Thermal properties and critical behaviour in rare-earth based magnetocaloric materials

Oleaga A[(1)*], Herrero A[(1)], Aseguinolaza IR[(1)], Apiñaniz E[(1)], García-Adeva AJ[(1)]

(1) Departamento de Física Aplicada, Escuela de Ingeniería de Bilbao, Universidad del País Vasco UPV/EHU, Bilbao, Spain

*Corresponding author's email: alberto.oleaga@ehu.es

The need to introduce environmentally friendly technology in the energy field has led to huge advances in the research and development of a new refrigeration technology based on the magnetocaloric effect, with the aim of replacing the classical gas compression-expansion cycles [1, 2]. Hence, a thorough search for magnetocaloric materials which present suitable properties for technological applications in different temperature ranges is currently under way. Different types of materials are being studied, among them a huge variety of intermetallics. We have been focusing our attention in the last years on rare-earth based intermetallic families which can compete in this field in a wide temperature span, from the gas liquefaction ranges to room temperature. There is a need to properly characterize the magnetic and magnetocaloric properties of these materials as well as their thermal ones. As the magnetocaloric materials will work in a cycle in a refrigeration system, the heat exchange between the magnetocaloric material and the fluid in the refrigerator must be efficient and quick, allowing high working frequencies, highlighting the relevant role of the thermal diffusivity, as it is a non-steady heat transfer situation. Besides, the study of the thermal behaviour at the phase transition will complement the magnetic one in order to understand the underlying physics, through the study of the critical behaviour of the second order magnetic transition.

This work will present a selection of results for the following families: R_6(Fe,Mn)X_2 (R=Tb, Gd, Ho, Dy; X=Sb, Bi, Te), R_3CoNi (R=Tb, Dy, Ho), Tb_3Co, Tb_3Ni, covering a wide range of temperatures, magnetic transitions and properties.

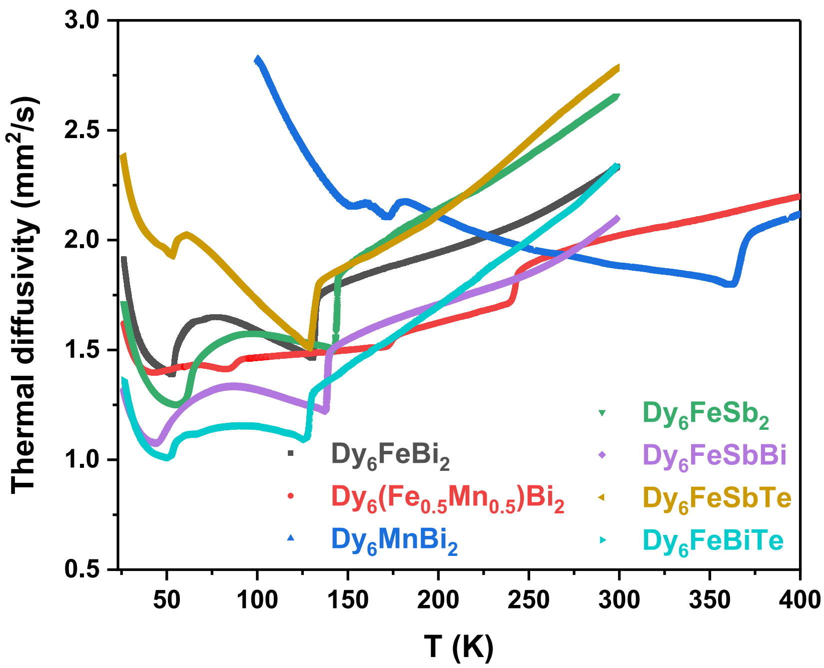

Fig. 1. Thermal diffusivity curves for Dy_6(Fe,Mn)X_2

Concerning the thermal properties, an ac photopyroelectric calorimeter in the back detection configuration has been used to measure thermal diffusivity (D) and specific heat (c_p), due to its high resolution and sensitivity. Fig. 1 shows an example of D for the $Dy_6(Fe,Mn)X_2$ family, where the paramagnetic to ferromagnetic (PM-FM) second order phase transitions are signalled as dips in the higher temperature part of each curve, while at lower temperature there are different spin reorientation transitions. These curves will be discussed in parallel to magnetization curves as a function of temperature [3]. Fig. 2 shows the succession of a second order PM-FM and a weakly first order FM-AFM transition in the case of Tb_3Co [4].

