alloys. It has to be noted that this extrapolation does not consist in a mere temperature shift of the $\Delta S_M(T)$ curves.

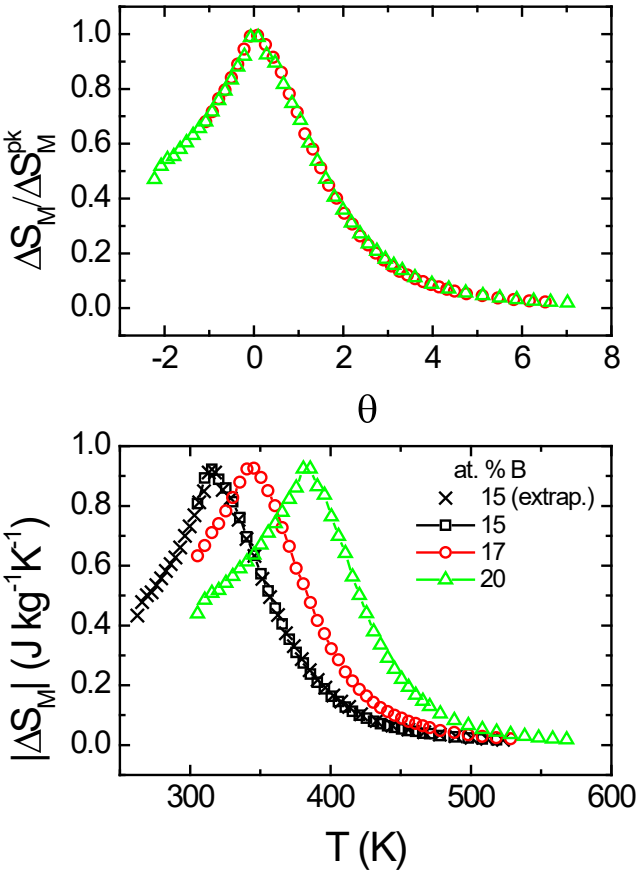



***Figure 7:*** *Upper panel: rescaled curves of the x=17 and x=20 alloys for a maximum applied field of 15 kOe. Lower panel: experimental magnetic entropy change values of the studied alloys and low temperature extrapolation of the x=15 sample (crosses).*

In addition to making extrapolations of the results up to fields or temperatures not available in the lab, this curve can be used for practical purposes, such as enhancing the resolution of the data, deconvoluting the response of overlapping magnetic transitions, etc.[11] This universal curve has been used to successfully determine the order of the phase transition of materials for which the purely magnetic Banerjee criterion was giving erroneous results, overcoming the need of complementary non-magnetic measurements to make this determination. Currently, there are attempts to extend this universal curve to materials with a first order phase transition[15] and, even if they are not based on the theory of critical phenomena, the curves obtained can lead in the future to practical applications in this field of research.

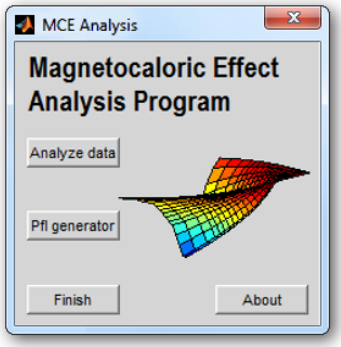



***Figure 8:*** *Main window of the magnetocaloric effect analysis program.*

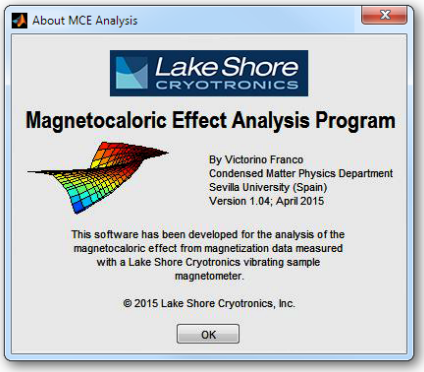



***Figure 9:*** *Details of the software version.*

It has to be noted, however, that there are several factors which could affect or even prevent the applicability of the universal curve, like the presence of different magnetic phases[16] or a large demagnetizing factor[17,18] in the sample under study. But even for perfectly pure samples with a negligible demagnetizing factor, trying to apply the scaling behavior at temperatures very far from the Curie temperature or for very large fields (typically above 15 T) could lead to artifacts in the results.

## 5. MCE analysis program

A program has been developed with the aim of helping VSM users perform experiments to characterize magnetocaloric materials and extract the relevant magnetocaloric parameters. It consists of two main parts, which are selected with different buttons on the main screen (Figure 8). The first part, selected with the button **Analyze data**, can be used for processing the magnetization curves measured with a Lake Shore VSM. The second part, **Pfl generator**, is a tool for the generation of the profiles that can be imported by the IDEAS VSM software in order to perform the measurements.

### 5.1 Data analysis software

The data analysis part allows calculating $\Delta S_M$ and *RC* (the latter calculated using the different accepted definitions) as a function of the maximum applied field. It is appropriate for the characterization of first and second order phase transition materials (if used in combination with the appropriate measurement protocol, as described in previous sections). 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.

In this section, a description of the usage of the 1.04 version of the data analysis software is provided. Whenever a major change of the software takes place, this section will be updated with the most current instructions.

#### 5.1.1. File selection

Data files saved by the IDEAS VSM software can be seamlessly imported directly into the MCE Analysis Program. At the moment, the kind of experiments that the program is able to interpret are:

- Isothermal magnetization curves *M(H)*
  - Magnetizing curves (0 to $H_{max}$)
  - Demagnetizing curves ($H_{max}$ to 0)
  - Loops (0-$H_{max}$-0 or $H_{max}$-0-$H_{max}$)
- Isofield magnetization curves *M(T)*
  - Increasing temperature ($T_{min}$ to $T_{max}$)
  - Decreasing temperature ($T_{max}$ to $T_{min}$)
  - Loops ($T_{min}$-$T_{max}$-$T_{min}$ or $T_{max}$-$T_{min}$-$T_{max}$)
  - Both as either point by point measurements or ramping temperature in background

