A constant magnetocaloric response in FeMoCuB amorphous alloys with different Fe/B ratios

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The magnetocaloric effect of $Fe_{91-x}Mo_8Cu_1B_x$ ($x=15,17,20$) amorphous alloys has been studied. The temperature of the peak of magnetic entropy change can be tuned by altering the Fe/B ratio in the alloy, without changing its magnitude, $|\Delta S_M^{pk}|$. The average contribution of the Fe atoms to $|\Delta S_M^{pk}|$ increases with increasing B content. This is correlated with the increase in the low temperature mean magnetic moment of Fe. A recently proposed master curve behavior for the magnetic entropy change is also followed by these alloys and is common for all of them. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2724804]

I. INTRODUCTION

The magnetocaloric effect (MCE), i.e., the temperature change of a magnetic material upon the application of a magnetic field, is a subject of current research interest[1–3] due to the promising application of magnetic refrigeration around room temperature, already materialized in some working prototypes.[4] In a scenario of increasing energy costs, there are two complementary research approaches trying to ease the situation: the search for alternative and less scarce energy resources, and the reduction of energy consumption by increasing the efficiency of the apparatus. MCE falls into the second line, as refrigeration based on MCE is energetically more efficient than that based on conventional gas compression-expansion refrigerators, and it is more environment friendly, as neither ozone-depleting nor global-warming volatile refrigerants are required.

There are two main present objectives in MCE research: the optimization of material properties and the reduction of material cost. In this respect, the peak entropy change ($|\Delta S_M^{pk}|$) has been maximized with the discovery of the so-called giant MCE[5,6] and giant inverse MCE,[7] while cost reduction is being investigated by using transition metal based alloys instead of rare-earth-based materials.[8] Recently, there is a growing interest in studying the applicability of soft magnetic amorphous alloys as magnetic refrigerants.[9–16] Albeit the maximum magnetic entropy change, $|\Delta S_M^{pk}|$, for these alloys is modest when compared to that of rare-earth-based materials, the remarkable difference in material costs is an incentive for studying their suitability as magnetic refrigerants. Besides their reduced magnetic hysteresis (virtually negligible), the high electrical resistivity (which would decrease eddy current losses), tunable Curie temperature, and, in the case of bulk amorphous alloys,[17–20] outstanding mechanical properties are beneficial characteristics for a successful application of the material.

The magnetocaloric response of soft magnetic amorphous alloys can be tuned by compositional changes in the different families of alloys. For example, the addition of Co in alloys with high metalloid content produces a decrease of the Curie temperature of the material, making it closer to room temperature, but at the expense of a reduction in both its $|\Delta S_M^{pk}|$ and its refrigerant capacity (RC).[18] A similar effect has been observed for Cr and/or Mo substitution in bulk amorphous alloys.[19] Therefore, the application of high-temperature magnetic refrigerants would require the search for alloying elements which would optimize the Curie temperature of the material without a detrimental effect on the MCE response. Moreover, composites with a constant entropy change between the hot and cold reservoirs have been considered among the optimum materials for active magnetic regenerative refrigerators.[21,22] Hence, materials with a constant value of $|\Delta S_M^{pk}|$ and different Curie temperatures could be a good starting point for the development of such composites. One of the objectives of this work is to show that the B substitution for Fe in nanoperm type alloys with low B content permits one to adjust the temperature at which MCE has a maximum response, keeping constant the peak entropy change of the alloys.

The field dependence of the magnetic entropy change, ΔS_M, in materials with a second order phase transition has also been recently studied, demonstrating that a master curve behavior is fulfilled for the ΔS_M curves measured up to different maximum fields.[23] The second objective of this work is to demonstrate that the $\Delta S_M(T)$ curves of different alloys from the same compositional series can also collapse in a master curve.

