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A universal curve for the magnetocaloric effect: an analysis based on scaling relations

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Abstract
The universal character of the recent experimentally found master curve for the magnetic entropy change, ΔS_M, in studies of the magnetocaloric response of materials is analytically justified by using scaling arguments. The validity of the obtained scaling relations is checked against experimental data as well as the mean field and Heisenberg models. The curves are unique for each universality class. It is shown that the universal curve can be practically constructed in two different ways, reducing the number of required parameters with respect to the previous phenomenological derivation. This opens the possibility of an inexpensive screening of the performance of magnetocaloric materials, as it allows extrapolations to magnetic fields or temperatures not available in some laboratories.

(Some figures in this article are in colour only in the electronic version)

The magnetocaloric effect (MCE), i.e. the temperature change of a magnetic material when it is magnetized/demagnetized [1], is a field of increasing research interest, mainly because magnetic refrigerators are expected to be more environmental friendly than those based on gas compression–expansion [2, 3]. From the materials science point of view, there are numerous attempts to find materials with enhanced magnetocaloric response (mostly associated with giant magnetocaloric effect, GMCE) [4–7] and to reduce material costs (by replacing rare earths by transition metal based alloys) [8]. However, in order to be able to apply a specific material in a real refrigerator, there are additional requisites which have to be considered [9–11] and this justifies why present refrigerator prototypes still employ almost exclusively MCE materials with a second-order magnetic phase transition (versus GMCE materials, with a first-order magneto-structural phase transition). Simultaneous to the search for advanced magnetocaloric materials, the field dependence of this effect is also being studied intensively, either experimentally [12–15], or from a theoretical point of view by restricting the description to a mean field approach [16, 17][3], as this can give further clues of how to improve the performance of refrigerant materials for the magnetic field range employed in actual refrigerators (generally 10–20 kOe). More recently, the limitation of a mean field approach has been overcome by using the equation of state for materials with a second-order magnetic phase transition [18]. Expressing the field dependence as $\Delta S_M \propto H^n$, this approach allowed us to find a relationship between the exponent n at the Curie temperature and the critical exponents of the material [18]:

$$n|_{T=T_C} = 1 + \frac{1}{\delta}\left(1 - \frac{1}{\beta}\right). \quad (1)$$

A phenomenological universal curve for the field dependence of ΔS_M was also proposed [18]: 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 main aspect of constructing the curve was the selection of the equivalent points of the experimental curves and for this purpose the peak entropy change, $|\Delta S_M^{pk}|$, has been taken as a reference. It was assumed that all points that are at the same level with respect to $|\Delta S_M^{pk}|$ should be in an equivalent state. In that way, two different reference points were found for each curve, one below T_C and

[3] For a comprehensive summary of the application to rare earth metals, see section 8.1.8 of [4].

the other above it. After normalizing the curves with respect to their peak, the test for the existence of the universal curve would be to impose a scaling law for the temperature axis which makes the equivalent points collapse and check if the remaining parts of the curves also collapse. The temperature axis was rescaled in a different way below and above T_C, just by imposing that the position of the two reference points of each curve correspond to $\theta = \pm 1$:

$$\theta = \begin{cases} -(T - T_C)/(T_{r1} - T_C); & T \leqslant T_C \\ (T - T_C)/(T_{r2} - T_C); & T > T_C \end{cases} \quad (2)$$

where T_{r1} and T_{r2} are the temperatures of the two reference points of each curve. This procedure has been successfully applied to different families of soft magnetic amorphous alloys [18, 19] and lanthanide based crystalline materials [20].

On the other hand, the search for universal curves and scaling laws permeates all fields of scientific research, ranging from economics [21], to seismicity [22] and condensed matter physics [23]. In materials science, the possibility of collapsing experimental data of different materials into a single curve allows us to make predictions for the response of a particular material under different experimental conditions (which is extremely useful for cases when those conditions are not locally available to the researcher or are heavily resource consuming), and to be used as a simple, cost-effective screening tool in the search for more efficient materials. In the field of magnetocaloric research, universal curves or scaling behaviours have being recently looked for, either from the previously described phenomenological approach [18] or from the theoretical description of some specific models [24–26]. However, universal curves achieve their higher degree as predictive tools only when their existence is analytically demonstrated, as this would prove to which extent it is universal or if it just an ad hoc developed tool for some specific families of materials. The aim of this work is to show that the existence of the above-mentioned universal curve for the magnetocaloric effect (which, up to now, was only based on phenomenological grounds) can be grounded theoretically, proving that the MCE data of different alloys of the same universality class should collapse onto the same curve, regardless of the applied magnetic field. This demonstration will allow us to reduce the number of parameters necessary to construct the curve and provides an alternative, more robust, method of constructing it.

