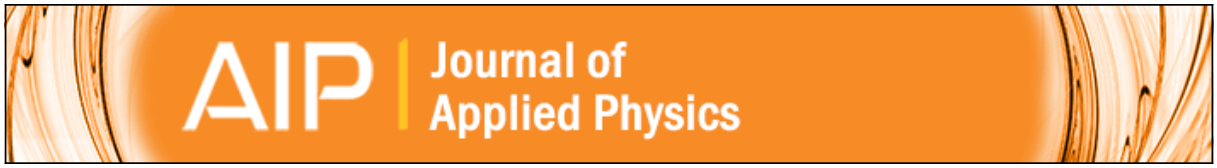

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The influence of Co addition on the magnetocaloric effect of Nanoperm-type amorphous alloys

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The effect of Co addition on the magnetocaloric effect of amorphous alloys with Nanoperm-type composition has been studied for temperatures above room temperature. Co addition produces an increase in the maximum magnetic entropy change and a shift of its associated temperature to higher temperatures. The maximum refrigerant capacity (RC) value obtained in this study is 82 J kg^{-1} for a maximum applied field $H=15$ kOe. This value is ~30% larger than that of a Mo-containing Finemet-type alloy measured under the same experimental conditions. However, the RC of the alloys, when calculated from temperatures corresponding to the half-maximum entropy change value, deteriorates with the presence of Co in the alloy. The field dependence of the magnetic entropy change has also been analyzed, showing a power dependence for all the magnetic regimes of the samples. This field dependence at the Curie temperature deviates from mean field predictions. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2337871]

INTRODUCTION

The magnetocaloric effect (MCE), reported by Warburg in 1881,[1] consists in the temperature change of a magnetic material upon the application of a magnetic field. When magnetized, the entropy of the spin subsystem is decreased and, under adiabatic conditions, the transfer of energy to the lattice provokes the heating of the material. Conversely, the adiabatic demagnetization of the material causes its cooling, an effect that has been employed for reaching temperatures below 1 K since 1933.[2]

MCE phenomenon is not new, and there were proposals for employing it at temperatures close to room temperature since 1976.[3] In 1998 a prototype was efficiently tested for room-temperature magnetic refrigeration.[4] This long delay in the application of the MCE at high temperatures was not due to conceptual difficulties, but to technological ones, the selection of adequate materials being among them.

To display a significant MCE response, a material needs to exhibit an appreciable temperature dependence of magnetization in the application temperature range. Therefore, for cooling at temperatures around 1 K, paramagnetic materials can be used as their magnetic response increases when approaching 0 K. However, their response is negligible at temperatures close to room temperature. In order to obtain materials with a noticeable temperature dependence of magnetization at higher temperatures, ferromagnetic materials can be used. When the Curie temperature of the material is approached, the ferromagnetic-paramagnetic transition causes a peak in the magnetic entropy change associated with the magnetization/demagnetization of the material. As the Curie temperature of Gd is close to room temperature (294 K) and its magnetic moment is large, this element was the material of choice for developing the initial room-temperature prototypes.[3,4] The efforts for finding materials which can be employed as high temperature magnetic refrigerants are not futile, because refrigeration based on MCE is energetically more efficient than that of conventional gas compression-expansion refrigerators and more environmental friendly as neither ozone-depleting nor global-warming volatile refrigerants are required. Therefore, currently there is an intensive research in this field,[5–7] with two main objectives: the maximization 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 so-called giant MCE (Ref. 8) and giant inverse MCE,[9] while cost reduction is being investigated by using transition metal based alloys instead of rare earth based materials.[10] In particular, there is a growing interest in studying the applicability of soft magnetic amorphous alloys as magnetic refrigerants[11–15] due to their reduced magnetic hysteresis (virtually negligible), enhanced electrical resistivity, and tunable Curie temperature. In the case of bulk amorphous alloys,[16,17] outstanding mechanical properties are also exhibited. All these characteristics are beneficial for a successful application of the material.

The aim of this work is to analyze MCE of soft magnetic amorphous alloys of the Nanoperm family, taking into consideration the influence of Co addition on the refrigerant capacity of the material, and to study the field dependence of the magnetic entropy change. As the magnetic moment and Curie temperature of Fe based amorphous alloys depend on Co addition, it could be expected that it will also have an influence on MCE.