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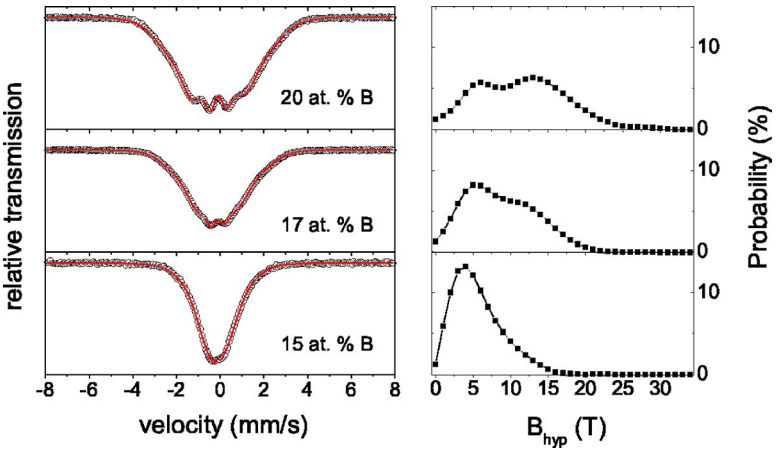

FIG. 1. (Color online) Mossbauer spectra and hyperfine field distributions for the studied alloys.

II. EXPERIMENT

Amorphous ribbons (~5 mm wide and 20–30 μm thick) of $Fe_{91-x}Mo_8Cu_1B_x$ ($x=15,17,20$) were obtained by melt spinning. The amorphous character of the as-quenched alloys was checked by x-ray diffraction (XRD) and Mössbauer spectroscopy (MS). MS spectra were recorded at room temperature in a transmission geometry using a ^{57}Co(Rh) source. The incident γ beam was perpendicular to the ribbon plane. The values of the hyperfine parameters were obtained by fitting with NORMOS program.[24] The low temperature (5 K) magnetic moment of the studied alloys was measured by superconducting quantum interference device (SQUID) magnetometry (Quantum Design MPMS-5S).

The field dependence of magnetization was measured by a Lakeshore 7407 vibrating sample magnetometer using a maximum applied field $H=15$ kOe with field steps of 50 Oe at constant temperatures in the range of 300–570 K with increments of 5 K. Prior to the measurements, the stress of the samples was relaxed by preannealing them at 625 K. The magnetic entropy change due to the application of a magnetic field H has been calculated from the numerical derivative of the $M(H,T)$ curves with respect to temperature, subsequently integrating it with respect to the field. The RC of the material has been calculated from the Wood and Potter definition,[25] $RC=\Delta S_M \Delta T$, where ΔS_M is the magnetic entropy change at the hot (T_h) and cold (T_c) ends of the cycle and $\Delta T=T_h-T_c$. The optimal refrigeration cycle is that maximizing RC.

III. RESULTS AND DISCUSSION

It has been recently shown that nanocrystallization of soft magnetic amorphous alloys does not enhance the magnetocaloric response of this kind of materials near room temperature.[13] Therefore, this study will be restricted to the alloys in their amorphous state. The nanocrystallization behavior of the studied alloys and its correlation with their soft magnetic properties will be reported elsewhere.[26] Mössbauer spectroscopy is a more sensitive technique than XRD to detect small amounts of quenched-in nanocrystals in nanoperm type alloys. In these alloys, the nanoparticle composition is close to pure Fe, and the outmost lines of the corresponding sextet would appear at velocities (~5.5 mm/s) clearly higher than those ascribed to the amorphous phase.

Figure 1 shows the room temperature Mossbauer spectra, fitted with a distribution of hyperfine magnetic fields, B_{hyp}, linearly correlated to that of isomer shift in all the studied cases. A broad distribution of hyperfine field contributions is characteristic of amorphous alloys, for which the local environment of Fe is not unique. As B content increases, the distribution extends to higher values of B_{hyp} and, consequently, the average over the distribution increases. For the 12 at. % B alloy, a single asymmetric maximum in the distribution is observed at ~5 T. It is worth mentioning that such low B_{hyp} contributions could be ascribed to paramagnetic sites, as the fitting procedure which has been used cannot distinguish between paramagnetic and low B_{hyp} sites. This feature can be ascribed to the lower Curie temperature of this alloy, as will be shown below. A bimodal character can be observed for the 17 and 20 at. % B alloys, as it is typically found for Fe–ET–B (ET=Zr,Nb, etc.).[27] The peak at lower fields could be ascribed to Fe in a Mo rich environment, while the peak at higher fields would correspond to Fe rich environments.

