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Influence of Mn on the magnetocaloric effect of nanoperm-type alloys

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In this paper, the influence of the Mn content on the magnetocaloric response of ribbon-shaped amorphous samples of $Fe_{80-x}Mn_xB_{20}$ (x=10, 15, 18, 20, and 24), has been studied. For this purpose, the temperature and field dependence of the magnetic entropy change (ΔS_M) have been obtained from magnetization curves. The partial substitution of Fe by Mn leads to a monotonous change in the Curie temperature (T_C) of the alloys from 438 K for x=10 to 162 K for x=24, in agreement with the coherent-potential approximation. These Curie temperatures could make them good candidates to be used for magnetic refrigeration at room temperature. For an applied field of 1.5 T, the maximum entropy change (ΔS_M^{pk}) passes from 1 J K^{-1} kg^{-1} (x=10) to 0.5 J K^{-1} kg^{-1} (x=24), and the refrigerant capacity varies between 117 J kg^{-1} (x=10) and 68 J kg^{-1} (x=24). A linear relationship between ΔS_M^{pk} and the average magnetic moment per transition metal atom ($\langle\mu\rangle_{Fe,Mn}$) has been presented. © *2010 American Institute of Physics*. [doi:10.1063/1.3489990]

I. INTRODUCTION

Magnetic refrigeration based on the magnetocaloric effect (MCE) is currently gaining an increasing interest due to the discovery of materials with remarkable magnetocaloric response close to room temperature. Among others, its main advantages with respect to the systems based on the compression-expansion gas cycle are an improvement in the energetic efficiency and the avoidance of ozone depleting and green-house effect gases.[1] The MCE describes the reversible temperature change ΔT_{ad} due to the application of an external magnetic field change ΔH under adiabatic conditions. Assumed an isobaric process at pressure P, as is usual in conventional magnetic refrigeration applications for solid state magnetic materials, the thermodynamic coefficient that controls the variation in the temperature T in the MCE is $(\partial T/\partial H)_{S,P}$, where S is the total entropy of the magnetic solids defined as the sum of the magnetic S_M, lattice S_L, and electronic S_E entropies.[2] Taking into account that S remains constant in closed systems in an adiabatic process, when the entropy associated to magnetic degrees of freedom decreases (increases) the contribution to the entropy associated to non magnetic degrees of freedom increases (decreases). In other words, the magnetic system experiments the aforementioned adiabatic temperature change ΔT_{ad} when the magnetic field changes ΔH in order to keep constant the total entropy S. Since the entropy is a state function, and considering the magnetic systems in which the S_L and S_E are field independent,[2] the magnetic entropy change ΔS_M experimented in the MCE can be calculated in an isothermal process as follows:

$$\Delta S_M(T,\Delta H) = \int_{H_o}^{H_f} \left[\frac{\partial \mu_0 M(T,H)}{\partial T}\right]_H dH, \tag{1}$$

where $\Delta H = H_f - H_o$ is the experimented magnetic field change, μ_0 is the magnetic permeability of vacuum, and $M(T,H)$ is the magnetization of the magnetic material.

The MCE characterization can be carried out through direct[3] measurements of ΔT_{ad}, or indirectly[4] by numerical approximation of Eq. (1) after measuring the temperature and field dependence of the magnetization. In this paper, only the latest method has been used to calculate ΔS_M. Taking into account that the heat transferred between the hot (at temperature $T=T_{hot}$) and cold (at temperature $T=T_{cold}$) reservoirs in the implemented thermodynamic cycle is an intrinsic property of the MCE, this magnitude can be used to characterize it, instead of the adiabatic temperature change ΔT_{ad}. The refrigerant capacity RC, defined as the heat transferred mentioned above, can be calculated from ΔS_M as follows:

$$\mathrm{RC}(\Delta H) = \int_{T_{cold}}^{T_{hot}} \Delta S_M(T,\Delta H)dT. \tag{2}$$

From this expression, the hysteresis losses have to be subtracted.[5] However, for the studied alloys these losses are negligible.

In accordance with that, the characterization of the magnetocaloric materials in which S_L and S_E are field independent is based on two parameters that can predict the goodness of a magnetic material to be used as magnetic refrigerant: the peak of the magnetic entropy change ΔS_M^{pk}, and the refrigerant capacity RC.

