

## The magnetocaloric effect in materials with a second order phase transition: Are $T_C$ and $T_{\text{peak}}$ necessarily coincident?

V. Franco,<sup>1,a)</sup> A. Conde,<sup>1</sup> M. D. Kuz'min,<sup>2</sup> and J. M. Romero-Enrique<sup>3</sup>

<sup>1</sup>*Departamento de Física de la Materia Condensada, ICMSE-CSIC, Universidad de Sevilla, P.O. Box 1065, 41080 Sevilla, Spain*

<sup>2</sup>*Leibniz-Institut für Festkörper- und Werkstoffforschung, IFW Dresden, PF 270116, D-01171 Dresden, Germany*

<sup>3</sup>*Departamento de Física Atómica, Molecular y Nuclear Área de Física Teórica, Universidad de Sevilla, P.O. Box 1065, 41080 Sevilla, Spain*

(Presented 12 November 2008; received 9 September 2008; accepted 30 October 2008; published online 12 February 2009)

Using the Arrott–Noakes equation of state it is shown that the Curie point ( $T_C$ ) and the temperature where the magnetic entropy change is maximum ( $T_{\text{peak}}$ ) coincide only in the mean field approximation, but the Heisenberg model implies that  $T_{\text{peak}} > T_C$  even for homogeneous materials. The distance between  $T_{\text{peak}}$  and  $T_C$  increases with applied magnetic field following a power law. In both cases,  $T_C$  corresponds to a singular point in the temperature dependence of the magnetic entropy change. The field dependence of the magnetic entropy change is exactly the same at the Curie temperature and at the temperature of the peak. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3063666]

Magnetocaloric effect (MCE) and its most straightforward application, magnetic refrigeration, are becoming fields of increasing research interest. On the one hand, there are reasonable expectations that these subjects will give rise to energy-efficient, environmentally friendly technological applications. On the other hand, the study of some model materials gives some more insight into the physics underlying these phenomena. The temperature change of a magnetic sample upon the application of an external magnetic field is associated with the temperature variation of magnetization. The latter is usually maximum near phase transitions; therefore, materials useful for applications are those with a phase transition close to the working temperature. This gives rise to the most important classification of MCE materials: the ones undergoing a second order magnetic phase transition versus those presenting a magnetostructural phase transition.<sup>1</sup> In the first case, there is no associated thermal or magnetic hysteresis. However, the second type of materials present a higher magnetocaloric response but at the expense of hysteretic losses.<sup>2,3</sup> This is the reason why most refrigerator prototypes are still using materials with second order phase transitions. From the technological point of view, the optimization of magnetic refrigerator appliances for domestic use should proceed toward the increase in the magnetocaloric response at low applied magnetic fields, which has motivated recent studies of the field dependence of the magnetic entropy change.<sup>4–7</sup>

In the literature about MCE, it is often assumed that the magnetic entropy change of a material with a second order magnetic phase transition has its peak value exactly at the Curie temperature,  $T_C$ . In some cases, the experimental separation between  $T_C$  and the temperature of the peak,  $T_{\text{peak}}$ , has been ascribed to compositional inhomogeneities in the stud-

ied sample.<sup>7,8</sup> The aim of this work is to show that this assumption is not the only possibility to explain this experimental fact. The magnetic entropy change due to the application of a magnetic field  $H$  can be calculated with the use of

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

In order to describe the temperature and field dependences of magnetization in the environment of the Curie temperature, the Arrott–Noakes equation of state can be used<sup>9</sup> as follows:

$$H^{1/\gamma} = a(T - T_C)M^{1/\gamma} + bM^{1/\beta+1/\gamma}, \quad (2)$$

where  $\beta$  and  $\gamma$  are the critical exponents. In the case of  $\beta = 0.5$ ;  $\gamma = 1$ , this coincides with the mean field approximation. Following Ref. 10, it is worth noting that this expression fits the three-dimensional Heisenberg scaling equation of state, with  $\beta = 0.367$  and  $\gamma = 1.388$ , and is essentially exact except for very large reduced temperatures and very small magnetic fields. After proper manipulation of the equation of state, Eq. (1) can be rewritten as

$$\Delta S_M = - \int_{M_s}^{M_{\text{max}}} a\gamma M(a(T - T_C) + bM^{1/\beta})^{\gamma-1} dM, \quad (3)$$

where  $M_s$  stands for the spontaneous magnetization and the upper limit of the integral is the magnetization corresponding to the maximum applied field at the given temperature. The use of Eq. (3) instead of Eq. (1) avoids numerical errors close to the transition temperature and it can be evaluated either by numerical integration or analytically in terms of hypergeometric functions.