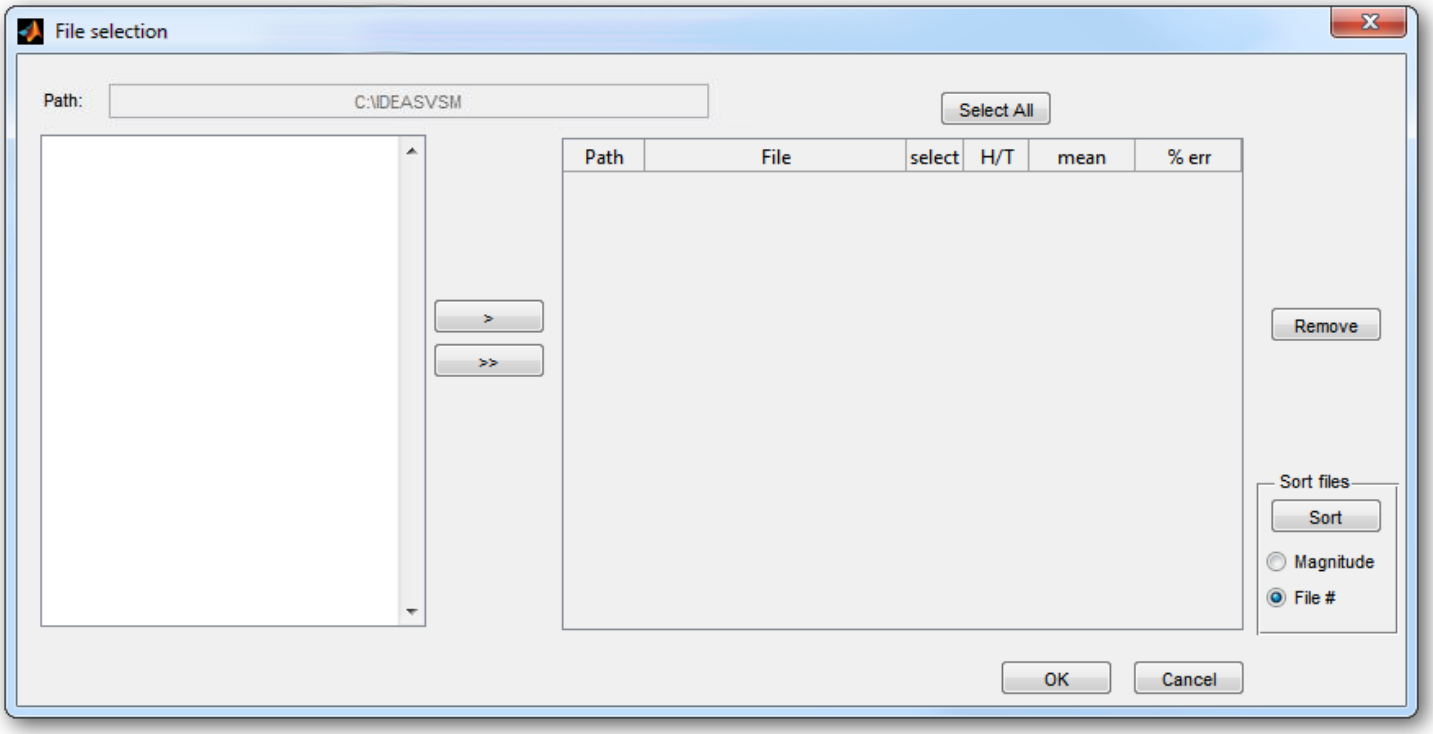



***Figure 10:*** *Window for the selection of the VSM data files.*

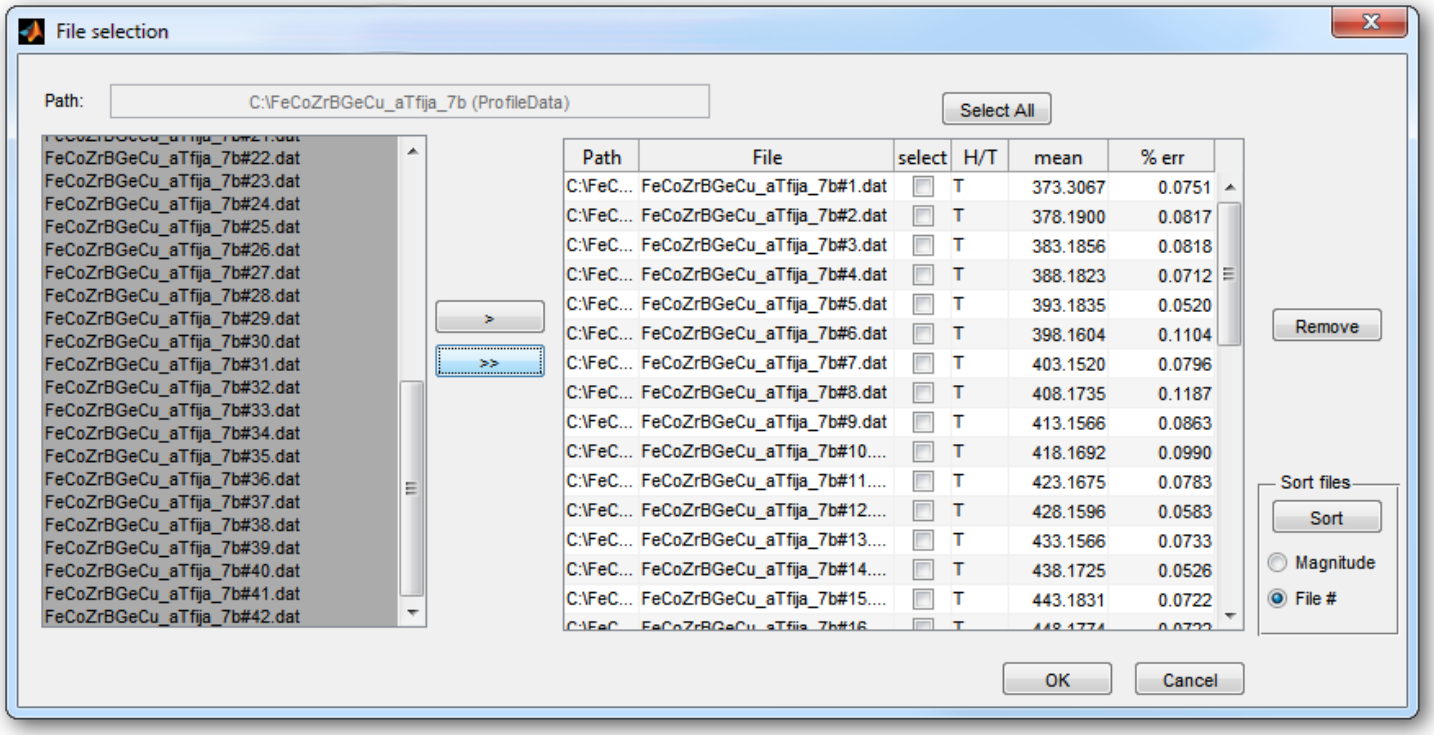



***Figure 11:*** *Example of a list of data files in the selection window.*

File selection is performed using a graphical user interface (Figure 10).

The selection of the directory where the files are located is performed by clicking on the **Path** textbox, which opens a pop-up window for graphically choosing the directory. Once this is done, the list box on the left of the window will include the .dat files present in that directory. They can be then selected partially (by marking one or several of them with the mouse and clicking on the **>** button), or all at the same time (by pressing on the **>>** button).