The study of amorphous materials to be used in magnetic refrigeration has been motivated by finding a compromise between the aforementioned parameters: a modest ΔS_M^{pk} with a high RC. These quantities together with their reduced magnetic and thermal hysteresis, high electrical resistivity,

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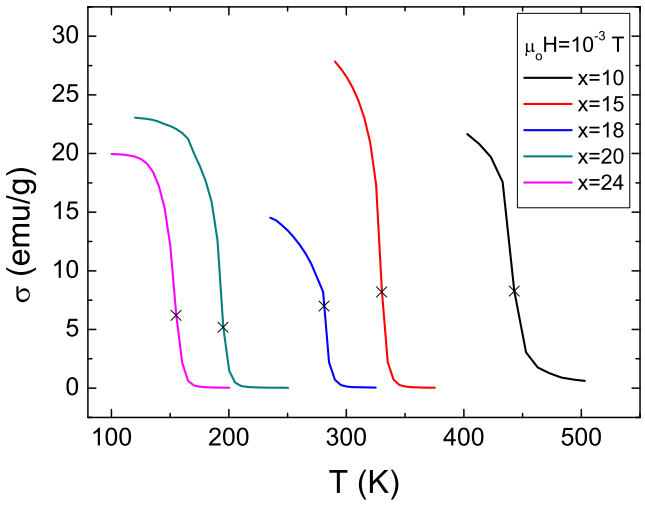

FIG. 1. (Color online) Temperature dependence of the magnetization σ of the studied amorphous quasibinary $Fe_{80-x}Mn_xB_{20}$ (x=10, 15, 18, 20, and 24) alloy series when a magnetic field of 10^{-3} T is applied. Crosses mark the Curie temperatures of the samples.

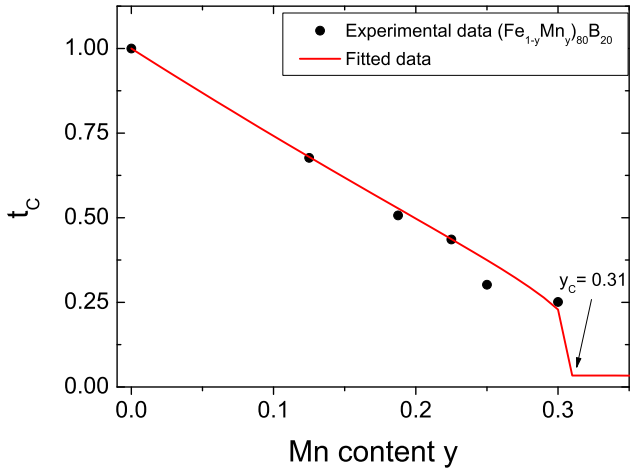

FIG. 2. (Color online) Mn concentration dependence of the reduced Curie temperature t_C of the amorphous quasibinary $(Fe_{1-y}Mn_y)_{80}B_{20}$ (y=0, 0.125, 0.1875, 0.225, 0.25, and 0.3) alloy series. Solid line indicates the t_C given by the CPA when $j_{Fe-Fe}=1$, $j_{Mn-Mn}=-0.25$, and $j_{Fe-Mn}=-0.1$. The critical Mn concentration of the studied alloys has been marked, being $x_C=80y_C \approx 25$ at. % Mn content.

good mechanical properties, and corrosion resistance, make these materials good candidates as magnetic refrigerators.[6]

Taking into account that a larger number of intermetallic Mn-based compounds present a great MCE response,[7,8] the aim of this work is to study the influence of the Mn content on the magnetocaloric behavior of the amorphous quasibinary ferromagnetic $Fe_{80-x}Mn_xB_{20}$ alloy series.