For generating the magnetization curves by means of Eq. (2), the values  $T_C = 370$  K,  $a = 1.228(\text{g/cm}^3)^{1/\gamma} \text{K}^{-1}$ , and

<sup>a)</sup>Electronic mail: vfranco@us.es.

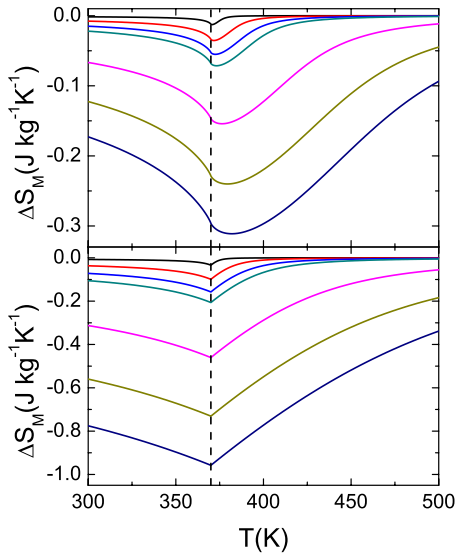


FIG. 1. (Color online) Temperature dependence of the magnetic entropy change for maximum applied fields of 100, 500, 1000, 1500, 5000, 10 000, and 15 000 Oe for the mean field (lower panel) and Heisenberg (upper panel) models. The vertical dashed line corresponds to the Curie temperature.

$b=7.70 \times 10^{-3} (\text{g/cm}^3)^{1/\gamma} (\text{emu/g})^{-1/\beta}$  have been used throughout this work. They correspond to those of a typical Fe-based soft magnetic amorphous alloy reported in the literature.<sup>11</sup> These three parameters do not alter the shape of the  $\Delta S_M$  curves.<sup>12</sup> Therefore, this particular choice does not impose any restriction on the conclusions extracted from this work. Figure 1 shows the temperature dependence of the magnetic entropy change for the Heisenberg (upper panel) and mean field (lower panel) models, for different values of the maximum applied field. It is seen that the generally accepted equality  $T_C = T_{\text{peak}}$  is only true for the mean field case, but the Heisenberg model implies  $T_{\text{peak}} > T_C$ . From an experimental point of view, the determination of the Curie temperature from magnetization curves usually implies the determination of their inflection point, which shifts to higher temperatures for increasing magnetic fields and gives rise to an apparent increase in  $T_C$  for high magnetic fields. This experimental fact is reproduced by the Heisenberg model (and not by the mean field model) and is responsible for the shift in  $T_{\text{peak}}$ . Figure 2 shows that the distance between  $T_C$  and  $T_{\text{peak}}$  increases with field following a potential law  $H^{1/\Delta}$  (with  $\Delta = \beta + \gamma$ ), as recently predicted by scaling laws.<sup>12</sup> In that figure, together with the results for the Heisenberg model, the values of the critical exponents ( $\beta=0.46$ ;  $\gamma=1.56$ ) of the FeCrB amorphous alloys studied in Ref. 11 has also been used. These latter values are inside the range of those found for other amorphous alloys.<sup>13</sup> For a maximum applied field of 15 kOe, the predicted shift in  $T_{\text{peak}}$  for these samples remains below 5 K, which is in agreement with the reported experimental results. It has to be taken into account that the use of numerical derivatives in calculating the  $\Delta S_M$  curves from magnetization data imposes a lower bound on the temperature increment (so that noisy curves are avoided), which is about 5 K for the experimental setup in Ref. 11.

