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Field dependence of the magnetocaloric effect in Gd and $(Er_{1-x}Dy_x)Al_2$: Does a universal curve exist?

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Abstract – The field dependence of the magnetic entropy change of ferromagnetic lanthanide-based materials has been studied. The recently proposed master curve for the field dependence of the magnetocaloric effect of Fe-based amorphous alloys can also be constructed for these lanthanide-based crystalline materials, suggesting a universal behavior. The exponent n controlling the field dependence of the magnetic entropy change can be used for the interpretation of results in the case of multiple magnetic ordering phenomena.

Introduction. – The discovery of the giant magnetocaloric effect [1] has accelerated the research on near-room temperature magnetic refrigeration, especially with respect to better understanding of advanced magnetocaloric materials [2–5]. The search for more efficient materials, *i.e.* materials with a large peak isothermal entropy change in response to a varying magnetic field, $|\Delta S_M^{pk}|$, and refrigerant capacity, has been ongoing for the past ten years and several families of materials, including some rare-earth–based alloys, have been identified [5]. Meanwhile, cost reduction has been investigated by replacing rare-earth elements by transition metals [6]. More recently, soft magnetic amorphous alloys have been investigated as promising candidates for low-cost magnetic refrigerants (ref. [7] and references therein). In this latter case, although $|\Delta S_M^{pk}|$ is not as high as for rare-earth alloys, the refrigerant capacity of the amorphous alloys can be comparable to that of iron substituted $Gd_5Si_2Ge_2$ polycrystalline materials, even for a similar temperature span of the refrigeration cycle [7].

Currently, the field dependence of the magnetocaloric effect is also being studied intensively [8] for two main reasons. From a fundamental point of view, the analysis of this field dependence for different types of materials can give further clues of how to improve the performance of refrigerant materials for the magnetic-field range employed in actual refrigerators (generally 10 to 20 kOe). From a practical point of view, the knowledge of the laws governing the field dependence of the magnetic entropy change, ΔS_M, can provide tools for making plausible extrapolations to magnetic-field values outside the available experimental range in some laboratories.

The study of the field dependence of ΔS_M has been usually made either experimentally [9,10], or from a theoretical point of view by using a mean-field approach [11][1]. More recently [12], in order to predict the field dependence of ΔS_M for materials which do not follow a mean-field approach, the magnetic equation of state of such a material in the proximity of the transition temperature can be approximately described by the Arrott-Noakes equation of state [13], which can be written as

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

where β and γ are the critical exponents and T_C is the Curie temperature. Expressing the field dependence as

$$\Delta S_M \propto H^n, \tag{2}$$

taking into account the relationship $\beta\delta = \beta + \gamma$ and after proper manipulation of eq. (1), this approach leads to a relationship between the exponent n at the Curie point and the critical exponents of the material [12],

$$n = 1 + \frac{1}{\delta}\left(1 - \frac{1}{\beta}\right). \tag{3}$$

[1] For a comprehensive summary of the application to rare-earth metals, see sect. 8.1.8 of ref. [2].

In the case of a mean-field model (*i.e.* $\beta = 0.5$, $\gamma = 1$ and $\delta = 3$), we obtained $n = 2/3$, as predicted by Oesterreicher and Parker with rather different arguments [11]. Equation (3) was successfully tested for soft magnetic amorphous alloys [12]. Moreover, a phenomenological universal (master) curve for the field dependence of ΔS_M was also proposed and its suitability was positively tested for different series of soft magnetic amorphous alloys. Not only did each single alloy follow the universal curve when measured to different maximum applied fields [12], but also the ΔS_M curves of different alloys with similar values of the critical exponents could be overlapped into a single curve [14]. Consequently, this universal curve has been used as a predictive tool for characterizing series of materials [15]. However, the materials used for these studies, although with a broad compositional range, were rather limited in two senses: they were all Fe or Fe-Co based alloys, and all of them were amorphous, while magnetic refrigerator prototypes mainly use rare-earth crystalline materials. The aim of this work is to test whether this recently proposed universal curve is applicable to the behavior of magnetocaloric materials with a second-order magnetic phase transition, or if it is just a peculiarity of either amorphous materials or transition metal-based alloys. For this purpose, we have selected single crystalline Gd and polycrystalline $(Er_{1-x}\ Dy_x)Al_2$ alloys, because they are well-known magnetic refrigerants which do not suffer from the aforementioned limitations of the previous test materials.

