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Enhanced magnetocaloric response in Cr/Mo containing Nanoperm-type amorphous alloys

V. Franco, C. F. Conde, and A. Conde[a)]
Departamento Física de la Materia Condensada, ICMSE-CSIC, Universidad de Sevilla, P.O. Box 1065, 41080 Sevilla, Spain

L. F. Kiss
Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, 1525 Budapest, Hungary

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The magnetocaloric effect of $Fe_{76}Cr_{8-x}Mo_xCu_1B_{15}$ $(x=0,4)$ alloys is studied. Although the combined addition of Cr and Mo is more efficient in tuning the Curie temperature of the alloy, the Mo-free alloy presents a higher magnetocaloric response. The refrigerant capacity (RC) for the Mo-containing alloy is comparable to that of $Gd_5Ge_{1.9}Si_2Fe_{0.1}$ (for a field of 50 kOe, RC $=273$ J kg^{-1} for the Mo alloy vs 240 J kg^{-1} for the Gd-based one), with a larger temperature span of the optimal refrigeration cycle (250 K vs 90 K, respectively). The restriction of the temperature span to 90 K gives RC$=187$ J kg^{-1} for the Mo alloy. A master curve behavior for the magnetic entropy change is also evidenced. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2437659]

Room temperature magnetic refrigeration is presently gaining an increasing interest due to the discovery of materials with remarkable magnetocaloric response for temperatures close to 300 K.[1–3] Among the advantages of the refrigerators based on the magnetocaloric effect (MCE) with respect to the systems based on the compression-expansion of gases are that they are more environment friendly and that their energetic efficiency is increased. The scenario of increasing energy costs makes the search for more efficient apparatuses inevitable, being complementary to the investigation of alternative and less scarce energy resources.

Current research in magnetocaloric materials has two main goals: the increase of material performance and the reduction in material cost. The peak entropy change $(|\Delta S_M^{pk}|)$ has been maximized with the discovery of the so-called giant MCE (Ref. 4) and giant inverse MCE.[5] Meanwhile, cost reduction is being investigated by using transition metal based alloys instead of rare earth based materials.[6] The characterization of magnetocaloric materials is based on two main parameters: the peak magnetic entropy change $|\Delta S_M^{pk}|$ and the refrigerant capacity (RC). A compromise between $|\Delta S_M^{pk}|$ and the width of the peak is necessary for a working prototype, as discussed by Wood and Potter.[7] RC is measured in the literature by different methods and, regardless of the specific definition used for calculating it, RC gives a measure of this aforementioned compromise, making it a suitable metric for comparing the performance of different materials. Moreover, hysteresis losses can be taken into account when evaluating the refrigerant material by subtracting them from the computed RC,[8] making the comparison between materials with different coercivities more straightforward.

Besides the peak entropy change, RC, and material cost, there are other factors that should be taken into account for a material to be efficiently applied,[3] such as mechanical properties, corrosion resistance, electrical resistivity, etc. In particular, there is a growing interest in studying the applicability of soft magnetic amorphous alloys as magnetic refrigerants[9–20] due to their reduced magnetic hysteresis (virtually negligible), higher electrical resistivity (which would decrease eddy current losses), and tunable Curie temperature T_{Curie}. Among the different compositional series of soft magnetic amorphous alloys, Nanoperm-type alloys are those that currently exhibit the highest RC values, having also among the highest values of $|\Delta S_M^{pk}|$.[21] Corrosion resistance of the alloys can be enhanced by Cr alloying,[22,23] facilitating their applicability. Simultaneously, T_{Curie} can be tuned by Cr and/or Mo alloying. Although both alloying elements produce a similar reduction in the Curie temperature of the amorphous alloy, displacing it to temperatures closer to room temperature,[24–26] it has been recently shown that the combined addition of Cr and Mo to a Nanoperm alloy has an increased efficiency in reducing T_{Curie} with respect to the Mo-free alloy.[27] Therefore, the purpose of this letter is to analyze the influence of Cr and Cr/Mo addition on the magnetocaloric effect of a Nanoperm-type amorphous alloy. It will be shown that both RC and $|\Delta S_M^{pk}|$ are reduced for the Mo-containing alloy, although the RC values presented in this letter are higher than those of other Nanoperm-type amorphous alloys, making the studied samples promising candidates for magnetic refrigerants. It will be also evidenced that the $\Delta S_M(T)$ curves for the studied alloys follow a master curve behavior, as recently proposed.[28]