Focusing our attention again on the models, the temperature derivative of the magnetic entropy change can also be

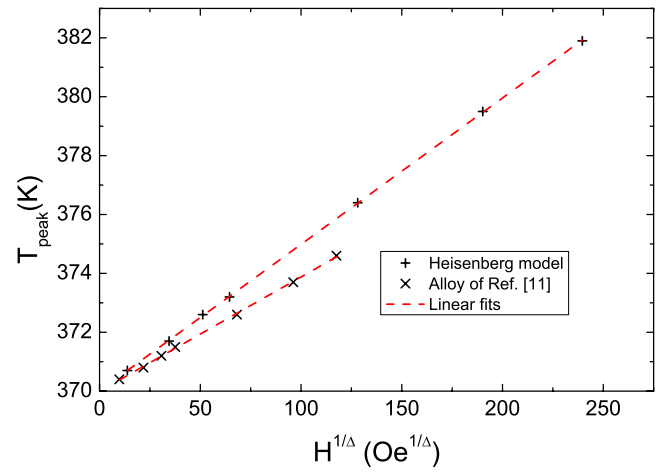


FIG. 2. (Color online) Field dependence of  $T_{\text{peak}}$  for the Heisenberg model (using  $\beta=0.367$ ;  $\gamma=1.388$ ) and predicted evolution for the B15 Fe-based amorphous sample of Ref. 11 (using  $\beta=0.46$ ;  $\gamma=1.56$ ). The dashed lines are linear fits to the data.

calculated from the temperature dependence of magnetization, without the need for numerical derivatives, as follows:

$$\frac{d\Delta S_M}{dT} = \frac{a^2 \gamma M_{\text{max}}^2 (a(T - T_C) + bM_{\text{max}}^{1/\beta})^{\gamma-1}}{\frac{a(T - T_C)}{\gamma} + b\left(\frac{1}{\beta} + \frac{1}{\gamma}\right)M_{\text{max}}^{1/\beta}} - \int_{M_s}^{M_{\text{max}}} a^2 \gamma (\gamma - 1) M (a(T - T_C) + bM^{1/\beta})^{\gamma-2} dM. \quad (4)$$

It can be shown that  $d\Delta S_M/dT|_{T=T_C} \propto H^{-\alpha/\Delta}$  and that  $d^2\Delta S_M/dT^2|_{T=T_C}$  diverges. This is a common feature of all the universality classes for which  $\alpha = 2 - \beta - \Delta < 0$ , the Heisenberg model being a particular case.

Figure 3 shows the temperature dependence of the de-

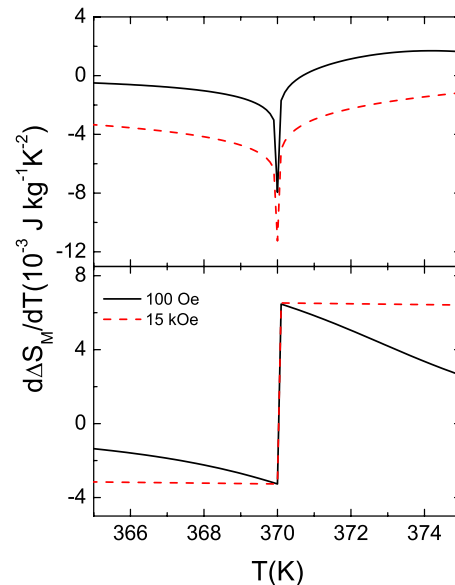


FIG. 3. (Color online) Temperature dependence of the slope of the magnetic entropy change curves for the mean field (lower panel) and Heisenberg (upper panel) models.

ivative of  $\Delta S_M$  [Eq. (4)] for the Heisenberg and mean field models, for different maximum applied fields. In both cases, the Curie temperature corresponds to the minimum value of the slope of the  $\Delta S_M$  curves, which is followed by an abrupt (discontinuous in the mean field case) increase in slope. It also accidentally coincides with the peak temperature of  $\Delta S_M$  for the mean field model but, as shown above, this coincidence is not a general feature.

When studying the field dependence of the magnetic entropy change, it is usually expressed as  $\Delta S_M \propto H^n$ . In most of the cases, this exponent is only calculated from experimental  $\Delta S_M$  data at the temperature of the peak of the curves. At the Curie temperature, a general expression for this field dependence has been given,<sup>5</sup> and its generality subsequently justified using scaling relations.<sup>12</sup> It is therefore worth considering whether or not  $n(T_C) = n(T_{\text{peak}})$ . By expressing  $\Delta S_M \propto H^{(1-\alpha)/\Delta} s((T-T_C)/H^{1/\Delta})$ , where  $s(x)$  is a scaling function, it was shown that the exponent  $n$  controlling the field dependence has the following scaling behavior:<sup>12</sup>

$$n = \frac{\partial \ln|\Delta S_M|}{\partial \ln H} = \frac{1-\alpha}{\Delta} - \frac{1}{\Delta} \frac{d \ln|s(x)|}{d \ln x} \Bigg|_{x=(T-T_C)/H^{1/\Delta}}. \quad (5)$$