Experimental. – The Gd single crystal was prepared by the Materials Preparation Center (MPC) of the Ames Laboratory using the strain anneal technique [16]. It was 99.85 at.% (99.98 wt.%) pure with the major impurities (in ppm atomic) as follows: O – 706, C – 470, N – 100, H – 63, Fe – 27, Si – 25, Cu – 25, and F – 20. The $(Er_{1-x}Dy_x)Al_2$ alloys were prepared by arc-melting stoichiometric amounts of pure components: high-purity Dy (major impurities were H – 800, F – 690, O – 500, N – 46, Mn – 24, Fe – 23, Cl – 23, Ta – 17, and C – 10) and Er (major impurities were H – 828, O – 546, F – 246, C – 97, N – 60, Fe – 19, and Cl – 14) prepared by MPC, Ames Laboratory, and 99.99 wt.% Al purchase from a commercial vendor. The samples were prepared by arc-melting the two lanthanide metals first to form the corresponding $Er_{1-x}Dy_x$ alloy, which then were arc-melted with Al to form the corresponding $(Er_{1-x}Dy_x)Al_2$ alloy. Annealing was not necessary since all dialuminide compounds melt congruently. According to X-ray powder diffraction and optical metallography, the samples were over 99% single phase.

The magnetic entropy change has been evaluated from the processing of the temperature and field-dependent magnetization curves using a numerical approximation to the equation

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H, \tag{4}$$

where the partial derivative is replaced by finite differences and the integration is performed numerically. The local values of the exponent n characterizing the field dependence of ΔS_M has been calculated as

$$n = \frac{\mathrm{d}\ln|\Delta S_M|}{\mathrm{d}\ln H}. \tag{5}$$

All materials examined are magnetically soft, thus ensuring single domain state over the range of magnetic fields used. Due to irregular shapes of samples, magnetic-field values were not corrected for demagnetization.

Results and discussion. – The phenomenological universal curve can be constructed by: 1) normalizing all the $\Delta S_M(T)$ curves using their respective peak entropy change; and 2) rescaling the temperature axis below and above Curie temperature, T_C, as defined in eq. (6) with an imposed constraint that the position of two additional reference points in the curve correspond to $\theta = \pm 1$:

$$\theta = \begin{cases} -(T - T_C)/(T_{r1} - T_C); & T \leqslant T_C, \\ (T - T_C)/(T_{r2} - T_C); & T > T_C, \end{cases} \tag{6}$$

where T_{r1} and T_{r2} are the temperatures of the two reference points. These can be selected from the temperatures corresponding to $\Delta S_M\left(T_r, H_{max}\right)/\Delta S_M^{pk}\left(H_{max}\right) = a$, where a is a real number between 0 and 1. For this study, $a = 0.4$ has been selected for the Gd samples and $a = 0.5$ for the rest of the compositions. The reason for selecting a lower value of a for the Gd samples was to avoid (as much as possible) the influence on the universal curve of the spin reorientation transition (see below).