After the files are selected, they populate the table on the right of the window (see Figure 11). This table contains information about the directory in which each file is located, its name, a check box for selecting some of the files, a column "H/T" which indicates if the data in that file are isothermal (T) or isofield (H), the mean value of that constant magnitude (temperature or field) in SI units (K or T, depending on the case), and the percentage indicating how much that magnitude (temperature or field) was deviating from the average value in each curve. Possible values for the H/T column are:

- H: temperature experiment for a given magnetic field value (isofield magnetization curves)
- T: field experiment for a given *T* value (isothermal magnetization curves)
- tH: time experiment for which the field is constant
- tT: time experiment for which the temperature is constant

Files of different types can be selected and displayed together in the table, but they cannot be analyzed simultaneously by the program. The only exception is the combination of T and tT files (isothermal in both cases) or H and tH files (isofield in both cases). However, this combination of files should be performed with care.

If the data files are located in different directories, the procedure for selecting them can be done sequentially, by navigating to the different directories and choosing the files as indicated above. Moreover, if the data files saved by the IDEAS software do not contain the value of the mass, the software will ask the user for that value and save it in the .dat file, overwriting the previous version. Therefore, it is important to be careful about the mass value introduced in the file as this current version of the software does not allow for changing the mass of a file which already has it (that should be done manually by editing the file outside this software).

Files which have the check box marked can be removed from the table with the **Remove** button. All the files in the table, regardless of their selection status, can be ordered either by file number (according to IDEAS file naming convention) or by the average value of the magnitude that

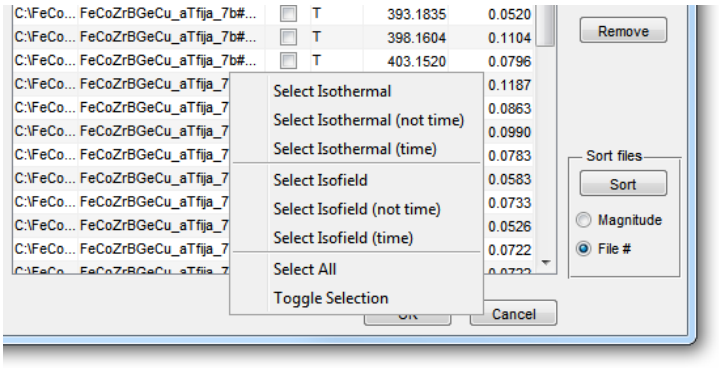



***Figure 12:*** *Different selection options appear when the table is right-clicked.*

defines the file (temperature or field). This latter option is particularly suitable for files measured with different profiles and for which the alphabetical order does not produce a monotonic variation of the magnitude.

Right clicking on the table allows selecting some or all of the files, using criteria associated to the type of experiment that the files contain (Figure 12).

Pressing **OK** will pass the check box-selected files to the data processing part of the program. If no files are selected, the program assumes that all the files in the list will be analyzed.

It is important to note that it is not advisable to import an experimental file that is being measured at the same moment by IDEAS, especially if the mass of the sample was not indicated in the .exp file. This is because both IDEAS and the data analysis software will try to write simultaneously on the .dat file, giving rise to unpredictable results and potential data loss.

### 5.1.2. Data analysis

The data analysis window (Figure 13) is divided into several parts:

- Table with the files to be processed (A)
- Panel with the type of calculations to be performed and shown (B)
- Panel with the results of the calculations (C)
- Four figures with the imported data and the magnetocaloric results (D)

Once the program opens this window, it will populate the table with all the magnetization curves which were passed to it from the file selection window. It will plot all of them in the upper left graph. The contents of the table are the same as in the previous window.

As in the file selection window, right clicking on the table opens a context menu that allows a more user-friendly selection of the curves to be processed (Figure 14). In the figure, only the odd-numbered files have been selected.

The magnetization curves presented in the figure are the originally imported ones, without any processing. Only those that appear in the figure will be used for performing the calculations. If the data selection is changed, the **Calculate** button has to be pressed in order to reprocess the calculations. However, there is no need to re-import the curves into the software. This processing of a partial subset of the curves is useful for removing outlier points in the magnetic entropy change curve.

The calculation of the magnetic entropy change curves is performed using a numerical approximation to Eq. (1). While the integral can be done using the trapezoidal integration, the numerical derivative can be performed in two main ways, which are sketched in Figure 15. We can assume that the derivative is made between two consecutive points and locate it at the central position between them (denoted "middle"):

$$\Delta S_M\left(\frac{T_{i+1}+T_i}{2}, H_{j_{\max}}\right) = \\ = \mu_0 \sum_{j=1}^{j_{\max}} \frac{M(T_{i+1},H_j) - M(T_i,H_j)}{T_{i+1}-T_i}(H_{j+1}-H_j) \quad (5)$$

or we can calculate the derivative of the points before and after the desired temperature, and place the derivative value at the temperature that we are studying (denoted "central"):

$$\Delta S_M\left(T_i, H_{j_{\max}}\right) = \\ = \mu_0 \sum_{j=1}^{j_{\max}} \frac{M(T_{i+1},H_j) - M(T_{i-1},H_j)}{T_{i+1}-T_{i-1}}(H_{j+1}-H_j) \quad (6)$$

If the experimental *M(T)* curve has N points, the middle derivative will have N-1 points, while the central one will have N-2 points. A possible solution for this loss of points in the curve is to use the middle method for the first and last points of the magnetic entropy change curve and the central method for the rest. This will provide a curve with N points and is denoted as "central (no loss)" in the software. Usually, magnetic entropy change curves calculated with the central method are smoother than those calculated using the middle method, without a relevant difference in the magnitude of the peak entropy change.

In order to perform the calculations, it is necessary that the field values for all the isothermal curves (the temperature values for all the isofield curves) are the same in all cases. For this purpose, the program performs an interpolation