Amorphous ribbons of nominal composition $Fe_{76}Cr_8Cu_1B_{15}$ and $Fe_{76}Cr_4Mo_4Cu_1B_{15}$ were prepared by single roller melt spinning. Their amorphous character was checked by x-ray diffraction. Prior to the measurements, samples were stress relaxed by heating them at 10 K/min up to 525 K in an Ar atmosphere. The field dependence of magnetization was measured by a Lakeshore 7407 vibrating sample magnetometer (VSM) using a maximum applied field $H=15$ kOe, for constant temperatures in the range of 300–520 K and by a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer using a maximum applied field $H=50$ kOe, for constant temperatures in the range of 50–400 K. The use of both magnetometers is necessary to be able to cover the complete mag-

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[a)]Electronic mail: conde@us.es

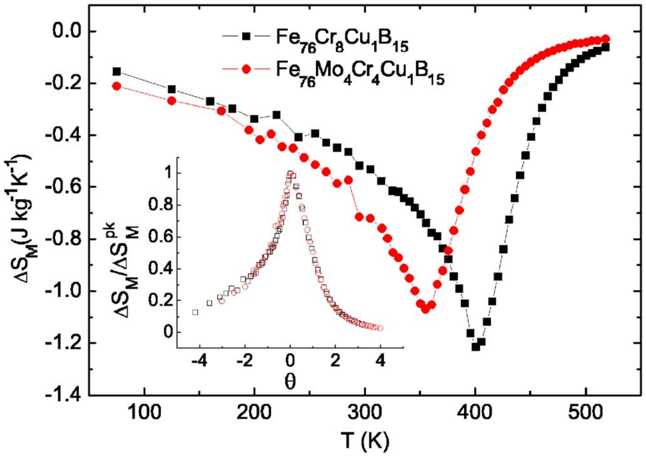

FIG. 1. (Color online) Temperature dependence of the magnetic entropy change of the studied alloys for a maximum applied field of 15 kOe. Inset: master curve behavior of the curves [for a definition of the rescaled temperature axis, see Eq. (3)].

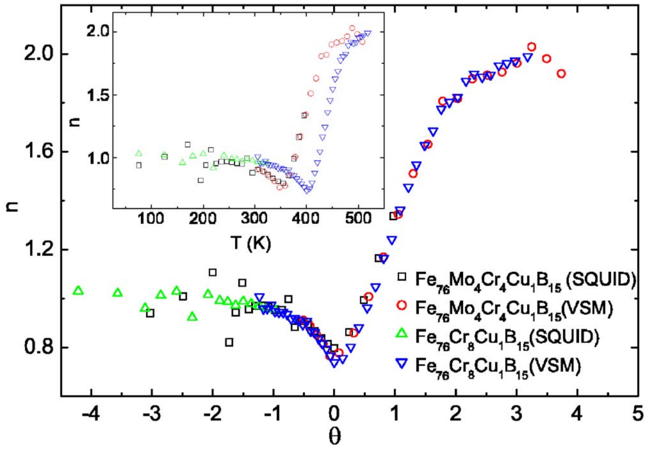

FIG. 2. (Color online) Inset: temperature dependence of the exponent characterizing the field dependence of ΔS_M for the studied alloys. Main panel: master curve behavior of n. Exponent values obtained from the VSM and SQUID measurements are presented separately.

netic entropy change curve for materials with peak temperatures close to room temperature.