This demonstration of the universality of the ΔS_M curve is based on the assumption of scaling near a second-order phase transition, which is strongly supported by experimental results and theoretical analysis (see for example [27]). For magnetic systems, the scaling equation of state takes the form [28]

$$\frac{H}{M^\delta} = h\left(\frac{t}{M^{1/\beta}}\right), \quad (3)$$

where $t = (T - T_C)/T_C$ is the reduced temperature, T_C is the Curie temperature, $h(x)$ is a scaling function and β and δ are critical exponents which characterize the magnetization behaviour along coexistence ($H = 0, t < 0$) and the critical isotherm ($t = 0$), respectively. We note that the scaling function is the same for each system in a given universality class if we choose the magnetization and magnetic field units in such a way that $h(0) = 1$ and $h(-1) = 0$. As the critical exponents, the scaling equation of state is characteristic of the universality class of the system. As a particular case, for mean field (i.e. infinite-ranged interactions) the scaling function in equation (3) is $h(x) = (1 + x)$. The scaling equation of state can be expressed in different ways. For example, equation (3) may be formally inverted as:

$$\frac{M}{|t|^\beta} = m_\pm\left(\frac{H}{|t|^\Delta}\right) \quad (4)$$

where $\Delta = \beta\delta$ is the gap exponent and the plus (minus) sign corresponds to $t > 0$ ($t < 0$), respectively.

The MCE can be characterized by the magnetic entropy change due to the application of a magnetic field H, which can be evaluated from the processing of the temperature and field dependent magnetization curves:

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \quad (5)$$

Assuming the scaling form of the equation of state given by equation (4), and after some algebra, this expression can be rewritten as:

$$\Delta S_M/a_M = \pm|t|^{1-\alpha} \int_0^{H/|t|^\Delta} \mathrm{d}x(\beta m_\pm(x) - \Delta x m'_\pm(x))$$
$$= |t|^{1-\alpha}\tilde{s}(t/H^{1/\Delta}) = H^{\frac{1-\alpha}{\Delta}} s(t/H^{1/\Delta}) \quad (6)$$

where $a_M = T_c^{-1} A^{\delta+1} B$, being A and B the critical amplitudes at coexistence ($M = A(-t)^\beta$) and along the critical isotherm ($H = BM^\delta$), respectively. Note that $1 - \alpha = \beta + \Delta - 1$ (Griffiths equality) and $s(x) = |x|^{1-\alpha}\tilde{s}(x)$. This equation shows that if the reduced temperature t is rescaled by a factor proportional to $H^{1/\Delta}$, and the magnetic entropy change by $a_M H^{(1-\alpha)/\Delta}$, the experimental data should collapse onto the same curve. Similarly, the exponent n controlling the field dependence has the following scaling behaviour:

$$n = \frac{\partial \ln|\Delta S_M|}{\partial \ln H} = \frac{1-\alpha}{\Delta} - \frac{1}{\Delta}\frac{\mathrm{d}\ln|s(x)|}{\mathrm{d}\ln x}\bigg|_{x=t/H^{1/\Delta}}. \quad (7)$$

Consequently, the values of n also collapse when plotted against the same rescaled temperature axis for which the normalized values of ΔS_M collapse onto the same universal curve. Experimental evidences of this collapse of n have been recently given for soft magnetic amorphous alloys [10, 29]. It is worth mentioning that equation (6) proves that the field dependence of the magnetic entropy change for $T = T_C$, which was recently derived from the Arrott–Noakes equation of state [18]

$$\Delta S_M|_{T=T_C} \propto H^{1+\frac{1}{\delta}(1-\frac{1}{\beta})} = H^{\frac{1-\alpha}{\Delta}}, \quad (8)$$

is valid for any magnetic system which follows a scaling equation of state.