A. Compositional dependence of MCE

Figure 2 shows the temperature dependence of the magnetic entropy change of the studied alloys. Increasing B content, the temperature of the peak entropy change (T_{pk}) is displaced to higher temperatures. This evolution of (T_{pk}) is in agreement with the evolution of Curie temperature calculated

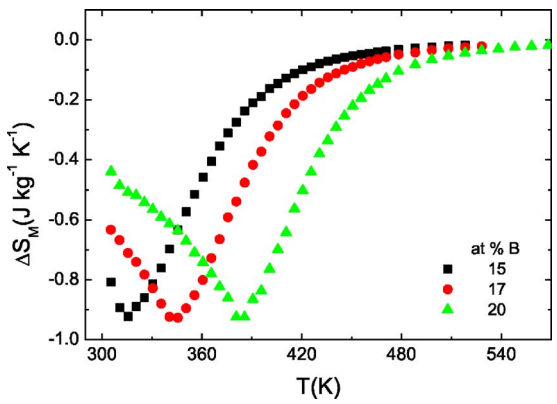

FIG. 2. (Color online) Temperature dependence of the magnetic entropy change for a maximum applied field of 15 kOe.

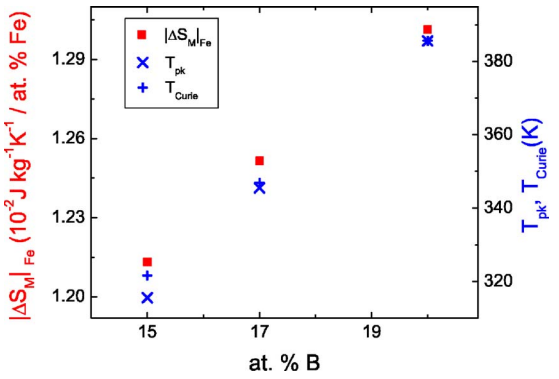

FIG. 3. (Color online) Compositional dependence of the average contribution of the Fe atoms to $|\Delta S_M^{pk}|$, temperature of the peak of magnetic entropy change, and Curie temperature of the alloys.

from the fit of the thermal dependence of the magnetization curve for $H=500$ Oe to a $(1-T/T_{Curie})^{\beta}$ law, leaving T_{Curie} and β as free parameters. The most remarkable feature of the Fig. 2 is that $|\Delta S_M^{pk}|$ remains constant, despite the shift in T_{pk}. Usually, compositional changes in an alloy series which produce a decrease in the Curie temperature are accompanied by a decrease in $|\Delta S_M^{pk}|$.[16] The observed constant value of $|\Delta S_M^{pk}|$ explained by an increasing average contribution of the Fe atoms to $|\Delta S_M^{pk}|$ (denoted as $|\Delta S_M|_{Fe}$ in Fig. 3) with increasing B content, which is balanced by the decreasing Fe content in the alloy as B content increases. A comparison between the compositional dependencies of T_{Curie} and T_{pk} is also shown in Fig. 3. The increasing value of the Curie temperature with increasing B content is usual for amorphous alloys with low B content.[28]

The increase in $|\Delta S_M|_{Fe}$ with increasing B content can be ascribed to the increase in the average magnetic moment per Fe atom with increasing B content in the alloy, which is also a general feature for Fe–ET–B (ET=Zr,Mo, etc.) alloys with low B content.[29] To check this correlation for the studied alloys, the average magnetic moment of Fe ($\langle\mu_{Fe}\rangle$) has been measured at 5 K by SQUID magnetometry, and the results are shown in Fig. 4. The compositional evolution of the low temperature magnetic moments has been also estimated from the Mossbauer results. Assuming a proportionality between $\langle B_{hyp}\rangle$ and the average Fe magnetic moment in the alloy, the low temperature average hyperfine field, $\langle B_{hyp}\rangle_0$, can be estimated by imposing the same thermal evolution as that of the spontaneous magnetization, $(1-T/T_{Curie})^{\beta}$, where T_{Curie} and β are those resulting from the previous fit of the magnetization data. Results for $\langle B_{hyp}\rangle_0$ are presented in Fig. 4, showing a reasonable correlation with the measured low temperature average magnetic moment of Fe.