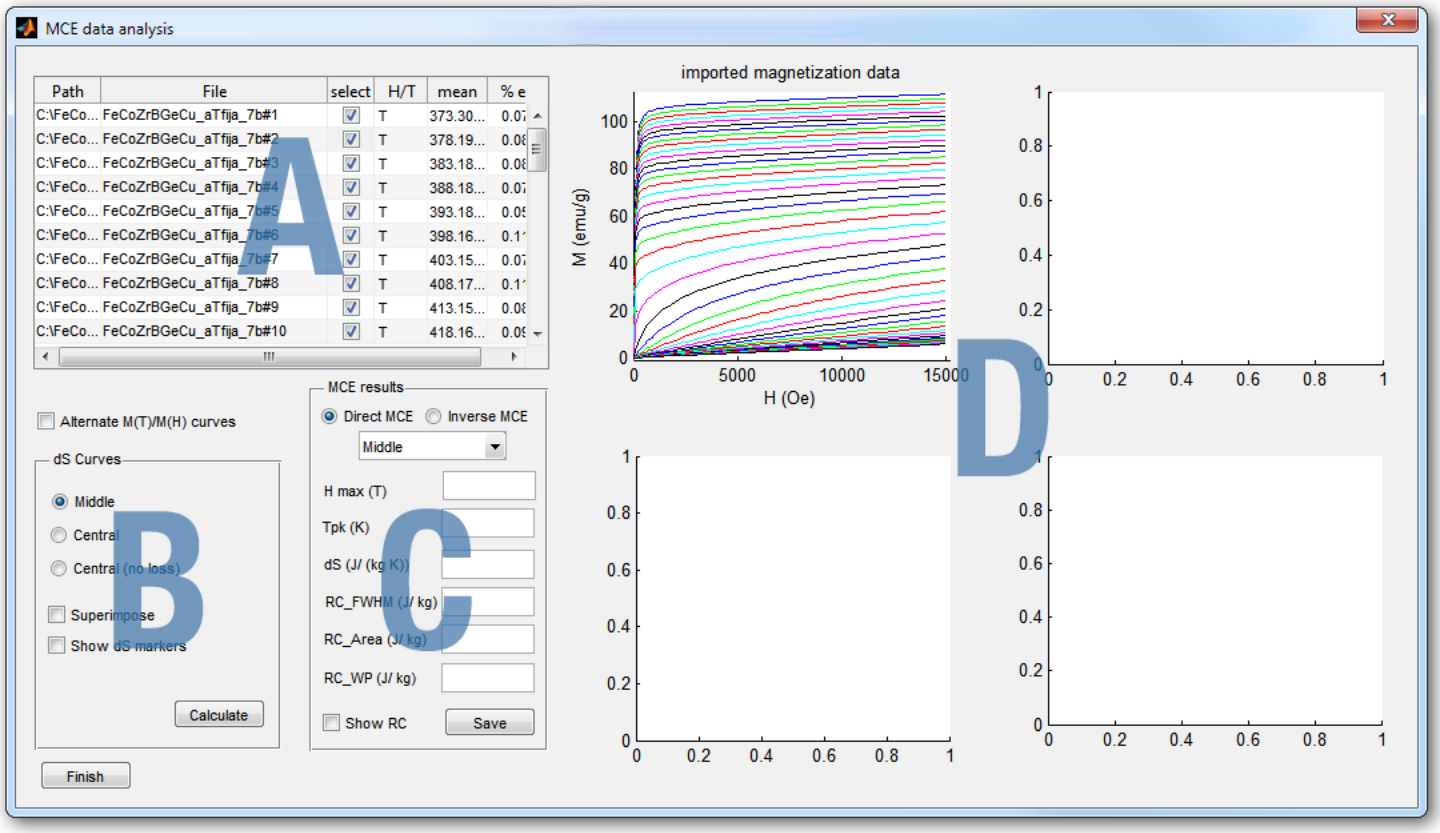



***Figure 13:*** *Data analysis window showing the files selected at the previous stage.*

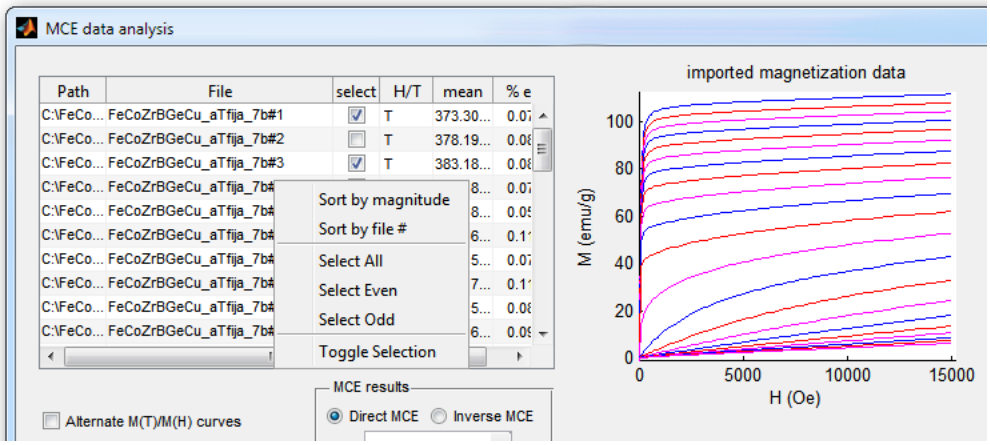



***Figure 14:*** *Menu options appear when the table is right-clicked. In the case shown, only odd-numbered files are plotted and will be used for the analysis.*

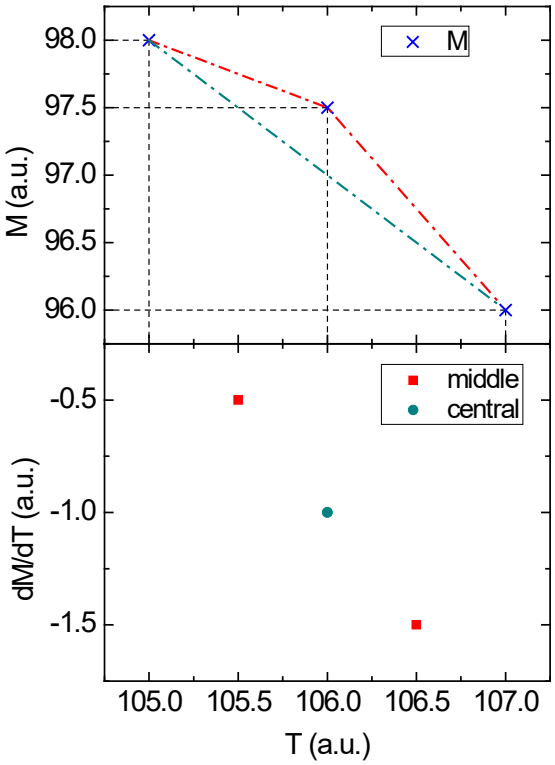



***Figure 15:*** *Sketch of the different methods for calculating the numerical derivative of the magnetization curves. Upper panel: magnetization curves. Lower panel: derivatives.*

of the data, which is displayed on the lower-left figure of the data analysis window (Figure 16). After calculation, this figure should essentially be the same as the imported data, unless the check box **Alternate M(T)/M(H) curves** is ticked. If this is the case, the lower-left figure will display *M(T)* curves if the measurements were taken isothermally, or *M(H)* curves if the measurements were made in isofield mode. This allows for a quick evaluation of the quality of the set of original data and of the resultant interpolation.

Once the **Calculate** button is pressed, the remaining figures will also be populated. The upper right figure corresponds to the temperature dependence of the magnetic entropy change for the maximum applied field, while the lower right curve is the three dimensional representation of the field and temperature dependence of the magnetic entropy change. The three methods are applied to calculate the magnetic entropy change curves, but only the method selected with the radio button will be displayed in the two graphs on the right. Selecting a different radio button will change the curve that is shown on the upper right corner, but the three dimensional surface and the values shown on the results panel will not change, unless the **Calculate** button is pressed again.