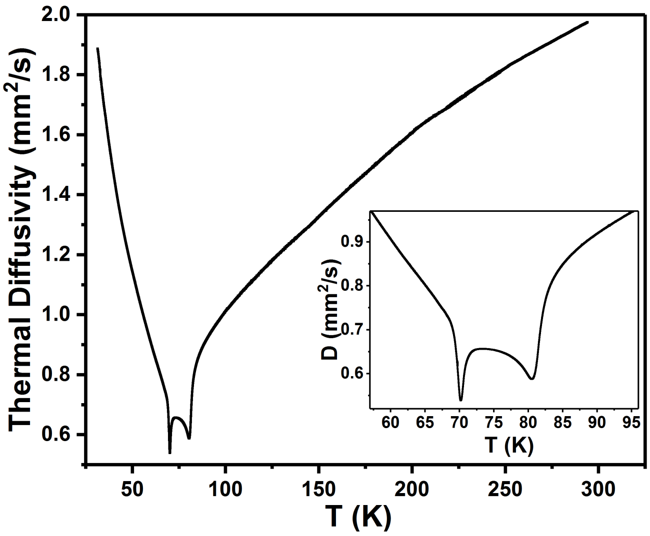

Fig. 2. Thermal diffusivity curve for Tb_3Co. The inset highlights the most relevant part.

The critical behaviour of the second order phase transitions has been analysed by thermal, magnetic and magnetocaloric techniques. According to the renormalization group theory, the critical behaviour of these transitions in the near vicinity of the critical temperature is characterized by a set of critical exponents (α, β, γ, δ, related to specific heat, spontaneous magnetization, inverse of the initial susceptibility and magnetization at the critical temperature, respectively) corresponding to different universality classes.

The magnetic interaction range, as well as the ordering of the spins, have therefore been studied using the different scaling equations, such as the following one for c_p:

$$c_p = B + Ct + A^{\pm}|t|^{-\alpha}(1 + E^{\pm}|t|^{0.5}) \qquad \text{Eqn. 1}$$

where t is the reduced temperature and $A^{\pm}$, B, C, $E^{\pm}$ are fitting parameters.

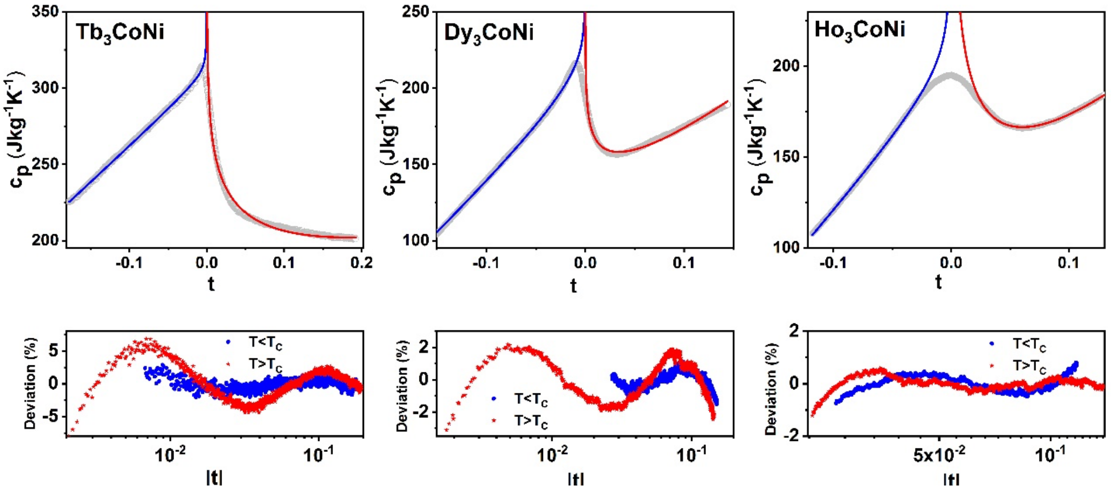

Fig. 3. Top line: Experimental (grey open circles) and fitted curves (continuous lines) of the specific heat as a function of the reduced temperature for the three compounds in the near vicinity of T_C. Bottom line: deviation plots for the fittings, blue circles correspond to $T < T_C$, red stars for $T > T_C$.

We will show that, among these families, we have found phase transitions belonging to the Mean Field class (long range order magnetic ordering), 3D Heisenberg (short range order, isotropic distribution of spins), Chiral classes (short range order with complex magnetic ordering), even unconventional critical behaviours with critical exponents whose values do not fit in any theorized universality class. Fig. 3 shows an example of the specific heat fittings for R_3CoNi [5].

We will show that the thermal diffusivity values of these families are among the highest in the magnetocaloric field, being competitive with High Entropy Alloys such as several Heusler alloys, which make them interesting even if the magnetocaloric variables (magnetic entropy change, refrigerant capacities) are not among the highest ones.

References

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