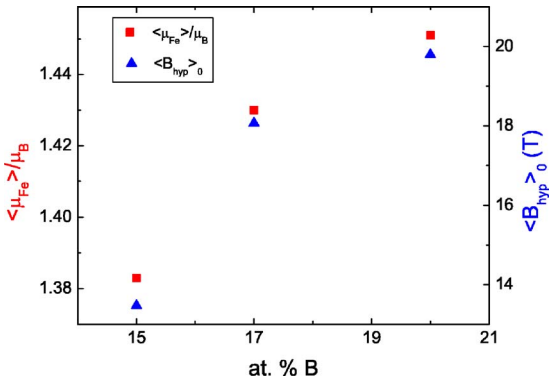

FIG. 4. (Color online) Compositional dependence of the low temperature average magnetic moment of iron and estimated low temperature hyperfine magnetic field.

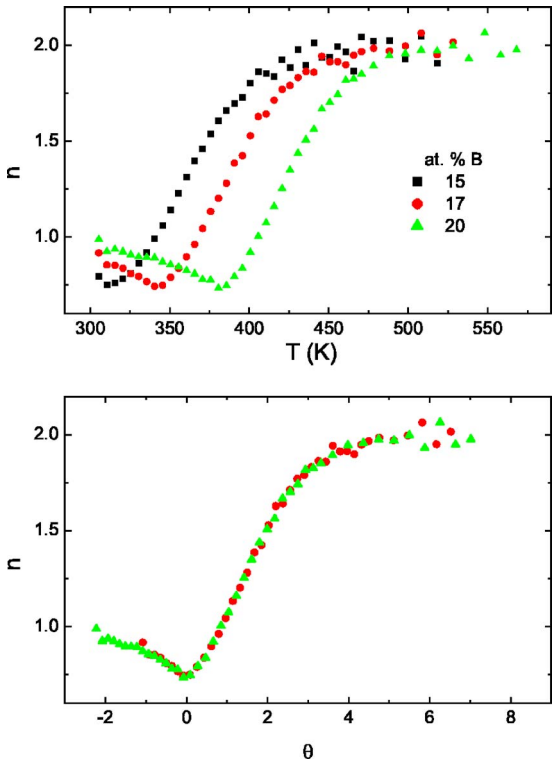

FIG. 5. (Color online) Upper panel: temperature dependence of the local exponent n for a maximum applied field of 15 kOe. Lower panel: dependence of n with the rescaled temperature θ.

The temperature dependence of the refrigerant capacity of these alloys indicates that the optimal refrigeration cycle is inside the experimentally available temperature range only for the higher B content alloy (due to its higher Curie temperature). In this case, for a maximum applied field of 15 kOe, RC=54 J/kg. Although this value is slightly smaller than that of a Mo-containing Finemet type alloy,[13] it has to be considered that the Curie temperature is decreased by ~85 K for the present case, making it closer to room temperature. Taking into account the practically linear field dependence of RC (regression coefficient $r=0.9992$), this value extrapolates to ~180 J/kg for a maximum applied field of 50 kOe, which has the same order of magnitude of that of $Gd_5Ge_{1.9}Si_2Fe_{0.1}$ (240 J/kg for $H=50$ kOe).[6]