The results panel indicates if the material exhibits direct or inverse magnetocaloric effect, the method of derivative

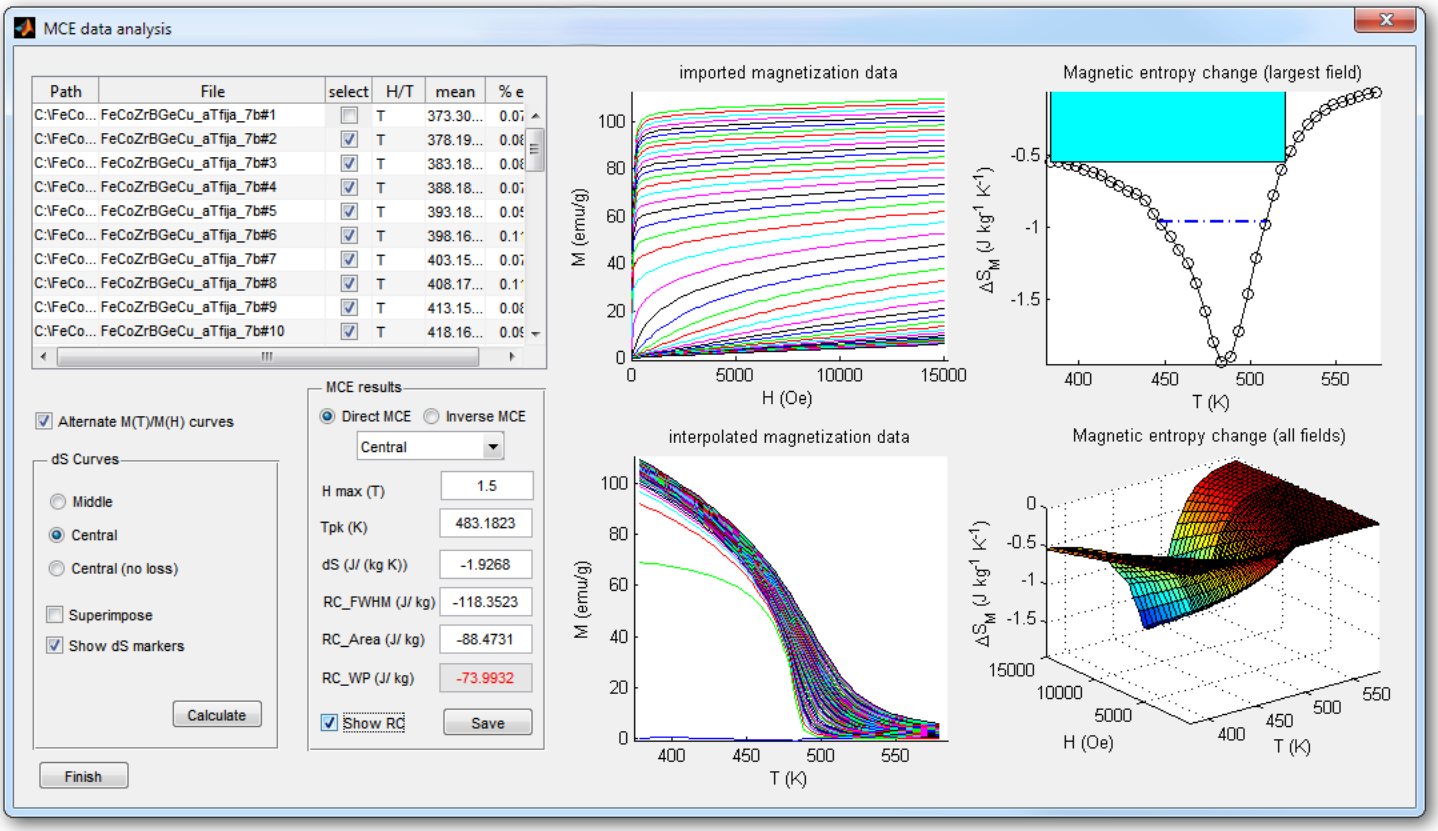



***Figure 16:*** *Results of the calculation of the magnetocaloric effect of the curves selected.*

used for the calculated results, the maximum value of the applied field and the most relevant magnetocaloric parameters, like the temperature of the peak, the magnetic entropy change peak and the refrigerant capacity (calculated using the three broadly accepted definitions mentioned above). This panel includes a **Show RC** check box that overlays on the upper right graph the full width at half maximum of the peak (used for calculating $RC_{FWHM}$ and $RC_{Area}$) and a rectangle representing the refrigerant capacity calculated using the Wood and Potter definition.

It is important to note that, regardless of the sign of the field variation (increasing or decreasing field), the program will calculate $\Delta S_M$ as if the field was increasing. This allows for a simple comparison of the curves of direct (negative peak) and inverse (positive peak) magnetocaloric materials.

There can be circumstances where the results cannot be properly calculated with the available experimental results, e.g., the full width at half maximum of the peak is not fully determined using the experimental temperature variation, or the maximum area of the inscribed rectangle is obtained using one of the temperature limits as one of the reservoirs. In these cases, the magnitude affected by the potential error is indicated in red.

If the data files contain different branches of data (e.g., loops with 0-$H_{max}$-0 or $H_{max}$-0-$H_{max}$ branches), after the **Calculate** button is pressed the software will ask the user which branch should be used for the calculations. In the case that the other branch should also be analyzed, there will be no need of re-importing data, as the program keeps both branches in memory and requests for the choice each time that the **Calculate** button is pressed.

The **Save** button in the results panel will generate ASCII files for the results calculated by the program, allowing the user to plot them with his/her preferred graphics software for publication.

### 5.1.3. Output data format

After pushing the **Save** button, four ASCII data files will be saved: MCE, MC3, MCH, and NLC files.

The units in all files will be tesla for the magnetic field, K for temperature and J $kg^{-1}$ $K^{-1}$ for the magnetic entropy change. All columns in the files are separated by tabulators.

The user will be asked for the directory and filename where he/she wants to save the files, although the software will append "_Mid," "_Ctr," or "_CtrNL" for calculations made using the middle, central, or no loss procedures (see previous section for a description).

#### 5.1.3.1. MCE files

MCE files (*.mce) contain the temperature dependence of the magnetic entropy change for the maximum applied field.

The first line of MCE files indicates the value for which that magnetic entropy change curve was calculated. The second line includes two columns with the headers of the subsequent data. Following lines are two columns with temperature and magnetic entropy change data.

#### 5.1.3.2. MC3 files

MC3 files (*.mc3) contain the temperature and field dependence of the magnetic entropy change (three dimensional surface).

The first line of the file contains the number of temperature values (nT) that are included in the file. The second line indicates the number of applied field values (nH). The third line has a header for the subsequent lines. After this, a set of nT*nH lines contain temperature, field, and magnetic entropy change values.

#### 5.1.3.3. MCH files

MCH files (*.mcH) contain the field dependence of the relevant magnetocaloric parameters.