When the critical exponents of the material are known, the rescaled temperature axis can be constructed using equation (6). One consequence of the above given deduction

is that there is no need to use two reference temperatures as in equation (2), because the scaling law is the same below and above the Curie temperature, but the whole temperature axis can be scaled using either of the expressions in equation (2). However, the noise of experimental data can be overcome by using the two well separated reference temperatures, making the existence of the universal curve more evident.

From a theoretical point of view, provided that we know the equation of state, the Curie temperature and the critical exponents of the studied material, the universal curve for the magnetic entropy change could be constructed without introducing any additional parameters. However, when experimentalists are characterizing the magnetocaloric response of a new material, neither the analytical form of the equation of state, nor the critical exponents are known *a priori*. Therefore, what from a theoretical point of view can be simply seen as introducing the value of the Curie temperature inside equation (6), becomes an intractable approach when the functional form of s is not known (the usual situation when experimentally investigating a new material for the first time).

The transformation from a theoretical model to the universal curve and, finally, to the calculated magnetocaloric response of a 'virtually fabricated material' is straightforward. However, the method of obtaining the universal curve from experimental data needs the use of additional parameters. To make a practical case, let us concentrate for a moment on a single hypothetical material whose equation of state is the empirical Arrott–Noakes (AN) equation: [30]

$$H^{\frac{1}{\gamma}} = a(T - T_C)M^{\frac{1}{\gamma}} + bM^{\frac{1}{\beta}+\frac{1}{\gamma}}. \tag{9}$$

The different ΔS_M curves for different applied magnetic fields can be univocally characterized by the Curie temperature (related to the position of the peak), and the parameters a and b appearing in equation (9). However, the identification of parameters a and b from the experimental ΔS_M curves is not straightforward. Therefore, an equivalent set of three parameters, more easily identifiable, should be defined. In our description, these parameters are $|\Delta S_M^{pk}|$, T_C and the previously defined reference temperature, T_r. This reference temperature is an instrumental parameter which allows the placement of equivalent points of the ΔS_M curves on the same position of the rescaled temperature axis. Although it lacks a physical meaning, its virtue is that even without knowing the analytical form of the equation of state, or the values of the critical exponents of the material, the procedure described in this work allows the extraction of the universal curve for the magnetocaloric effect.

In order to select the reference temperature, taking into account that the overlap of ΔS_M curves is intimately associated to that of the n curves, an alternative method for constructing the universal curve can be proposed: to select the reference temperature as that corresponding to a specific value of the exponent n. When normalizing the ΔS_M curves, as there can be cases where the peak is not properly determined (e.g. few data points in that temperature range), it is also advisable to normalize with respect to the ΔS_M value corresponding to the reference temperature.

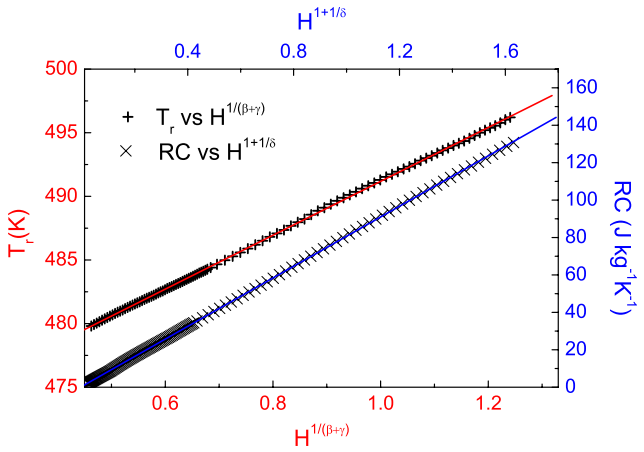

Figure 1. Scaling laws controlling the field dependence of the reference temperature and the refrigerant capacity for a $Fe_{78}Co_5Zr_6B_5Ge_5Cu_1$ amorphous alloy. The values of the critical exponents were previously determined using the Kouvel–Fisher method. Lines are a linear fit to the data.

