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Field dependence of the magnetocaloric effect in materials with a second order phase transition: A master curve for the magnetic entropy change

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The field dependence of the magnetic entropy change can be expressed as $\Delta S_M \propto H^n$. For soft magnetic amorphous alloys $n=1$ well below the Curie temperature (T_C), $n=2$ in the paramagnetic range, and $n \approx 0.75$ for $T=T_C$. The first value can be explained with simple arguments, $n=2$ is a consequence of the Curie-Weiss law, but $n(T_C)$ deviates from mean field predictions. From the Arrott-Noakes equation of state, a relation between $n(T_C)$ and the critical exponents has been obtained, showing remarkable agreement with experimental data (for an example alloy, predicted $n=0.72$ versus experimental $n=0.73$). A master curve behavior for the temperature dependence of ΔS_M measured for different maximum fields is proposed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2399361]

Magnetic refrigeration at temperatures close to room temperature, based on exploiting the magnetocaloric effect (MCE), is a field of intensive research.[1–3] Not only do these systems have an enhanced efficiency with respect to conventional gas compression-expansion refrigerators but they are also more environment friendly, as they do not require gases associated with greenhouse effect or ozone depletion. Current trends in material research related to this field go through the enhancement of materials performance[4,5] and cost reduction.[6] A compromise between the magnitude of the magnetic entropy change and the width of the peak is necessary for a working prototype, as discussed by Wood and Potter,[7] giving rise to the refrigerant capacity as a suitable metrics for comparing the performance of different materials. Recently, soft magnetic amorphous alloys[8–18] have been proposed as low cost candidates for high temperature magnetic refrigeration. Their MCE is associated with the second order magnetic phase transition which takes place at the Curie temperature T_C of the alloy. The possibility of tuning T_C with minor compositional changes, their extremely reduced magnetic hysteresis, and their enhanced electrical resistivity (which would reduce eddy current losses) are all beneficial characteristics for their application as magnetic refrigerants.

When comparing the published characteristics of different materials, one of the problems that arise is associated with the different experimental capabilities from one laboratory to another. In particular, when comparing the peak magnetic entropy change, $|\Delta S_M^{\mathrm{pk}}|$, experimental data are usually reported only for the maximum available magnetic field. A work around for comparing experimental values for different applied fields has been to quote the $|\Delta S_M^{\mathrm{pk}}|/H_{\mathrm{max}}$. However, little information is available regarding the field dependence of this magnitude and its relationship with the physical characteristics of the materials. Therefore, a detailed study of this subject will provide a means for a better comparison of experimental results, as well as it can give a deeper insight into the physics of the magnetocaloric effect at the transition temperature.

An initial attempt to explain the field dependence of $|\Delta S_M^{\mathrm{pk}}|$ for materials with a second order phase transition was made by Oesterreicher and Parker,[19] proposing that for a mean field case $|\Delta S_M^{\mathrm{pk}}| \propto H^n$, where $n=2/3$. To deduce this law they introduced the field dependence of magnetization at the Curie point inside an expression of ΔS_M obtained for temperatures well above T_C, where the Curie-Weiss law is valid. However, recent experimental results for soft magnetic amorphous alloys deviate from this value of n.[14,17] An alternative approach was made by Romanov and Silin,[20] analyzing the MCE in the case of inhomogeneous ferromagnets, but limiting their study to a mean field approach, as they based the analysis on the Landau theory of second order phase transitions. However, for some field and temperature regions, the obtained expressions are rather complex, making it difficult to fit to experimental data. For materials with a first order phase transition, scaling laws are also sought from an experimental approach[21] and by the application of Landau theory.[22,23] The aim of this letter is to describe the field dependence of MCE in materials with a second order phase transition, expressed as $\Delta S_M \propto H^n$, in the three characteristic regions of interest (i.e., temperatures well below, well above, and at T_C).

Recent experimental results on different families of soft magnetic (bulk) amorphous alloys show that the field dependence of ΔS_M has the following features in all cases:[12,14,17] for temperatures well below T_C, $n=1$; well above T_C, $n=2$; and at the temperature corresponding to $|\Delta S_M^{\mathrm{pk}}|$, T_{pk}, $n \approx 0.75$. As an example, Fig. 1 shows the temperature dependence of n of $Fe_{83}Zr_6B_{10}Cu_1$ amorphous alloy. Measurements were performed on disks with a diameter of ~3 mm and a thickness of ~20 μm. Further details about sample preparation and experimental methods of sample characterization are given elsewhere.[14]

The high temperature limit of the curve, $n=2$, is a well known consequence of the Curie-Weiss law.[1] As magnetization has a linear field dependence in this temperature region, the calculation of the magnetic entropy change from