For each value of the applied field, the following magnitudes are calculated (a header is given in the first line of the file; for a description of how they are calculated or their physical meaning, see section 2):

**T_pk(K):** temperature for which the magnetic entropy change has a peak.

**RCArea(J/kg):** refrigerant capacity calculated using the area under the curve.

**RCFWHM(J/kg):** refrigerant capacity calculated as the peak times the full width at half maximum of the curve.

**T1(K):** low temperature of the full width at half maximum of the curve.

**T2(K):** high temperature of the full width at half maximum of the curve.

**dSmax(J/kg K):** magnetic entropy change peak.

**RC_WP(J/kg):** refrigerant capacity calculated using the Wood and Potter definition.

**T1WP(K):** low temperature reservoir corresponding to the Wood and Potter definition.

**T2WP(K):** high temperature reservoir corresponding to the Wood and Potter definition.

**dS_WP(J/kg/K):** magnetic entropy change corresponding to the Wood and Potter definition.

**Err:** This column indicates if there is any potential error associated to the calculation of the different parameters. It can contain the following values (or their combinations):

- "Pk": the set of data produces an extreme of the magnetic entropy change at one of the extremes of the temperature range. Therefore, it is probable that the magnetic entropy change peak is not properly recorded.
- "Tl": the lower part of the full width at half maximum of the peak is not reached. The lowest experimental temperature has been used for calculating $RC_{Area}$ and $RC_{FWHM}$, probably underestimating these two magnitudes.
- "Th" the upper part of the full width at half maximum of the peak is not reached. The highest experimental temperature has been used for calculating $RC_{Area}$ and $RC_{FWHM}$, probably underestimating these two magnitudes.
- "WP": the maximum area of the inscribed rectangle in the calculation of $RC_{WP}$ is found at the extreme of the temperature range. Therefore, it is probable that $RC_{WP}$ is underestimated.

#### 5.1.3.4. NLC files

NLC files (*.nlc) contain the exponent of the field dependence of the magnetic entropy change, as decribed in section 4: $\Delta S_M^{pk} \propto H^n$. Exponent $n$ is locally calculated as

$$n = \frac{d \ln |\Delta S_M|}{d \ln H} \tag{7}$$

The first line in the file contains a header, followed by lines with temperature, field, and $n$ values. These can be used for the extrapolation or interpolation of data, as well as for determination of critical exponents.

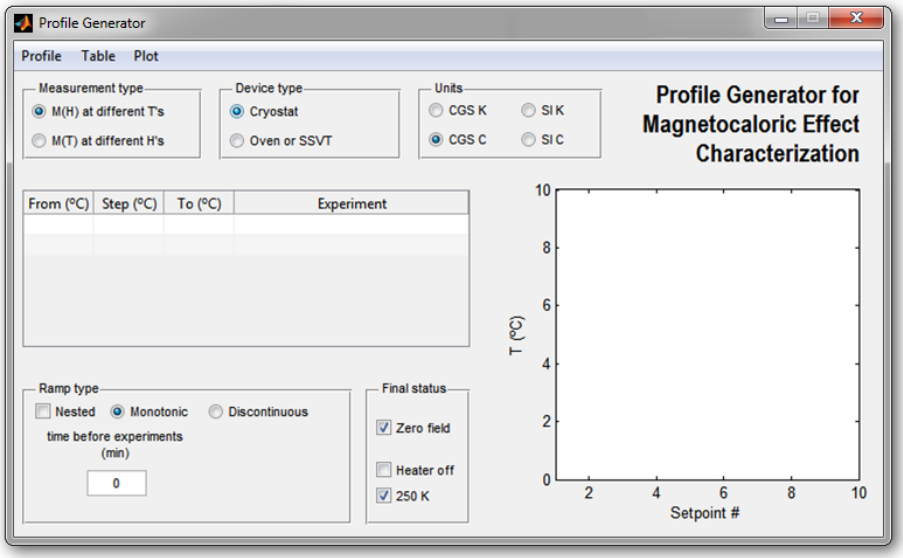



***Figure 17:*** *Profile generator tool screen.*

## 5.2. Profile generation tool

It is currently possible to program the profiles and experiments to be used in the IDEAS VSM software through the profile editor incorporated in that software. However, magnetocaloric experiments imply that either thermomagnetic curves have to be repeated numerous times for different applied magnetic fields, or isothermal magnetization curves need to be measured for a large series of temperatures. Therefore it is advisable to use a helper program to generate the profiles (pfl files of IDEAS VSM) in a more user friendly way. The profile generator is invoked from the **Pfl generator** button of the main window of the MCE Analysis Software (Figure 8). This will open a window (Figure 17) in which the type of measurement, configuration of the device, and sets of ramps and experiments can be defined, eventually producing a .pfl file which can be imported by IDEAS through the **add profile** option of the profile editor*. Users should familiarize themselves with the usage of the IDEAS VSM software and its experiments and profiles editor before using the MCE profile generator software.

### 5.2.1. Device configuration

One important point of the profile generation tool is the appropriate choice of the device configuration. IDEAS .pfl files should contain different codes if a cryostat is used when compared to the furnace or cryofurnace options.

It is also important to notice that .pfl files used in IDEAS do not include information about units. Therefore, it is necessary to create the profiles in the proper set of units that the VSM is using. The profile generator tool allows selecting the unit system manually, reconverting all predefined values from one set of units to the newly selected one. By default, the program will open with the last set of units which were used in the VSM (if the computer detects a VSM installation).

### 5.2.2. Measurement type

Two different types of measurements can be programmed using this tool. The most common one is a set of isothermal M(H) curves which are measured at different temperatures. These kind of profiles were described in Sections 3.1 (for SOPT materials) and 3.2.2 (for FOPT materials). While this procedure gives appropriate results for the former case, samples exhibiting first order phase transitions should be measured in combination with a discontinuous measurement protocol (see Section 5.2.5).

Alternatively, thermomagnetization curves at different fields can be programmed, as described in Section 3.2.1. This kind of experiment is usually more time consuming than isothermal magnetization curves measured using a monotonic temperature ramp and, therefore, should be reserved for FOPT materials.

### 5.2.3. Ramp selection

Ramps are defined in the table appearing in the tool window. Regardless of the type of experiment, there are four columns. The first column is the initial setpoint of each ramp, the second column is the increment that will be used, and the third column corresponds to the last point of each ramp. These three columns should contain numerical values (or empty values while the table is being filled up), which are checked by the software while typing. Simple numerical operations are allowed inside the cells while the table is being filled up (additions, subtractions, multiplications, and quotients). The last column corresponds to the experiment that will be executed at each of the setpoints of the ramps. To select the experiment, click on the cell, and choose the directory where the IDEAS .exp file is located. The creation of .exp files is a user task and should be previously done using the experiment editor inside IDEAS.