In order to check the accuracy of the given scaling relations for experimental data, a $Fe_{78}Co_5Zr_6B_5Ge_5Cu_1$ amorphous alloy has been selected. Details about sample preparation and measuring techniques can be found elsewhere [31, 32]. The reference temperature for each applied field was selected as that which corresponds to $n = 1.25$. The values of the critical exponents and the Curie temperature were determined using the Kouvel–Fisher method [33], obtaining $\beta = 0.42 \pm 0.01$; $\gamma = 1.39 \pm 0.01$; $T_C = 467 \pm 2$ K. Figure 1 shows the field dependence of the reference temperature and of the refrigerant capacity, RC, defined as the product of the peak entropy change times the full width at half maximum of the peak. According to equation (6), the reduced temperature axis should scale with field as $H^{1/\Delta}$. Therefore, the reference temperature calculated in the phenomenological approach should also scale with field in this same way. Figure 1 shows a good agreement between the T_r values determined from the experimental curves and the scaling law predicted by equation (6). For constructing the figure, the previously quoted values of the critical exponents have been used, together with the relationship $\Delta = \beta + \gamma$. Equation (6) also predicts that RC should scale with an exponent of $1/\Delta + (1 - \alpha)/\Delta = 1 + 1/\delta$ (the addition of the exponents controlling the field dependence of the peak entropy change and of the reduced temperature axis). A good agreement between the experimental RC data and the scaling law predicted by equation (6) is also evidenced.

In the literature, accurate expressions of the equation of state for the 3D Ising [34], XY [35] and Heisenberg [36] models have been proposed, and for the Ising and XY cases they are in excellent agreement with computer simulations [35, 37]. The empirical Arrott–Noakes (AN) equation also obeys scaling with $h(x) = (1 + x)^{\gamma}$, where $\gamma = \beta(\delta - 1)$. Following reference [36], it is worthwhile noting that the AN expression fits the 3D Heisenberg scaling equation of state for $x < 0.75$ with a relative error less than 3%, which implies that it is essentially exact except for $t \gg 0$ and very small magnetic fields. For $\beta = 0.5$ and $\gamma = 1$, the AN expression is exactly coincident with the mean field case.

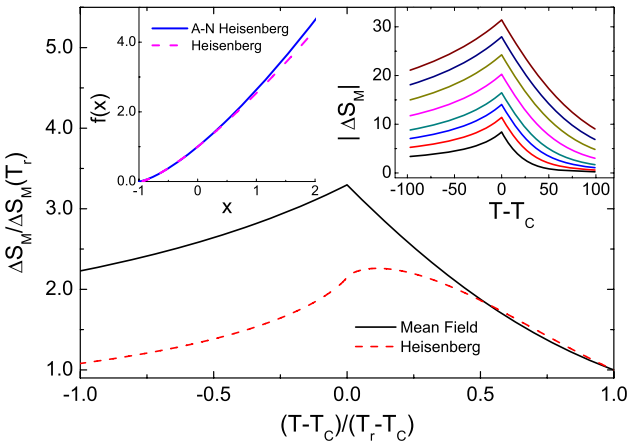

Figure 2. Universal curves for the mean field and Heisenberg models obtained from the numerically generated magnetization curves. The reference temperature has been selected in all cases as that corresponding to $n = 1.5$. Left inset: comparison between the scaling equation of state corresponding to the Heisenberg model and to the Arrott–Noakes equation of state with the critical exponents of the Heisenberg model. Right inset: some of the original curves used for generating the universal curve for the mean field model.