B. Field dependence of MCE

The field dependence of $|\Delta S_M^{pk}|$ can be studied by assuming a $\Delta S_M \propto H^n$ law, where n depends on the magnetic state of the sample. Local values of n can be extracted from the experimental data[17] by using

$$n = \frac{d\ln|\Delta S_M|}{d\ln H}. \quad (1)$$

The upper panel of Fig. 5 shows the thermal dependence of n

for the different studied alloys. In agreement with previous experimental data,[15–19] the general behavior consists in (a) a value of n close to 1 for temperatures well below the transition temperature (b) a smooth decrease of n down to values close to 0.75 at T_{pk}, and (c) a subsequent increase to $n=2$ in the paramagnetic region. These values have been ascribed[23] to (a) the temperature independent magnetization for moderate magnetic fields at low temperatures, (b) a relationship between n and the two critical exponents controlling the field dependence of magnetization at the Curie temperature (δ) and the thermal dependence of magnetization (β), of the form $n=1+(1/\delta)(1-1/\beta)$, and (c) a consequence of the linear field dependence of magnetization where the Curie-Weiss law is valid, respectively.

C. Master curve behavior

It has been established that the field dependence of the magnetic entropy change is characterized by the previously described n values. Taking into account that the temperature dependence of ΔS_M also changes when crossing T_{Curie} (an inverse quadratic dependence at high temperatures[1] and a behavior related to an effective β exponent at low temperatures), it was demonstrated[23] 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 was to normalize all the $\Delta S_M(T)$ curves with their respective peak entropy change and to rescale the temperature axis as

$$\theta = \begin{cases} -(T-T_{Curie})/(T_{r1}-T_{Curie}), & T \leq T_{Curie} \\ (T-T_{Curie})/(T_{r2}-T_{Curie}), & T > T_{Curie}, \end{cases} \quad (2)$$

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 $0.7\Delta S_M^{pk}$. The election of the factor (0.7 in this case) used for selecting the reference points has to be made in such a way that the curves to be overlapped have experimental values above that reference entropy change for temperatures below and above T_{Curie}. It has to be noted that a factor close to 1 will enhance the effect of experimental noise in the resulting master curve.

As an example, Fig. 6 shows the magnetic entropy change of the $x=20$ alloy measured for maximum applied fields ranging from 2.5 up to 15 kOe (102 experimental curves), together with the overlapping of the curves after rescaling them with the above-mentioned procedure.

Taking into account that the critical exponents remain practically constant for alloys of the same compositional series, it is expected that this master curve for the field dependence of ΔS_M also holds for different alloys of the series. Following the same scaling procedure with the ΔS_M curves measured with a maximum applied field of 15 kOe, Fig. 7 evidences that this master curve can be also applied to the $x=17$ and $x=20$ alloys. The $x=15$ alloy, due to the small number of experimental points below T_{Curie}, was not included in this master curve to avoid the need of using reference temperatures too close to T_{Curie}. However, assuming that this alloy also follows the master curve, its temperature dependence can be extrapolated below room temperature by

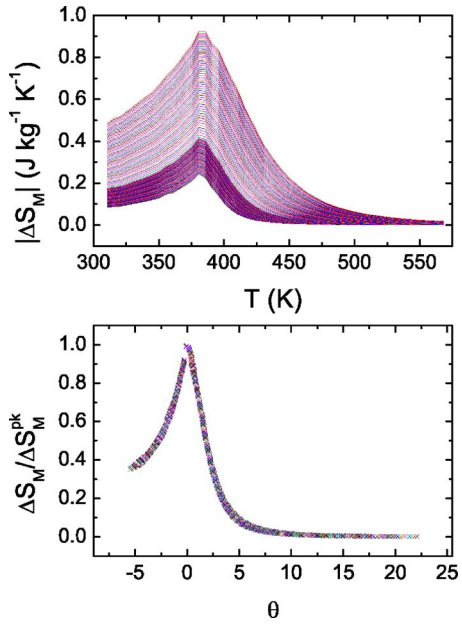

FIG. 6. (Color online) Upper panel: temperature dependence of the magnetic entropy change curves of the $x=20$ amorphous alloy for maximum applied fields ranging from 2.5 up to 15 kOe (102 curves). Lower panel: master curve behavior of all the data.