* *At the moment, importing a pfl file into IDEAS might show an empty list of experiments. If this happens, the user should disregard this fact and click OK. The main window of IDEAS should then show the list of experiments to be run. This is a general fact for pfl files edited outside IDEAS.*

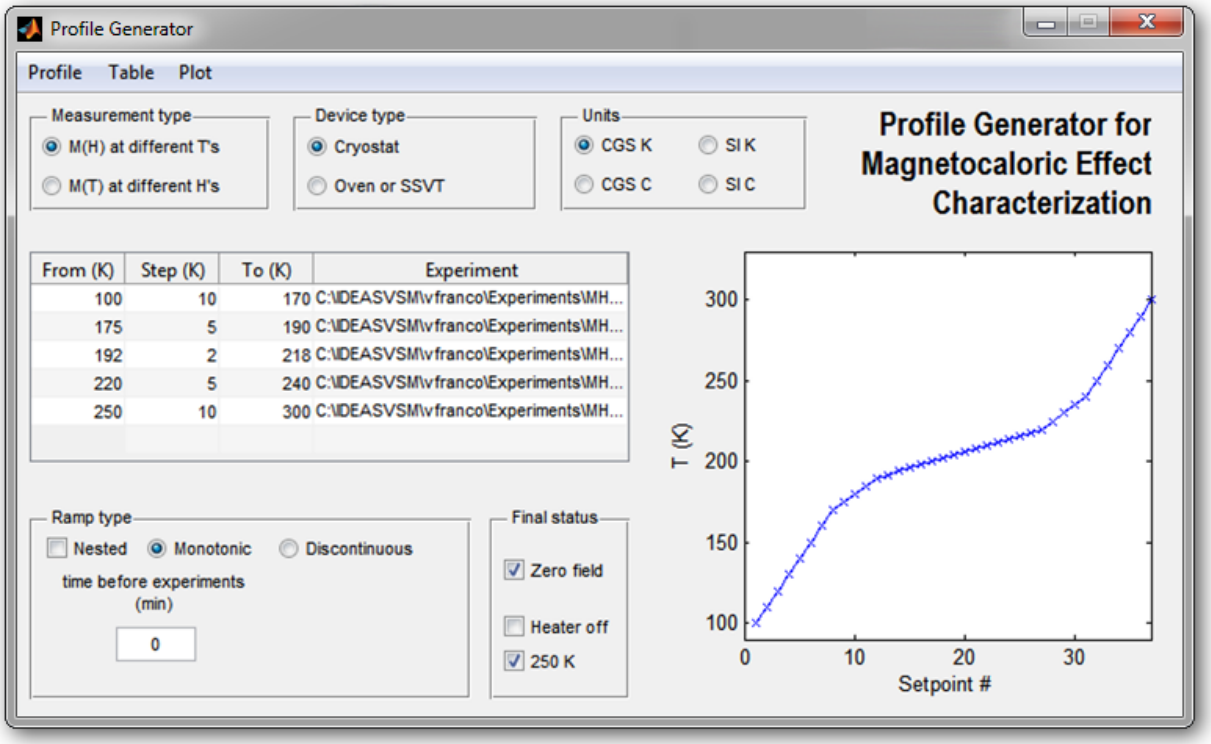



***Figure 18:*** *Definition of ramps which are not nested.*

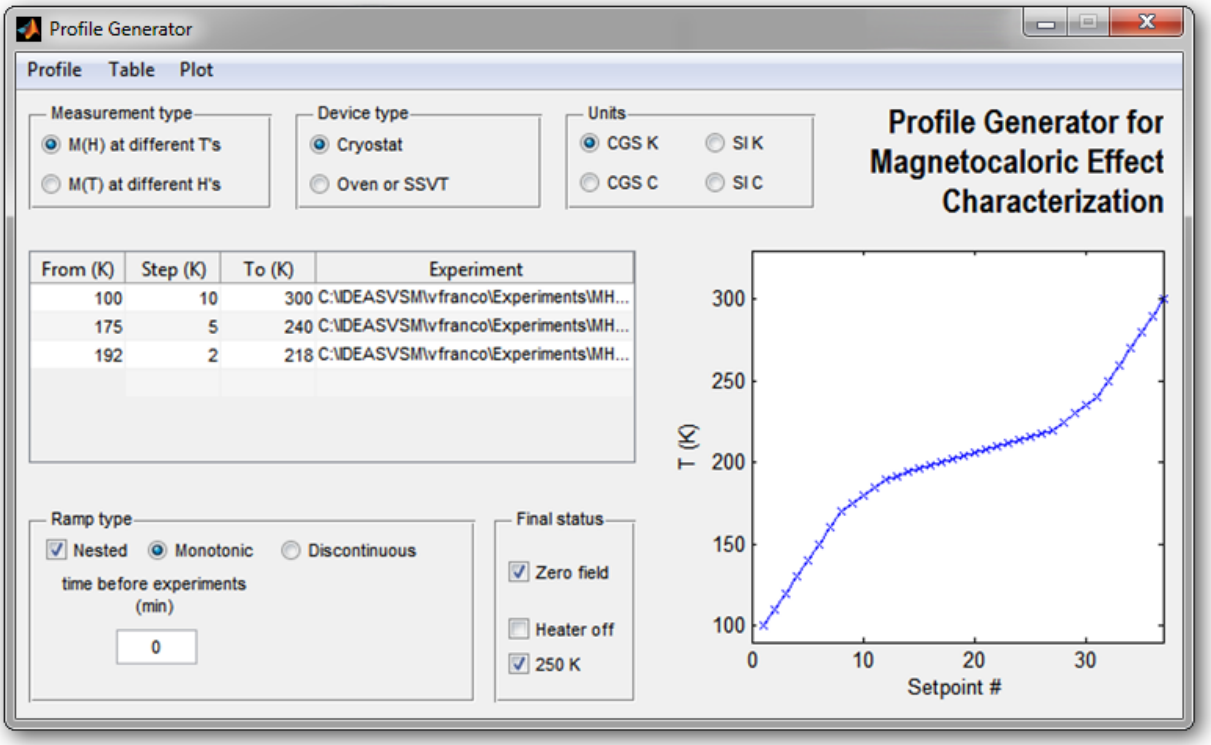



***Figure 19:*** *Definition of nested ramps. Notice that the result is identical to the one of Figure 18, requiring less typing in the ramps table.*