II. EXPERIMENTAL

Amorphous ribbons of $Fe_{80-x}Mn_xB_{20}$ (1 mm wide and ~12 μm thick) and compositional range x=10, 15, 18, 20, and 24, were obtained by a melt-spinning technique. The field and temperature dependence of magnetization $M(T,H)$ of 3 mm long ribbon samples have been measured (up to $\mu_0 H=5$ T and from 5 to 573 K) in a superconducting quantum interference device and in a vibrating sample magnetometer, restricted in this case to $\mu_0 H \leq 1.5$ T and $T \geq 303$ K. Measurements of the ac susceptibility $\chi(T)$ in ac magnetic field of amplitude 10 mOe at frequency of 7 kHz have been obtained by a conventional induction technique. Microstructural analysis of the samples was performed by transmission electron microscopy (TEM) in a Philips CM200 operated at 200 kV.

III. RESULTS AND DISCUSSION

The amorphous character of the whole studied $Fe_{80-x}Mn_xB_{20}$ (x=10, 15, 18, 20, and 24) alloy series was checked by TEM. The temperature dependence of the magnetization σ (at $\mu_0 H=10^{-3}$ T) of these alloys is presented in Fig. 1, indicating that whole studied compositional range seems to be ferromagnetic at low T. The values of the Curie temperatures (T_C) have been obtained from the inflection point of the experimental magnetization data (x=10, 15, 18, 20, and 24) at low field (marked with crosses in Fig. 1), and also from the experimental ac susceptibility $\chi(T)$ data (x=18, 20, and 24) in ac magnetic field, obtaining a good agreement between both techniques.

Figure 2 shows the dependence of the experimental values of the Curie temperatures on the Mn content. Using the coherent-potential approximation (CPA), the dependence of the T_C of an amorphous quasibinary ferromagnetic alloy $(A_{1-y}B_y)_{100-z}C_z$ (y=x/80, z=20 for the studied samples) on the variable concentration y (at a given value of the concentration z), is given as a solution of the cubic equation[9]

$$\alpha^2 t_C^3 + [\alpha s - \alpha(1+\alpha)\langle j\rangle]t_C^2 + \left[(1+\alpha)p\langle j^{-1}\rangle - \alpha\left(\frac{p}{j_{Fe-Mn}} + \frac{p}{j_{Mn-Mn}} + \frac{p}{j_{Fe-Fe}}\right)\right]t_C - p = 0, \quad (3)$$

where t_C is the reduced T_C of the system to the one in the pure binary compound $Fe_{100-z}B_z$ (y=0), that is, $t_C=T_C(y \neq 0)/T_C(y=0)$, z′ is the number of the average nearest neighbors in this pure binary amorphous compound (y=0), $\alpha=(z'/2)-1$, j_{ik} with i, k=Fe, Mn, are the exchange integrals confined to the nearest neighbors in the amorphous matrix B and reduced to the one in the pure binary crystal, i.e., j_{Fe-Fe}, and p, s, and involved mean values ($\langle\ \rangle$) are given by

$$p = j_{Fe-Fe} j_{Mn-Mn} j_{Fe-Mn},$$

$$s = j_{Fe-Fe} + j_{Mn-Mn} + j_{Fe-Mn},$$

$$\langle j\rangle = (1-y)^2 j_{Fe-Fe} + y^2 j_{Mn-Mn} + 2y(1-y) j_{Fe-Mn},$$

$$\langle j^{-1}\rangle = (1-y)^2 j_{Fe-Fe}^{-1} + y^2 j_{Mn-Mn}^{-1} + 2y(1-y) j_{Fe-Mn}^{-1}. \quad (4)$$

Taking the values of T_C (Ref. 10) and z′ (Ref. 11) of $Fe_{80}B_{20}$ presented in the literature, $T_C=647$ K and z′=12.4, and the values of the exchange integrals $j_{Fe-Fe}=1$, $j_{Mn-Mn}=-0.25$, and $j_{Fe-Mn}=-0.1$ (negative values of the exchange integrals indicate antiferromagnetic interactions), the coherent potential approximation gives values of t_C in a good agreement with the experimental data, as it is presented in Fig. 2 by the solid