Figure 1 shows the magnetic entropy change of a Gd single crystal with the applied field oriented along the [010]-direction and whose maximum value ranges from 10 to 56 kOe. The lower panel of this figure shows the rescaled curves. It is evident that the overlapping of the different curves is remarkable, being only less clear in the $-4 \leqslant \theta \leqslant -1$ range. This departure from the universal curve over this range is associated with the spin reorientation transition observed at ~ 230 K [17], and is more evident in the magnetocaloric effect data with the magnetic field applied along the [001]-direction. (According to ref. [18], the easy magnetization vector departs from the [001]-direction below 230 K, and the angle between the sixfold symmetry axis is temperature dependent). The lack of perfect overlap of the curves below the Curie temperature (its value, $T_C = 294$ K was employed for scaling according eq. (6)) is not a failure of the universal curve model, but it is simply the evidence that there are different magnetic transitions with different field dependencies in this sample. It should be mentioned that the magnetic-field values used for constructing the universal curve are much higher than the coercivity of the samples, as otherwise the histeretic nature of the magnetization curves below T_C need to be taken into account.

In order to discuss in more detail the influence of the overlapping of different magnetic transitions, the pseudo

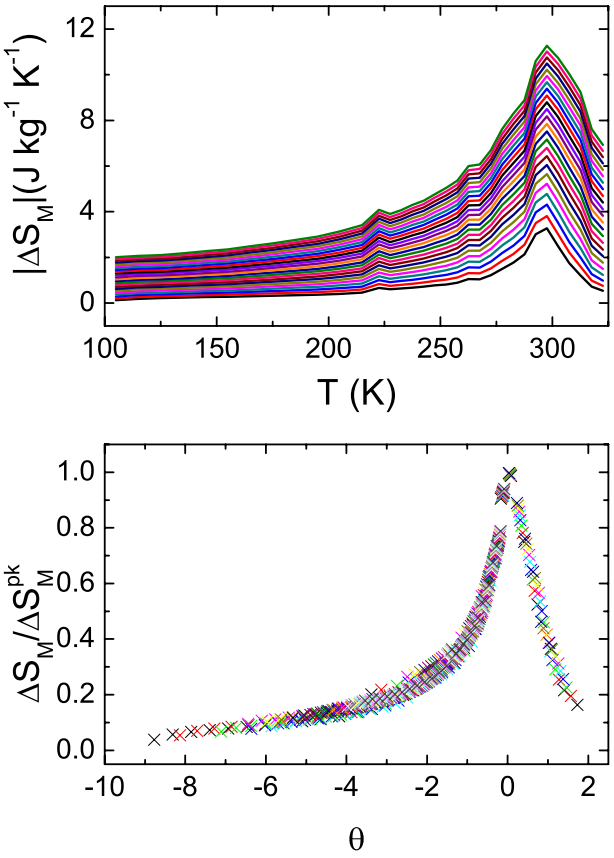

Fig. 1: Upper panel: temperature dependence of the magnetic entropy change of a Gd single crystal measured for applied fields (H ∥ [010]) ranging from 10 kOe up to 56 kOe with 2 kOe steps. Lower panel: the universal curve for all of the data.

binary alloy series $(Er_{1-x}Dy_x)Al_2$ has also been studied. In this case, the various magnetic ordering temperatures have been described as follows [19,20]: For $x = 0$, only a sharp peak in the heat capacity curves at the Curie temperature is detected; for $x = 0.85$ and $x = 1$, together with the ferromagnetic ordering transition, a spin reorientation transition (at 40 K) and a peak associated with the crystalline electric field, CEF (around ∼10 K) can be found. It is worth mentioning that the contribution emerging from the CEF should be sensitive to local structural perturbations of each particular sample. Therefore, minor deviations in the position of this peak can be expected. Figure 2 shows the field and temperature dependence of the magnetic entropy change of the $Er_{0.15}Dy_{0.85}Al_2$ sample. The main features are a main peak at the Curie temperature of the alloy and a shoulder at low temperatures, which looses importance as the applied field is increased (this hump can be detected from both the constant H grid lines and the distortion of the isolevel lines for low fields and temperatures).