EXPERIMENT

Amorphous ribbons (~5 mm wide and 20–30 μm thick) of $Fe_{83}Zr_6B_{10}Cu_1$ and $Fe_{78}Co_5Zr_6B_{10}Cu_1$ were obtained by melt spinning. The amorphous character of the as-quenched alloys was checked by x-ray diffraction. The field dependence of magnetization was measured in a Lakeshore 7407 vibrating sample magnetometer using a maxi-

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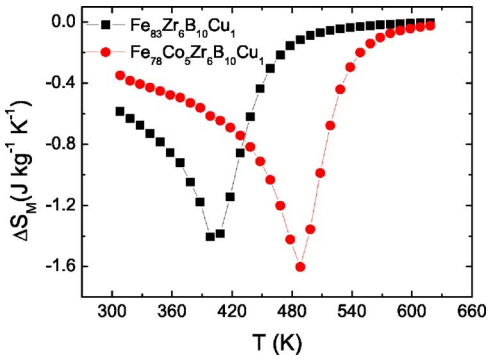

FIG. 1. (Color online) Temperature dependence of the magnetic entropy change for a maximum applied field of 15 kOe.

mum applied field $H=15$ kOe with field steps of 50 Oe, for constant temperatures in the range of 300–625 K with increments of 10 K. Prior to the measurements, the stress of the samples was relaxed by preannealing them at 700 K.

The MCE can be characterized by the magnetic entropy change due to the application of a magnetic field H, which can be evaluated from the processing of the temperature and field dependent magnetization curves using a numerical approximation to the equation

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

where the partial derivative is replaced by finite differences and the integration is performed numerically.

In order to compare the performance of different materials, either the peak entropy change $|\Delta S_M^{pk}|$ or the refrigerant capacity (RC) is used. The refrigeration at low temperatures requires a narrow temperature span of the refrigeration cycle, making $|\Delta S_M^{pk}|$ the parameter of choice for comparing low temperature materials, while high temperature refrigeration implies a wider temperature range and, consequently, RC is employed for comparison. According to Wood and Potter,[18] the RC of a reversible refrigeration cycle operating between T_h and T_c (the temperatures of the hot and cold reservoirs, respectively) is defined as $RC=\Delta S_M \Delta T$, where ΔS_M is the magnetic entropy change at the hot and cold ends of the cycle and $\Delta T=T_h-T_c$. Moreover, hysteresis losses can be taken into account when evaluating the refrigerant material by subtracting them from the computed RC,[19] making the comparison between materials with different coercivities more straightforward. The optimal refrigeration cycle is that which maximizes the RC.

RESULTS AND DISCUSSION

Temperature dependence of the magnetic entropy change

Figure 1 shows the temperature dependence of the magnetic entropy change corresponding to an applied field $H=15$ kOe for the two studied samples. Co addition produces an enhancement in the temperature at which the maximum entropy change takes place, in agreement with the influence of Co content on the Curie temperature of the amorphous phase (T_C^{am}) for these alloys.[20] It is worth mentioning that, in contrast to this behavior, amorphous alloys with larger metalloid concentration exhibit a monotonous decrease of T_C^{am} with increasing Co content.[21–23] In the case of the studied alloys, Co addition leads to an increase of the $|\Delta S_M^{pk}|$ value, unlike the observed behavior for the FeCoSiAlGaPCB alloy series, with larger metalloid content.[17] It has to be noted that an estimate of the error in $|\Delta S_M^{pk}|$ is below 3%, which is below the differences observed for both samples. The explanation of this influence of the metalloid content on T_C^{am} and $|\Delta S_M^{pk}|$ should be ascribed to the change in the local environment of Fe and Co atoms and its effect on the exchange interaction between atoms.[23] The $|\Delta S_M^{pk}|$ value of the Co-containing Nanoperm-type alloy is ~50% larger than that of a Mo-containing Finemet-type alloy, with a comparable T_C^{am}, measured under the same experimental conditions,[14] while the Co-free Nanoperm-type alloy increases the peak entropy change by ~31% with respect to the same Finemet-type alloy. Comparing with the $Fe_{70}B_5C_5Si_3Al_5Ga_2P_{10}$ amorphous alloy,[17] the Co-containing alloy presents a comparable value of $|\Delta S_M^{pk}|$, with the advantage of a peak temperature T_{pk}, which is 100 K closer to room temperature for the alloy studied in the present work.

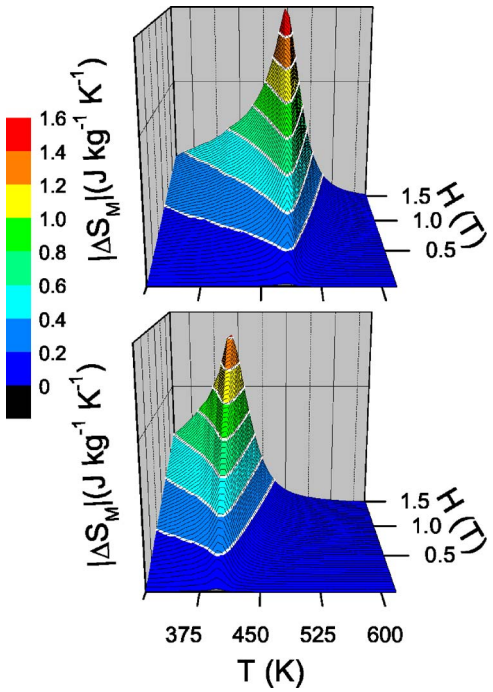

FIG. 2. (Color online) Field and temperature dependences of the magnetic entropy change for $Fe_{83}Zr_6B_{10}Cu_1$ (bottom) and $Fe_{78}Co_5Zr_6B_{10}Cu_1$ (top).