the following procedure: (1) calculating the $\Delta S_M/\Delta S_M^{pk}$ ratio for the first experimental point; (2) obtaining the corresponding θ value from the master curve; (3) calculating the reference temperature from Eq. (2) (T_{r1} in the present case); and

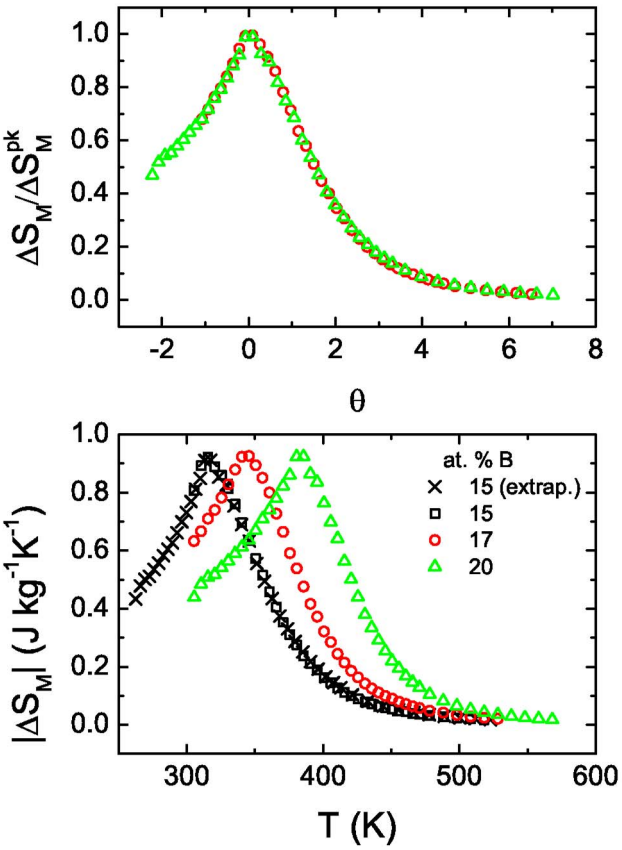

FIG. 7. (Color online) Upper panel: rescaled curves of the $x=17$ and $x=20$ alloys for a maximum applied field of 15 kOe. Lower panel: experimental magnetic entropy values of the studied alloys and low temperature extrapolation of the $x=15$ sample (crosses).

(4) performing the inverse transformation of the master curve with the adequate values of T_{Curie}, reference temperatures, and ΔS_M^{pk} for this alloy. Figure 7 shows the extrapolated data for the $x=15$ alloy together with the experimental values for all the studied alloys. It has to be noted that this extrapolation does not consist in a mere temperature shift of the ΔS_M.

A complementary confirmation of the accuracy of the master curve for different alloy compositions is presented in the lower panel of Fig. 5, where the n exponent values have been plotted as a function of θ, the rescaled temperature of the ΔS_M master curve. It is evidenced that the exponent controlling the field dependence of ΔS_M is the same for the $x=17$ and $x=20$ alloys ($x=15$ has not been included in the plot for the same reasons given in the case of the ΔS_M master curve), which supports the assumption of a common behavior for alloys of the same compositional series.

IV. CONCLUSIONS

It has been shown that controlling the Fe/B ratio in soft magnetic FeMoCuB amorphous alloys with low B content permits one to tune the temperature at which the maximum magnetocaloric effect takes place, without altering the magnitude of the magnetic entropy change. This constancy of the value of $|\Delta S_M^{\text{pk}}|$, which can be employed for designing composite materials with optimal performance, is ascribed to an increasing average contribution of the Fe atoms to $|\Delta S_M^{\text{pk}}|$ with increasing B content, related to the increasing average magnetic moment of iron in the alloy. The studied alloys follow a master curve for the magnetic entropy change measured up to different maximum applied fields, which is common for the alloys in the series. A procedure for making extrapolations of ΔS_M curves with the help of the master curve is also presented.

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