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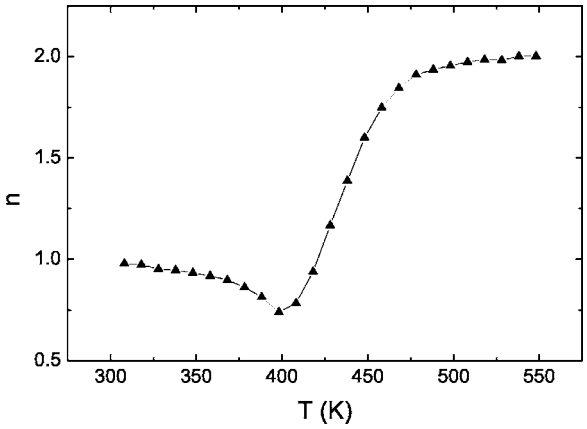

FIG. 1. Temperature dependence of the exponent characterizing the field dependence of ΔS_M for a $Fe_{83}Zr_6B_{10}Cu_1$ amorphous alloy.

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

has the consequence of a quadratic field dependence of ΔS_M.

The low temperature limit can also be explained with simple arguments: at temperatures well below the Curie temperature and moderate applied fields, magnetization does not show a strong field dependence. Experimental data in this temperature range show that magnetization is indeed not field independent, although this dependence is maintained for different temperatures in this low-temperature range. Assuming that the magnetization can be written as $M(H,T)=M_S(T)+\xi(H)$, where M_S is the spontaneous magnetization, the argument of the integral in Eq. (1) will be field independent if the function ξ is temperature independent (for the present experimental data, ξ seems to be linear in H and temperature independent). This has the consequence of $n=1$. Romanov and Silin[20] arrived to a linear field dependence of the magnetic entropy change in the low temperature region of inhomogeneous ferromagnets by directly imposing the field independence of magnetization, which is a much stronger condition, not fulfilled by our experimental data.

To predict the field dependence of ΔS_M at $T=T_C$ for materials which do not follow a mean field approach, let us consider that 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,[24] which can be written as

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

where β and γ are the critical exponents.

Differentiating Eq. (2) with respect to temperature, a closed expression for $\partial M/\partial T$ can be obtained for any temperature. For $T=T_C$, using the equilibrium value of magnetization at that temperature,

$$\left.\frac{\partial M}{\partial T}\right|_{T=T_C} = \frac{-a\beta\gamma}{b^{(\beta+\gamma\beta)/(\beta+\gamma)}(\beta+\gamma)} H^{(\beta-1)/(\beta+\gamma)}. \tag{3}$$

By introducing this expression into the defining Eq. (1), the magnetic entropy change at the Curie temperature can be obtained,

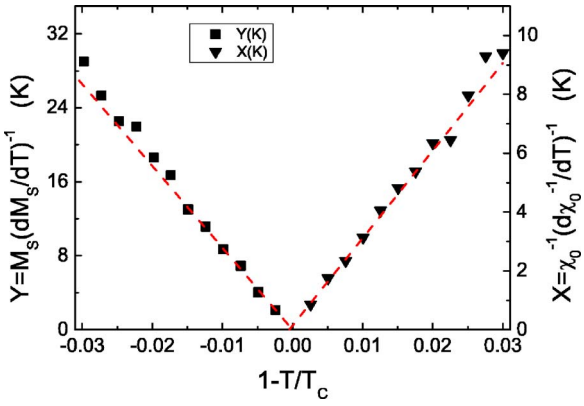

FIG. 2. Determination of the critical exponents and Curie temperature from the Kouvel-Fisher method.

$$\Delta S_M|_{T=T_C} = \frac{-a\beta\gamma}{b^{(\beta+\gamma\beta)/(\beta+\gamma)}(2\beta+\gamma-1)} H^{(\beta-1)/(\beta+\gamma)+1}. \tag{4}$$

Therefore, the present deduction predicts

$$n = 1 + \frac{\beta-1}{\beta+\gamma}, \tag{5}$$

which can be transformed using the relation $\beta\delta=\beta+\gamma$ to

$$n = 1 + \frac{1}{\delta}\left(1 - \frac{1}{\beta}\right). \tag{6}$$

In the case of a mean field model (i.e., $\beta=0.5$, $\gamma=1$, and $\delta=3$), $n=2/3$ is reobtained, as predicted by Oesterreicher and Parker with rather different arguments.