Field dependence of the magnetic entropy change

The magnetic entropy change not only depends on the measuring temperature but also on the value of the maximum applied field. Figure 2 shows the combined field and temperature dependence of $|\Delta S_M|$ for the two studied alloys. For all temperatures, the magnetic entropy change increases with increasing maximum applied field H. The field dependence can be expressed as

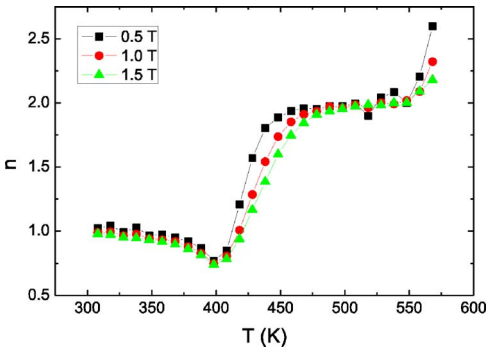

FIG. 3. (Color online) Temperature dependence of the local exponent determining the field dependence of the magnetic entropy change of the $Fe_{83}Zr_6B_{10}Cu_1$ alloy for three different maximum applied fields. The lines are a guide to the eyes.

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

where n depends on the magnetic state of the sample. For ferromagnets above their Curie temperature, the direct integration of the Curie-Weiss law indicates that $n=2$.[5] However, for temperatures below the Curie temperature no analytical expression is available. Moreover, the intrinsic irreversible behavior of ferromagnetic materials has to be taken into account in order to derive a thermodynamical model,[24] a consideration which is specially important for materials with non-negligible hysteresis (which is not the case in the present study). Nevertheless, on the basis of a mean field approach, the field dependence of the magnetic entropy change at the Curie temperature has been predicted to correspond to $n=2/3$.[25] In order to determine the field dependence of the experimental $|\Delta S_M|$ data for the different magnetic regions of the studied samples, a local exponent[16] can be calculated as

$$n = \frac{d \ln|\Delta S_M|}{d \ln H}. \tag{3}$$

Figure 3 shows the temperature dependence of the local exponents for the Co-free alloy for applied fields of 0.5, 1, and 1.5 T. Some general features of the curves, also fulfilled for the Co-containing alloy, are worth mentioning. In the ferromagnetic regime the local exponent is $n \approx 1$. At the Curie temperature of the amorphous alloy, a decrease in n is observed. However, it does not reach 2/3, as predicted by the mean field approach, but decreases only to ~0.74. Above T_C^{am} the local exponent increases up to $n \approx 2$, as predicted by the Curie-Weiss law. It should be recalled that this law is accurate for low fields and high temperatures, which explains the faster increase of n for smaller applied fields, as the high temperature condition is achieved at lower temperatures for smaller applied fields. The final increase in the exponent is ascribed to numerical errors, as the magnetic entropy change is negligible at these temperatures.

The field dependence of ΔS_M at T_{pk} for the Co-free alloy is also analyzed in Fig. 4 by representing ΔS_M^{pk} versus field and fitting the curve to a power law (equivalent results are obtained for the Co-containing alloy). The value obtained for the exponent (~0.76) is comparable to the minimum in Fig. 3. This value of the exponent, higher than the mean field predictions, could be due to local inhomogeneities in the amorphous alloy, causing a distribution of Curie temperatures, although the amorphous character of the alloy can also have an effect. On the other hand, discrepancies with mean field theories in the vicinity of a transition temperature can be expected.

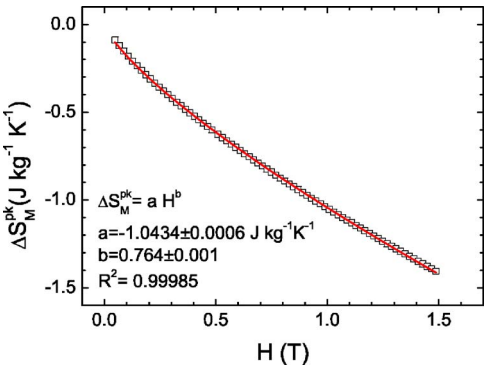

FIG. 4. (Color online) Field dependence of the peak entropy change for the $Fe_{83}Zr_6B_{10}Cu_1$ alloy. The line is the fitting to the data.