Figure 3 shows the rescaled magnetic entropy change curves of this alloy for applied magnetic fields ranging from 5 kOe up to 55 kOe. The curves corresponding to low applied fields depart from the universal curve for

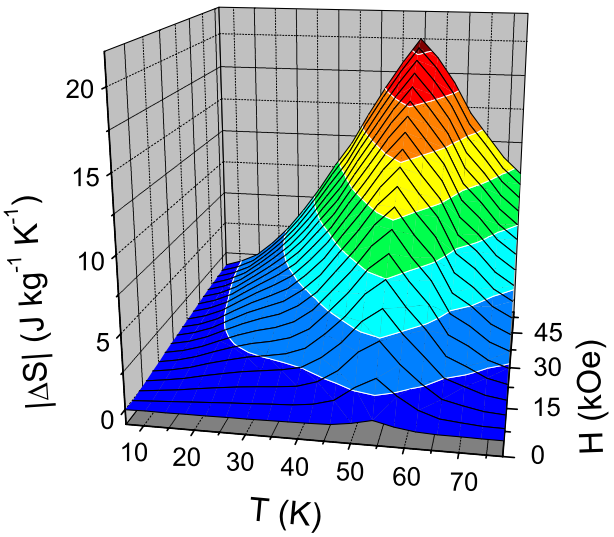

Fig. 2: Temperature and field dependence of the magnetic entropy change of a polycrystalline $Er_{0.15}Dy_{0.85}Al_2$ sample.

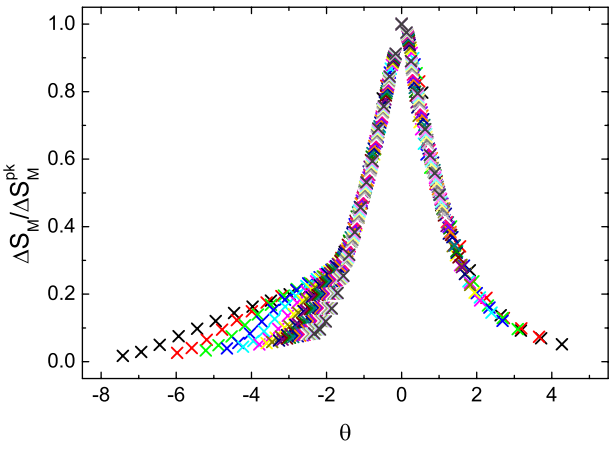

Fig. 3: Rescaled magnetic entropy change curves for a polycrystalline $Er_{0.15}Dy_{0.85}Al_2$ sample for applied fields ranging from 5 kOe up to 55 kOe with 2 kOe steps.

$\theta \leqslant -1.4$, while the overlapping in this reduced temperature range is enhanced with increasing applied field. This is in agreement with the previously mentioned decreasing importance of the low-temperature hump for higher applied fields. This change in the quality of the overlapping hints at a field-dependent magnetic effect, which can be further studied from the calculation of the local exponent n controlling the field dependence of ΔS_M. Figure 4 shows the temperature dependence of n for different values of the maximum applied field. Two minima can be found for all curves. The high-temperature one, which is nearly field independent, corresponds to the Curie transition of the alloy; the low-temperature minimum, with strong magnetic-field dependence, is associated with the CEF peak. This displacement of the minimum to lower temperatures with increasing applied fields explains the enhanced overlapping of the rescaled ΔS_M curves for higher fields.

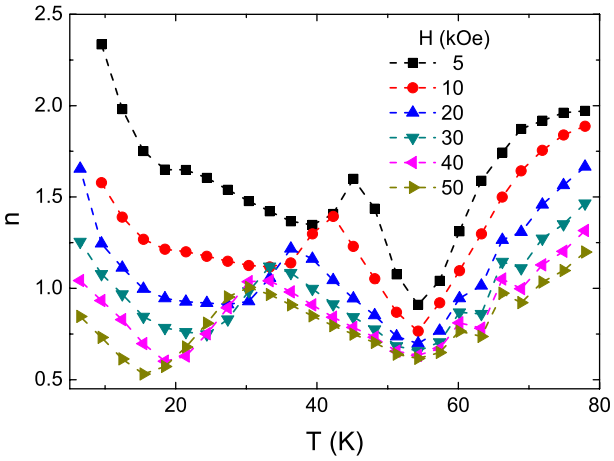

Fig. 4: The temperature dependence of the exponent n for a polycrystalline $Er_{0.15}Dy_{0.85}Al_2$ sample measured up to different maximum fields. The lines are a guide to the eye.