Two different temperatures make the second term vanish. One is  $T=T_C$ , as in that case  $x=0$ ; the other is  $T=T_{\text{peak}}$  because in that case, as  $\Delta S_M$  has a peak,  $ds(x)/dx=0$ . Therefore, the field dependences of the magnetic entropy change at the Curie transition and at the temperature of the peak of the  $\Delta S_M$  curve are exactly the same. In between those temperatures,  $n$  reaches its minimum value.

In conclusion, numerical calculations using the Arrott–Noakes equation of state have shown that for single phase materials, the generally assumed equality  $T_C = T_{\text{peak}}$  is not necessarily valid. It is correct for the mean field case, but not for the Heisenberg model, which implies  $T_{\text{peak}} > T_C$ . The distance between these two temperatures increases with field following a power law. In all cases,  $T_C$  corresponds to a singular point in the temperature dependence of the magnetic entropy change: either a minimum for the mean field model

or a point of minimum slope for the Heisenberg and mean field models. Scaling law arguments also show that the field dependence of the magnetic entropy change is exactly the same at these two temperatures: a power law with an exponent  $n=(1-\alpha)/\Delta$ . This does not exclude the fact that inhomogeneity of real samples is another reason for having different peak and Curie temperatures. More detailed experimental studies to discern the prevailing reason for this temperature difference in specific cases are currently under way.

This work was supported by the Spanish Ministry of Science and Innovation and EU FEDER (Projects Nos. MAT 2007-65227, ENE2007-6804-C03-02, and CIT-420000-2008-9), the PAI of the Regional Government of Andalucía (Projects Nos. P06-FQM-01823 and P06-FQM-01869), and by the German DFG (Project No. RI 932/4-1). J.M.R.-E. acknowledges a ‘‘Ramón y Cajal’’ Fellowship from the Spanish MEC.

<sup>1</sup>A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and Its Applications* (Institute of Physics Publishing, Bristol, 2003).

<sup>2</sup>V. K. Pecharsky and K. A. Gschneidner, Jr., *Phys. Rev. Lett.* **78**, 4494 (1997).

<sup>3</sup>V. Provenzano, A. J. Shapiro, and R. D. Shull, *Nature (London)* **429**, 853 (2004).

<sup>4</sup>A. M. Tishin, A. V. Derkach, Y. I. Spichkin, M. D. Kuz'min, A. S. Chernyshov, K. A. Gschneidner, Jr., and V. K. Pecharsky, *J. Magn. Magn. Mater.* **310**, 2800 (2007).

<sup>5</sup>V. Franco, J. S. Blázquez, and A. Conde, *Appl. Phys. Lett.* **89**, 222512 (2006).

<sup>6</sup>Q. Y. Dong, H. W. Zhang, J. R. Sun, B. G. Shen, and V. Franco, *J. Appl. Phys.* **103**, 116101 (2008).

<sup>7</sup>M. D. Kuz'min, M. Richter, and A. M. Tishin, *J. Magn. Magn. Mater.* **321**, L1 (2009).

<sup>8</sup>A. Y. Romanov and V. P. Silin, *Phys. Met. Metallogr.* **83**, 111 (1997).

<sup>9</sup>A. Arrott and J. E. Noakes, *Phys. Rev. Lett.* **19**, 786 (1967).

<sup>10</sup>M. Camprostrini, M. Hasenbusch, A. Pelissetto, P. Rossi, and E. Vicari, *Phys. Rev. B* **65**, 144520 (2002).

<sup>11</sup>V. Franco, A. Conde, and L. F. Kiss, *J. Appl. Phys.* **104**, 033903 (2008).

<sup>12</sup>V. Franco, A. Conde, J. M. Romero-Enrique, and J. S. Blázquez, *J. Phys.: Condens. Matter* **20**, 285207 (2008).

<sup>13</sup>S. N. Kaul, *J. Magn. Magn. Mater.* **53**, 5 (1985).