Refrigerant capacity

As previously mentioned, the comparison between different materials for high temperature magnetic refrigeration should be based on the refrigerant capacity. Figure 5 shows the refrigerant capacity of the studied alloys as a function of the temperature of the cold reservoir, T_c, ranging from room temperature up to T_{pk} of each alloy. As T_c separates from T_{pk}, the refrigerant capacity of the material increases. An optimal refrigeration cycle can be found for the Co-containing alloy in the experimental temperature range, as evidenced by a maximum in RC. The maximum RC values obtained in this study are 77 and 82 J/kg for the Co-free and Co-containing alloys, respectively, indicating a superior performance of the Co-containing alloy for refrigeration cycles with T_c above room temperature. However, the shape of the curve for the Co-free alloy suggests a maximum RC below room temperature for this alloy.

Instead of comparing the maximum obtained RC values, if we compare the RC values of refrigeration cycles with temperatures corresponding to half of $|\Delta S_M^{pk}|$ (i.e., the temperature span of the cycle corresponds to the width at half-

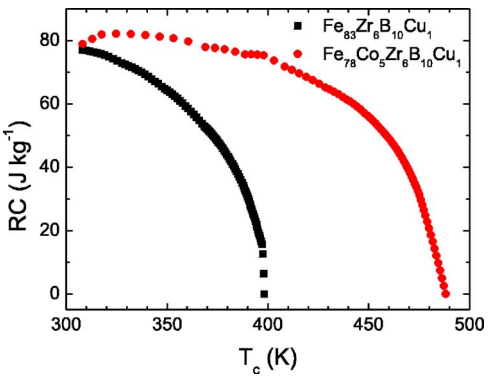

FIG. 5. (Color online) Dependence of the refrigerant capacity on the temperature of the cold end of the refrigeration cycle for the $Fe_{83}Zr_6B_{10}Cu_1$ and $Fe_{78}Co_5Zr_6B_{10}Cu_1$ alloys.

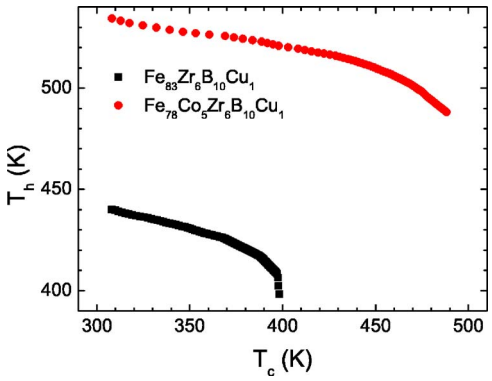

FIG. 6. (Color online) Temperature of the hot end of the refrigeration cycle which produces the maximum refrigerant capacity for a given temperature of the cold end.

maximum), the consideration of the Co-containing alloy as the one with a better performance no longer holds. In this case RC values are 71 and 63 J/kg for the Co-free and Co-containing alloys, respectively. This is in agreement with the previous suggestion of an optimal cycle for the Co-free alloy with a cold end below room temperature. These values are comparable to recent results on the magnetocaloric effect of Co–Cr containing Nanoperm-type alloys.[15]

Figure 6 presents the relationship between T_h and T_c for cycles which produce the maximum RC for a given T_c. For the Co-containing alloy, the optimal refrigeration cycle corresponds to $T_h \approx 531$ K and $T_c \approx 325$ K, while for the Co-free alloy the maximum obtained RC corresponds to $T_h \approx 440$ K and $T_c \approx 308$ K.

The maximum RC value measured in this work favorably compares to the previously mentioned Finemet-type and $Fe_{70}B_5C_5Si_3Al_5Ga_2P_{10}$ amorphous alloys, being ~30% larger in the present case.

CONCLUSIONS

The effect of Co addition on the magnetocaloric effect of $Fe_{83}Zr_6B_{10}Cu_1$ and $Fe_{78}Co_5Zr_6B_{10}Cu_1$ amorphous alloys has been studied. The temperature at which the maximum magnetic entropy change takes place is shifted to higher temperatures with Co addition, simultaneously increasing the value of this peak entropy change. However, the refrigerant capacity of the alloys, when calculated from the half-maximum temperatures, deteriorates with the presence of Co in the alloy. These alloys favorably compare to other amorphous materials considered as candidates for high temperature magnetic refrigeration, such as Finemet-type and FeCoSiAlGaPCB alloys. The refrigerant capacity is increased by ~30% for the present case.

The field dependence of the magnetic entropy change has also been analyzed, showing a power dependence for all the magnetic regimes of the samples. In the ferromagnetic range the exponent is 1. In the paramagnetic regime, well above the Curie temperature, the power is 2, in agreement with the Curie-Weiss law. However, the field dependence at the Curie temperature deviates from mean field predictions.

ACKNOWLEDGMENTS

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