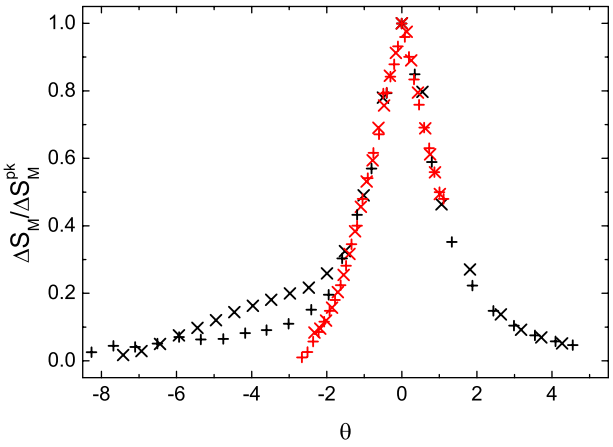

Fig. 5: Rescaled magnetic entropy change curves for polycrystalline $Er_{0.15}Dy_{0.85}Al_2$ (×) and $DyAl_2$ (+) samples for applied fields of 5 kOe (curves with low-temperature tails) and 55 kOe (without low-temperature tails).

For $x = 0$, the CEF minimum in n is not detected, while for $x = 1$ the results are similar to those presented for the $x = 0.85$ alloy.

For samples in which the only magnetic phenomenon that takes place in the studied temperature range is the ferromagnetic ordering transition, the field dependence of the magnetic entropy change is eliminated with the construction of the universal curve and the temperature dependence of these curves is connected to the critical exponents of the material. Initially, it was proposed that alloys with similar values of the critical exponents should follow the same universal curve [12]. This was experimentally observed in a series of amorphous alloys [14]. For the $(ErDy)Al_2$ system, changes in the alloy composition should not significantly alter the values of the critical exponents. However, the overlapping of different magnetic phenomena with different field dependences should prevent the complete overlapping of the rescaled magnetic entropy change curves. Figure 5 represents the results for the $Er_{0.15}Dy_{0.85}Al_2$ and $DyAl_2$ samples for applied fields of 5 and 55 kOe. As expected from the previous reasoning, the peaks of the curves (associated with the ferromagnetic ordering transition) collapse onto the same universal curve, while the low-temperature parts associated with the CEF peak exhibit different behaviors for the two compositions. As indicated above, the low-temperature tails for the low-field measurements are due to the large contribution of the CEF peak in these cases.

The experimental evidence of a universal curve for the magnetic entropy change of materials with a second-order magnetic phase transition constitutes an incentive to study analytically under which conditions this universal behavior should hold. Although for the mean-field case a simple expression connects the magnetic entropy change and the magnetization of the sample, for a general case the mathematical description goes through the hypergeometric function, which introduces numerous complications into the analytical procedure. This line of study is currently being undertaken and results will be given elsewhere [21].

Conclusions. – It has been shown that a universal curve of the field dependence of ΔS_M also holds for materials whose magnetocaloric response is due to a second-order magnetic phase transition, and is independent of the sample composition or any structural order/disorder. A study of the local exponent controlling the field dependence of ΔS_M can also be considered as a powerful tool for studying overlapping magnetic phenomena. Response to the question raised in the title of this article, it appears that the method proposed in refs. [12,14,15] and utilized in this paper is a qualified yes. But additional materials need to be evaluated to test its universality further.

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