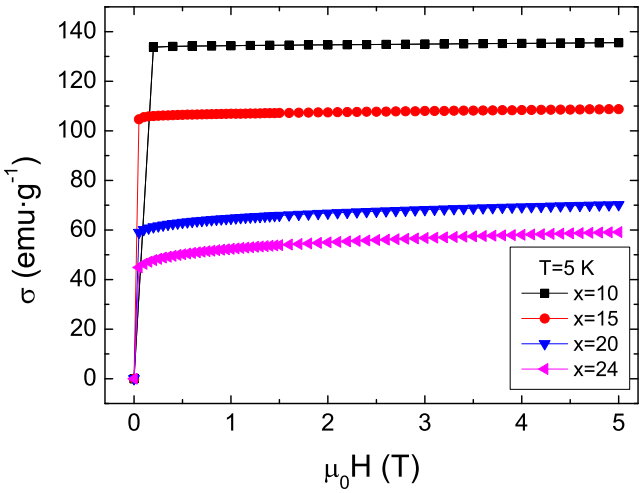

FIG. 3. (Color online) Field dependence, at 5 K, of the magnetization of the amorphous quasibinary $Fe_{80-x}Mn_xB_{20}$ (x=10, 15, 20, and 24) alloy series.

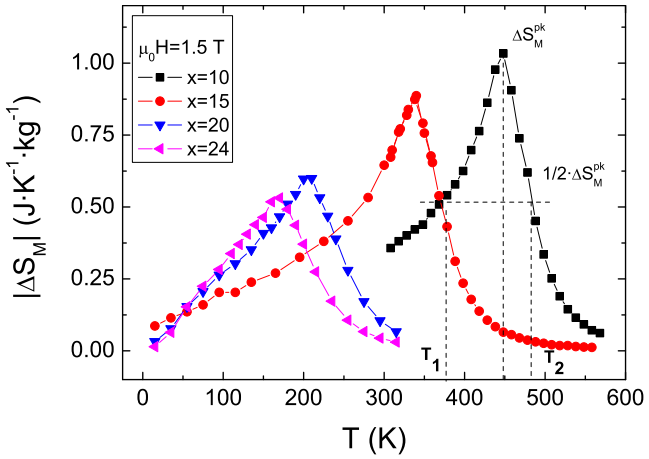

FIG. 4. (Color online) Temperature dependence of the magnetic entropy change corresponding to an applied field $\mu_0 H=1.5$ T of the amorphous quasibinary $Fe_{80-x}Mn_xB_{20}$ (x=10, 15, 20, and 24) alloy series. The maximum of the magnetic entropy change and the values of the temperatures determined at half maximum of the peak are presented for the x=10 composition.

line. It should be marked that the critical concentration y_C defined as the maximum concentration of Mn below which ferromagnetism exists, is an exchange integral dependent property. In this way, the temperature drop observed for the fitted experimental data indicates a critical Mn concentration $y_C=0.31$, corresponding to $x_C \approx 25$ at. % Mn content. It is worth mentioning that the maximum Mn content in the amorphous quasibinary ferromagnetic alloy series is greater in $(Fe_{1-y}Mn_y)_{100-z}B_z$ (Refs. 12 and 13) than in $(Fe_{1-y}Mn_y)_{100-z}Zr_z$.[14] Therefore, the differences found for the critical concentration of the alloys studied in this paper with respect to mentioned literature data may be due to the different method to obtain the Curie temperature (Mössbauer effect versus inflection point in $M(T)$ at low field),[12] the different value of concentration z,[13] and the different element in the amorphous phase C used (B versus Zr).[14] The critical concentration could be even different in samples with the same composition made by different methods because of the non-uniqueness of the amorphous structure[15] and the existence of inhomogeneities.

Figure 3 shows the field dependence of the magnetization at 5 K of the studied $Fe_{80-x}Mn_xB_{20}$ (x=10, 15, 20, and 24) alloy series, and indicates that an increase in Mn content determines an increase in the magnetic field to get the saturating behavior. The Mn content dependence of the saturation magnetization extrapolated to $\mu_0 H=0$ T at $T=5$ K, σ_0, follows a nearly linear behavior. The extrapolated value for x=0 is in agreement with the result presented in literature.[16] For the analysis of the field and Mn content dependence of the magnetization of the studied samples, the empirical law of the approach to ferromagnetic saturation[17] can be used

$$M(T,H) = M(T,0)\left[1 - \frac{a(T)}{H_{eff}} - \frac{b(T)}{H_{eff}^2}\right] + c(T)H_{eff}, \qquad (5)$$