In order to check the validity of Eqs. (5) and (6), isothermal magnetization curves of an $Fe_{83}Zr_6B_{10}Cu_1$ amorphous alloy have been measured every 1 K for temperatures close to T_C, both above and below it. The Curie temperature and the exponents β and γ have been determined in the following way. The extrapolation of the high field portion of the $M^{2.5}$ vs $(H/M)^{0.75}$ curves (Arrott-Noakes plot) was used to obtain the spontaneous magnetization and initial susceptibility from the intercepts with the $(H/M)^{0.75}=0$ and $M^{2.5}=0$ axes, respectively. These values were subsequently processed following the Kouvel-Fisher method[25] (Fig. 2) to obtain the critical exponents and a consistent determination of T_C. The results are $T_C=400.6\pm0.5$, $\beta=0.45\pm0.01$, and $\gamma=1.35\pm0.07$. The values of the critical exponents are inside the range of those found for other amorphous alloys.[26] The use of Eq. (5) predicts $n=0.70\pm0.05$ for the studied alloy. The use of Eq. (6) goes through the calculation of the critical exponent δ, which can be determined independently by making the $\ln M$ vs $\ln H$ plot for the critical isotherm and fitting it to a straight line, giving $\delta=4.329\pm0.002$. In this way, Eq. (6) predicts $n=0.72\pm0.05$. These results can be compared with the minimum value of the temperature dependence of n obtained from the magnetic entropy change curves. When isothermal magnetization data in the vicinity of T_C are processed in 2 K intervals (smaller intervals provoke an increase in the noise due to the numerical derivatives of the curves), the minimum value of n is 0.73, in remarkable agreement with the previously predicted value using Eq. (6).

It has been established that ΔS_M has three distinct temperature regions regarding its field dependence, which is

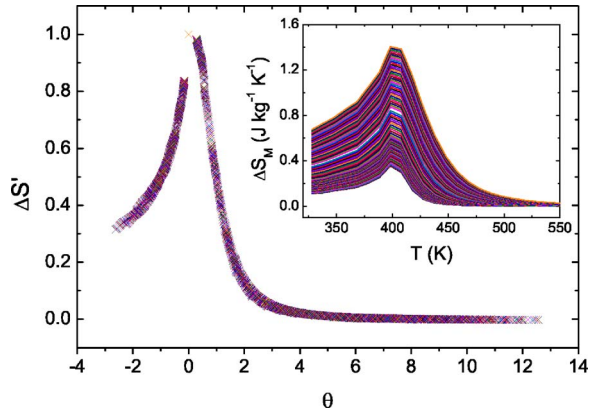

FIG. 3. Inset: temperature dependence of the magnetic entropy change curves of a $Fe_{83}Zr_6B_{10}Cu_1$ amorphous alloy for maximum applied fields ranging from 2.5 up to 15 kOe. Main figure: master curve behavior of all the data.

characterized by the exponent n. Its temperature dependence also changes when crossing T_C: an inverse quadratic dependence at high temperatures[1] and a behavior related to an effective β exponent at low temperatures. Therefore, it can be expected that the $\Delta S_M(T)$ curves measured with different maximum applied fields can collapse into a single master curve when properly rescaled. A phenomenological way of doing this would be to normalize all the $\Delta S_M(T)$ curves with their respective peak entropy change (which is field dependent, as previously shown), $\Delta S'(T,H_{\max}) = \Delta S_M(T,H_{\max})/\Delta S_M^{\mathrm{pk}}(H_{\max})$.

The temperature axis has to be rescaled in a different way below and above T_C, just by imposing that the position of two additional reference points in the curve correspond to $\theta = \pm 1$,

$$\theta = \begin{cases} -(T-T_C)/(T_{r1}-T_C), & T \leqslant T_C \\ (T-T_C)/(T_{r2}-T_C), & T > T_C, \end{cases} \tag{7}$$

where T_{r1} and T_{r2} are the temperatures of the two reference points that, for the present study, have been selected as those corresponding to $\frac{1}{2}\Delta S_M^{\mathrm{pk}}$. Figure 3 shows the untransformed $\Delta S_M(T)$ and transformed $\Delta S'(\theta)$ curves for applied fields from 0.25 up to 1.5 T (a total of 96 curves is plotted in each panel). This procedure can be used in the case that, provided that at least one of the curves can be fully characterized, the rest can only be explored in a limited field and/or temperature range (at least the three fixed points need to be measured: the peak and the two for a fixed rescaled height). In this way, properties of the incomplete curves such as the refrigerant capacity can be estimated by undoing the transformation. This can be particularly useful for studying families of similar materials, such as alloy series with minor compositional changes: in the cases that the critical exponent β, controlling the thermal dependence in the low temperature region, does not change much from one alloy to the other (that is the usual situation in some experimental cases[26]), the properties of some of the alloys can be inferred from the master curve (for example, when the compositional evolution of the Curie temperature pushes the curve of some of the samples out of the available experimental range).

In conclusion, the field dependence of the magnetic entropy change of materials with a second order phase transition has been explained. With the help of the Arrott-Noakes equation of state, an expression for the exponent controlling this field dependence at the Curie temperature has been proposed, $n = 1 + 1/\delta(1-(1/\beta))$, which is able to reproduce the experimental value obtained for a soft magnetic amorphous alloy. This allows one to find a master curve behavior of the thermal dependence of the magnetic entropy change measured for different maximum applied fields.

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