The magnetic entropy change due to the application of a magnetic field H has been calculated from the numerical approximation to the equation

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

where the partial derivative is replaced by finite differences and the integration is performed numerically. The refrigerant capacity has been calculated using the Wood and Potter definition [$\mathrm{RC}=\Delta S_M(T_h-T_c)$], where T_h and T_c are the temperatures of the hot and cold reservoirs, respectively, and ΔS_M is the magnetic entropy change at the hot and cold ends of the cycle.[7]

Figure 1 shows the temperature dependence of the magnetic entropy change for both studied alloys for a maximum applied field of 15 kOe. While both curves present the same qualitative behavior, two main differences should be mentioned: Cr substitution by Mo produces a displacement of the peak temperature of the magnetic entropy change towards room temperature, due to the reduction in the Curie temperature of the alloy, and a simultaneous reduction in $|\Delta S_M^{\mathrm{pk}}|$.

The magnetic entropy change not only depends on the measuring temperature but also on the value of the maximum applied field. The field dependence can be expressed as

$$\Delta S_M \propto H^n, \qquad (2)$$

where n depends on the magnetic state of the sample. It has been shown that three characteristic exponent values can be found for materials with a second order phase transition: $n \approx 1$ for temperatures well below the Curie temperature of the alloy, $n=2$ for temperatures where the Curie-Weiss law is applicable, and $n=1+(1/\delta)(1-(1/\beta))$ for the Curie temperature, where β and δ are the critical exponents.[28] The inset of Fig. 2 shows the temperature dependence of n, evidencing the previously mentioned regimes. In the figure, the experimental points corresponding to the SQUID and VSM measurements are plotted separately evidencing the overlapping of the data obtained from both equipments.

Having established that ΔS_M has three distinct temperature regions regarding its field dependence, characterized by the exponent n, and taking into account that its temperature dependence also changes when crossing the Curie temperature (an inverse quadratic dependence at high temperatures[1] and a behavior related to an effective β exponent at low temperatures), it was demonstrated that the ΔS_M curves measured with different maximum applied fields collapse into a single master curve when properly rescaled.[28] This phenomenological master curve is obtained by plotting the normalized $\Delta S_M(T)$ curves versus a temperature axis rescaled in a different way below and above T_{Curie} by imposing that the position of two additional reference points in the curve correspond to $\theta = \pm 1$:

$$\theta = \begin{cases} -(T-T_{\mathrm{Curie}})/(T_{r1}-T_{\mathrm{Curie}}), & T \leqslant T_{\mathrm{Curie}} \\ (T-T_{\mathrm{Curie}})/(T_{r2}-T_{\mathrm{Curie}}), & T > T_{\mathrm{Curie}} \end{cases}, \qquad (3)$$

where T_{r1} and T_{r2} are the temperatures of the two reference points which, for the present study, have been selected as those corresponding to $(1/2)\Delta S_M^{\mathrm{pk}}$. It was also proposed that the ΔS_M curves of alloys from families of similar materials, such as alloy series with minor compositional changes, should collapse into the same master curve. The inset of Fig. 1 shows the master curve behavior of the magnetic entropy change curves of the studied alloys, confirming the predictions of a master curve behavior for different alloy compositions of the same series. Once the rescaled temperature axis θ has been calculated in the previously mentioned way, it can also be used to rescale the temperature dependence of the exponent n, as shown in the main panel of Fig. 2. This overlapping of the n curves also reveals that the field and temperature dependences of the magnetic entropy change are common features for both alloys.