where H_{eff} is the effective magnetic field (applied field minus demagnetizing field), and a, b, and c are temperature-dependent constants related to the presence of structural inhomogeneities, to the magnetic anisotropy, and to the so-called paraprocess,[18] respectively. Since the ribbon-shaped samples have been magnetized in the plane of the ribbons, the influence of the demagnetizing factor N can be neglected due to the large aspect ratio. A non linear fit of the experimental data $M(T,H)$ have been carried out according to the Eq. (5) at temperature $T=5$ K, showing that the term $b(T)/H^2$ plays a negligible role, and that an increase in the Mn content produces an increase in the coefficient $M(T,0)$ $a(T)$. Therefore, an increase in Mn content determines an increase in the required field to get the saturating behavior (Fig. 3), which, according to the usual interpretation,[17] should be ascribed to structural inhomogeneities.

To characterize the MCE in the studied system, the ΔS_M^{pk} and RC have been measured. The temperature dependence of the ΔS_M obtained according to the thermodynamic Eq. (1), and caused by the variation in a external magnetic field from 0 to 1.5 T, has been plotted in Fig. 4 for the studied alloy series in the compositional range x=10, 15, 20, and 24. The field dependence of the ΔS_M has been obtained at the temperature of the peak of the magnetic entropy change ΔS_M^{pk} and is presented in Fig. 5 for the studied compositional range. This field dependence of the ΔS_M has been proposed in several works[19,20] as $\Delta S_M^{pk}(H) \propto H^n$, where the exponent n is field independent at the temperature of ΔS_M^{pk}.[21] Although the variation in ΔS_M in the close proximity of the temperature of the peak is small, the field dependence of the exponent n is very sensitive to the temperature. However, at high fields it tends asymptotically to a constant value n_{pk} when the temperature is close to the temperature of the peak. The experimental $n(H)$ curves for x=15 (Fig. 6) are not field independent because the temperature is not exactly that of the peak, but n_{pk} can always be extracted as the asymptotic value of $n(H)$.

Although the ΔS_M in the x=10 studied alloy has been measured only for a variation in an external magnetic field from 0 to 1.5 T (solid symbols ■ for x=10 in Fig. 5), its ΔS_M^{pk} values can be extrapolated through the abovementioned power law for the field dependence of the exponent n to a range of higher values of field (open symbols □ for x=10 in Fig. 5). For x=15, the ΔS_M^{pk} data can be fitted from 0 to 1.5 T

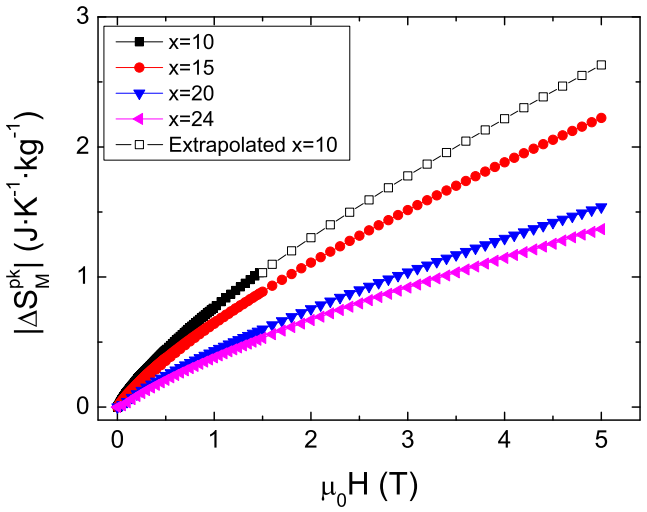

FIG. 5. (Color online) Field dependence of the maximum entropy change in the studied $Fe_{80-x}Mn_xB_{20}$ (x=10, 15, 20, and 24) alloy series. Open symbols indicate the non linear fit corresponding to experimental data of the x=10 composition sample.