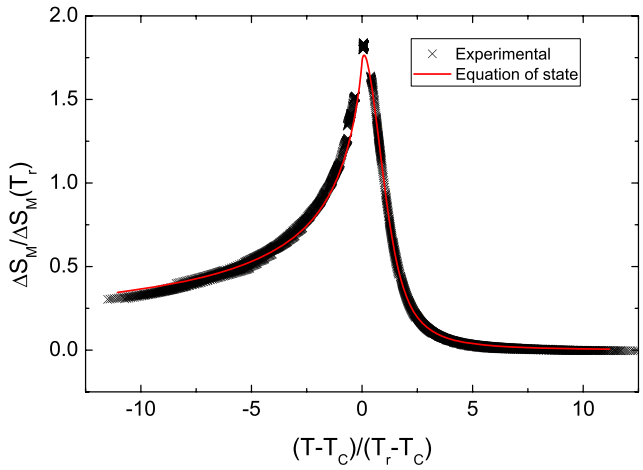

Figure 3. Experimentally determined universal curve for a $Fe_{78}Co_5Zr_6B_5Ge_5Cu_1$ amorphous alloy measured up to different maximum applied fields ranging from 2.5 to 15 kOe with increments of 125 Oe (crosses) and prediction of the Arrott–Noakes equation of state by using the critical exponents of the material (line).

To test the difference between the curves associated with different universality classes, magnetization curves have been numerically generated using the AN equation of state for the mean field and Heisenberg models (the accuracy of the AN equation of state for describing the Heisenberg model can be inferred from the left inset of figure 2, which confirms the previously mentioned agreement between the AN description and the exact scaling function [36]) and their magnetocaloric response has been calculated using a numerical approach to equation (5). Following the above described procedure, selecting the reference temperatures as those corresponding to $n = 1.5$ and normalizing the ΔS_M curves with respect to their value at $T = T_r$, figure 2 shows the universal curves corresponding to the different models. For each universality class, the curve is unique (i.e. changing the values of the Curie temperature or the parameters a and b in the equation of state does not alter the curve) but it is different from one class to another. The parameters used for generating the magnetization curves from which this figure was calculated were $a = 1$, $b = 1$ for both models—these values are chosen due to simplicity, as the universal curve is not dependent on them—and the critical exponents were $\beta = 0.5$; $\gamma = 1$ and $\beta = 0.367$; $\gamma = 1.388$ for the mean field and Heisenberg models, respectively. Although for the mean field model the peak entropy change corresponds to the Curie temperature, in the Heisenberg case the peak occurs at higher temperatures. A similar effect is found for the minimum value of n, which can be displaced from the Curie temperature.

Figure 3 shows the collapse of the experimental magnetic entropy change curves of the amorphous alloy measured up to different maximum magnetic fields ranging from 2.5 to 15 kOe with increments of 125 Oe, together with the rescaled ΔS_M curve corresponding to the AN equation of state with the values of the critical exponents previously calculated for this alloy. The description of the experimental data given by the equation of state is remarkably good. The differences in the peak value are inside the experimental error margin for ΔS_M (3%). The poorer agreement at lower temperatures can be ascribed either to the distance from the transition temperature, or to the appearance of different magnetization mechanisms associated to the disordered structure in the alloy. However, the maximum error in the collapse of the experimental data on a single curve is ∼5% for the whole temperature span of the figure and the separation between the experimental data and the AN curve remains below 5% up to a reduced temperature axis of 9. With respect to the scaling of the refrigerant capacity, this range of rescaled temperatures is broad enough to allow the proper reproduction of the field dependence, as shown in figure 1. Nevertheless, it is worth mentioning that corrections to scaling may appear if the temperature is far from the critical value. Such corrections can be explained by the presence of irrelevant operators in the renormalization-group sense and are characterized by correction-to-scaling exponent [38]. However, the actual range in which these corrections are nonnegligible depends on the details of the system. Our experimental data show that these corrections are less than the experimental error bar in the region of interest (i.e. close to the magnetic entropy change peak).

In conclusion, it has been analytically demonstrated that there exists a universal curve for the magnetic entropy change which is the same for any material in the same universality class. The rescaled temperature axis is the same as that which makes the curves of the exponent n or the magnetization curves collapse. This demonstration confirms the validity of the experimentally found universal curves for specific families of magnetocaloric materials. The phenomenological construction of the universal curve (i.e. without *a priori* knowledge of the critical exponents of the material) can be made with the use of a single reference temperature (apart from the Curie temperature) and an alternative procedure for the cases where the peak is not properly defined is also given. This opens the possibility of an inexpensive screening

of the performance of magnetocaloric materials, as it allows extrapolations to magnetic fields or temperatures not available in some laboratories.

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