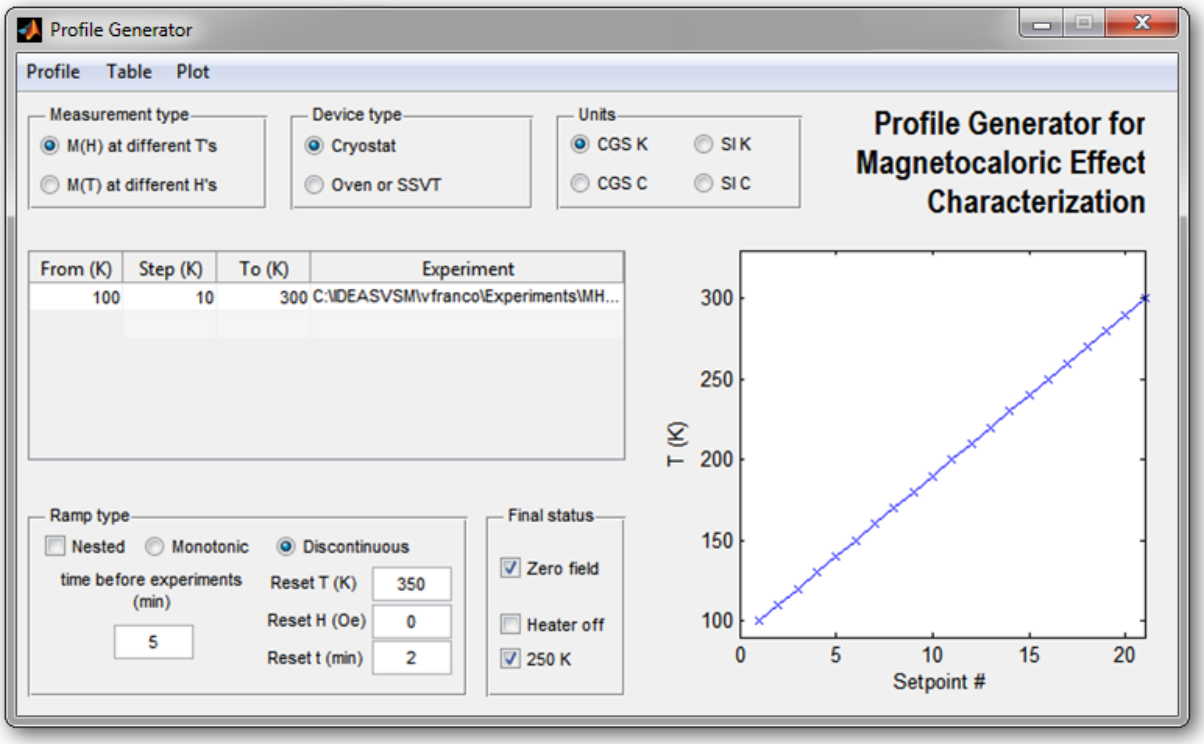



***Figure 20:*** *Additional options appear when a discontinuous protocol is selected.*

It is worth mentioning that the directory selection is initially set to be the experiments directory of the previous VSM user. If the profile is being created for another user, the directory should be changed accordingly. The use of experiment files of one user by another one inside IDEAS will have an unpredictable effect and should be avoided (users can import experiments from colleagues using the IDEAS experiment editor before selecting them for profile creation using this tool).

By default, ramps are added sequentially one after the other, and setpoints can be seen in a graph by selecting **Plot** in the tool menu. Only sets of ramps that are complete can be plotted; otherwise, there will be a warning message. Empty lines in the ramps table are ignored and do not produce errors in the plot.

A wait time before running the experiment after the setpoint is stabilized can be entered into **time before experiments (min)**.

### 5.2.4. Nested ramps

Ramps can be sequential (default) or they can be **Nested**. This option is useful when a certain sub-range of a broader ramp has to be measured with a different resolution. The creation of such a set of nested ramps can be done with less typing than the equivalent creation of the same setpoint profile (compare Figure 18 to Figure 19).

### 5.2.5. Monotonic vs. discontinuous

As indicated above, second order phase transitions can be measured using M(H) experiments at different temperatures, with temperatures changing monotonously. However, for first order phase transitions, the sample has to be "prepared" before each isothermal measurement. This can be done by selecting **Discontonuous** ramps, which opens up the possibility of selecting the field and temperature that should be used for preparing the sample (Figure 20): first the reset field is set, followed by ramping the sample temperature to the reset temperature. At that point, a wait time before the sample is ramped back to the measuring setpoint can be introduced. When this setpoint is reached, the experiment indicated in the fourth column of that ramp table will be run and, subsequently, the reset procedure will be repeated before the next setpoint.

### 5.2.6. Final status

At the end of the profile, the system can be set to **zero field** and leave the temperature controller either in **Heater off** (preferable when the furnace is used) or at **250 K** (indicated for cryostat operation). If none of these options are selected, the system will remain at the last measuring setpoint.

### 5.2.7. Other menus

In addition to the **Plot** menu function already indicated, there are two additional menus in the tool:

#### Profile

- **Load Profile:** loads a previously saved profile generator file (.pfg) that contains all the necessary parameters to generate an IDEAS profile using this tool.
- **Save Profile:** saves the .pfg file that can be loaded by this tool.
- **Generate IDEAS pfl file:** runs the profile generator and saves the .pfl file that can be imported by IDEAS at a later stage. By default, the directory to save the file is the profile directory of the last VSM user. The file should be saved in the profile directory of the user who will use it.
- **Exit:** exits the tool and returns to the main window of the Magnetocaloric Effect Analysis program.

#### Table

- **Clean up table:** removes empty lines from the table to enhance visibility.
- **Empty table:** removes all parameters included in the table.
- **Remove wrong lines:** eliminates any line of the table which contains an empty cell. Therefore, if a line of the table is to be removed from the profile, the simplest option is to replace one of its cells with an empty cell or with a space and then use this function.
- **Reset all parameters:** resets the tool to its default state.

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## About the author

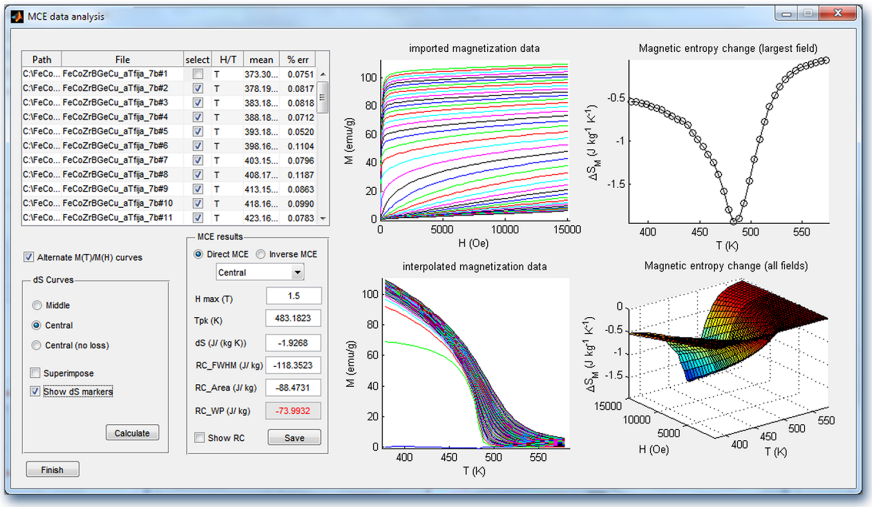
Victorino Franco obtained his PhD in Physics from Sevilla University (Spain) in 1999, where he is now a Professor at the Condensed Matter Physics Department.

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Victorino is the Past Chair of the Magnetic Materials Committee of the Minerals Metals and Materials Society (TMS), the Conference Coordinator of the Spain Section of IEEE, and the Secretary and Treasurer of the Spain Chapter of IEEE Magnetic Society. He is also Editor of the journal Metallurgical and Materials Transactions E: Materials for Energy Systems.

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