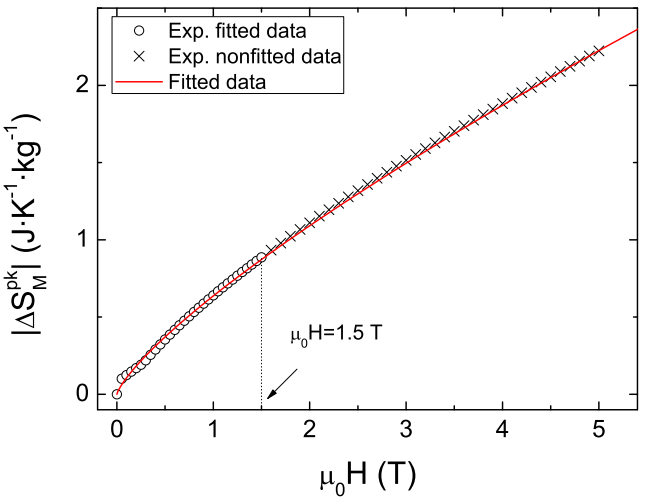

FIG. 7. (Color online) Extrapolation of the fitted data from 0 to 1.5 T for x=15 according to the expression $\Delta S_M^{pk}(T_{pk},H)=c_{15}(T_{pk})H^{n15}$, and comparison with the experimentally known ΔS_M^{pk} data from 1.5 to 5 T.

according to the expression $\Delta S_M^{pk}(T_{pk},H)=c_{15}(T_{pk})H^{n15}$ and, in order to check the goodness of this expression, the fitted data for x=15 can be compared to the experimentally known ΔS_M^{pk} data from 1.5 to 5 T. This comparison is presented in Fig. 7 and shows a good agreement between both extrapolated and experimentally known data. In accordance with this fitting procedure for x=10, cross sections of Fig. 5 at magnetic field $\mu_0 H=1.5$ T and 5 T has been obtained, showing a nearly linear behavior as a function of the Mn content.

On the other hand, a proportional relationship between the average magnetic moment per transition metal atom ($\langle\mu\rangle_{Fe,Mn}$) and the magnetic entropy change has been recently proposed.[22,23] Therefore, there should be a relationship between ΔS_M^{pk} and σ_0. Figure 8 confirms the validity of this relationship for ΔS_M^{pk} measured at $\mu_0 H=1.5$ and 5 T.

Considering that S_E and S_L are field independent in the system under study, and that the hysteresis losses are negligible for these alloys, an estimation of the RC given from Eq. (2) has been obtained from the product of ΔS_M^{pk} times the full temperature width at half maximum of the peak: $RC_{FWHM}=\Delta S_M^{pk}\times\Delta T_{FWHM}=\Delta S_M^{pk}\times(T_2-T_1)$, as is indicated in Fig. 4 for the composition with x=10. Other estimations of the RC calculated by the Wood and Potter definition[24] (RC_{WP}), and by the numerical integration of the area under the ΔS_M versus T curves (RC_{AREA}), using the full temperature width at half maximum of the peak as the integration limits, have been obtained and the results indicate approximately the same dependence on the applied field. Figure 9 presents the Mn content dependence of the different RCs for a magnetic field of $\mu_0 H=1.5$ T of the $Fe_{80-x}Mn_xB_{20}$ (x=10, 15, 20, and 24) alloy series showing a nearly linear behavior. However, as RC depends not only on the magnetization at T_C but also on that at other temperatures, it is not easy to give a theoretical justification for this phenomenological result.

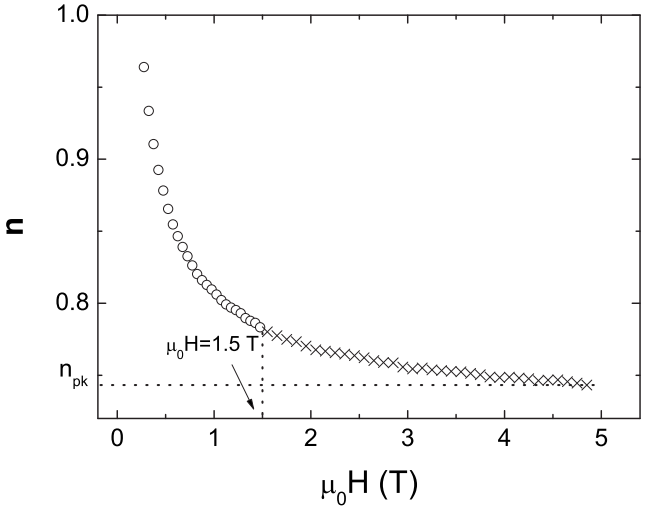

FIG. 6. Field dependence of the exponent n in the x=15 studied sample at the temperatures of the peaks of ΔS_M from $\mu_0 H=0$ to 5 T.