The measured values of $|\Delta S_M^{\mathrm{pk}}|$ for a maximum applied field of 15 kOe are 1.07 and 1.21 J kg^{-1} K^{-1} for the Mo-containing and Mo-free alloys, respectively. The value for the Mo-containing alloy could be measured up to 50 kOe in the SQUID magnetometer, giving an experimental value of 2.73 J kg^{-1} K^{-1}. The extrapolation of the VSM measurements (with a maximum applied field of 15 kOe) up to 50 kOe using the minimum n value of the main panel of Fig. 2 gives 2.61 J kg^{-1} K^{-1}, within 4% of the measured value. The extrapolated value up to 50 kOe for the Mo-free alloy is 2.95 J kg^{-1} K^{-1}.

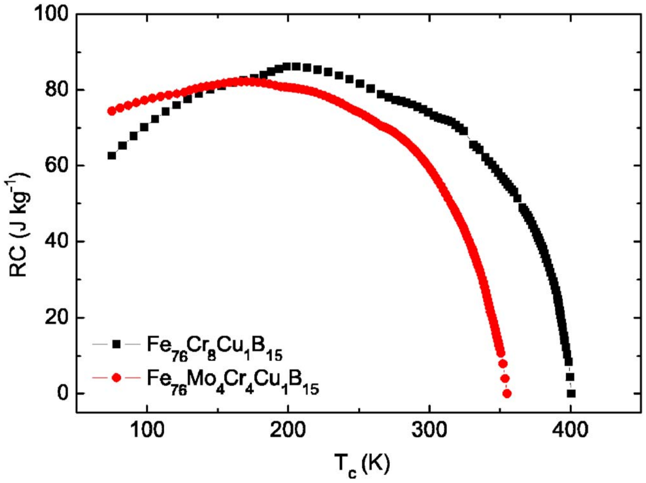

FIG. 3. (Color online) Dependence of the refrigerant capacity on the temperature of the cold end of the refrigeration cycle for the studied alloys for a maximum applied field of 15 kOe.

Figure 3 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 temperatures below that of $|\Delta S_M^{\mathrm{pk}}|$, T_{pk}, of each alloy, i.e., below their Curie temperature (according to the above given definition of RC, for $T_c = T_{\mathrm{pk}}$ the refrigerant capacity is zero). The corresponding T_h is selected by imposing $\Delta S_M(T_h) = \Delta S_M(T_c)$. As T_c separates from T_{pk}, the refrigerant capacity of the material increases. An optimal refrigeration cycle can be found for all the alloys in the experimental temperature range, as evidenced by a maximum in RC. For a maximum applied field of 15 kOe, the refrigerant capacities are 82 and 86 J kg^{-1} for the Mo-containing and Mo-free alloys, respectively. Taking into account the linear field dependence of RC, these values extrapolate to 273 and 287 J kg^{-1}, respectively, for a maximum field of 50 kOe, comparable to that found for $Gd_5Ge_{1.9}Si_2Fe_{0.1}$ (240 J kg^{-1} for $H = 50$ kOe). The temperature span for the present alloys $\Delta T = T_h - T_c \approx 250$ K is much larger than that of $Gd_5Ge_{1.9}Si_2Fe_{0.1}$ ($\Delta T \approx 90$ K), but restricting the temperature span to 90 K, the Mo-containing alloy exhibits a measured RC=187 J kg^{-1} for 50 kOe, still comparable to that of the Gd based material. Taking into account the 15 times reduction in cost of the soft magnetic amorphous alloy, these alloys stand as promising candidates for magnetic refrigerants.

In conclusion, it has been shown that the magnetic entropy change of $Fe_{76}Cr_8Cu_1B_{15}$ and $Fe_{76}Cr_4Mo_4Cu_1B_{15}$ amorphous alloys overlaps in the same master curve behavior. Combined Cr and Mo addition is more efficient in tuning the Curie temperature of the material but is deleterious for the magnetocaloric response. Refrigerant capacities of these alloys are comparable to that of $Gd_5Ge_{1.9}Si_2Fe_{0.1}$, even for a constrained temperature span. Therefore, the strong reduction in the price of the alloy, while keeping a comparable RC, is an incentive for studying the applicability of these Nanoperm-type alloys as room temperature magnetic refrigerants.

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