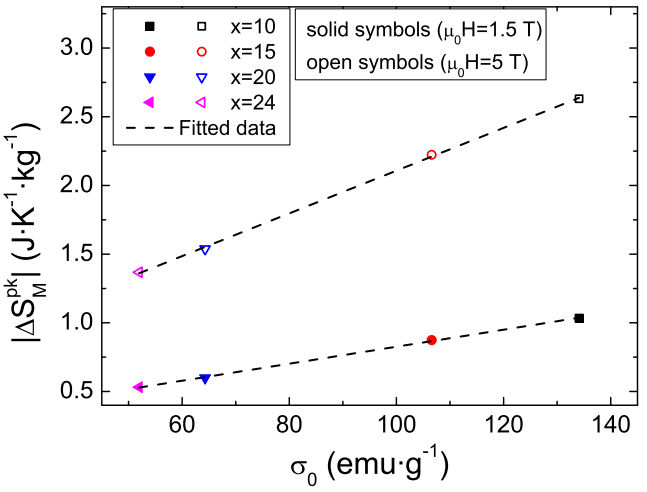

FIG. 8. (Color online) Dependence of the ΔS_M^{pk} on the saturation magnetization extrapolated to $\mu_0 H=0$ T at $T=5$ K, σ_0.

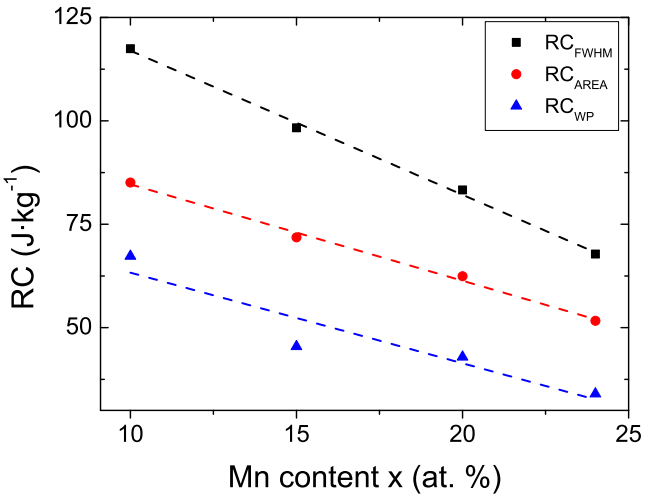

FIG. 9. (Color online) Mn content dependence of the refrigerant capacity RC_{FWHM}, RC_{WP}, and RC_{AREA} of the $Fe_{80-x}Mn_xB_{20}$ (x=10, 15, 20, and 24) alloy series when a field $\mu_0 H=1.5$ T is applied.

IV. CONCLUSIONS

In conclusion, the Mn content dependence of the thermomagnetic properties of the amorphous quasibinary ferromagnetic $Fe_{80-x}Mn_xB_{20}$ (x=10, 15, 20, and 24) alloy series have been shown. The Mn addition can be used to tune T_C close to room temperature, but at the expense of reducing ΔS_M^{pk} and RC. The dependence of the Curie temperature of the studied alloys on the Mn concentration is in agreement with the CPA, and a linear relationship between the ΔS_M^{pk} at $\mu_0 H=1.5$ and 5 T of the studied alloys and the saturation magnetization extrapolated to $\mu_0 H=0$ T at $T=5$ K, σ_0, has been shown. The results indicate a nearly linear dependence on the Mn content x of the Curie temperature T_C, the maximum magnetic entropy change ΔS_M^{pk}, and the refrigerant capacity RC_{FWHM}, with approximate slopes of −20 K/at. % Mn, −0.04 J K^{-1} kg^{-1}/at. % Mn, and −3.5 J kg^{-1}/at. % Mn, respectively.

ACKNOWLEDGMENTS

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