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Enhanced refrigerant capacity and magnetic entropy flattening using a two-amorphous FeZrB(Cu) composite

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The temperature dependence of the isothermal magnetic entropy change, ΔS_M, and the magnetic field dependence of the refrigerant capacity, *RC*, have been investigated in a composite system $x\mathrm{A}+(1-x)\mathrm{B}$, based on $Fe_{87}Zr_6B_6Cu_1$ (A) and $Fe_{90}Zr_8B_2$ (B) amorphous ribbons. Under a magnetic field change of 2 T, the maximum improvement of the full-width at half maximum of $\Delta S_M(T)$ curve (47% and 29%) and the *RC* (18% and 23%), in comparison with those of the individual alloys (A and B), is observed for $x \approx 0.5$. Moreover, a flattening over 80 K in the $\Delta S_M(T)$ curve around room temperature range is observed, which is a key feature for an Ericsson magnetic refrigeration cycle. © *2011 American Institute of Physics*. [doi:10.1063/1.3665941]

Nowadays, the search for new materials with enhanced magneto-caloric effect (MCE) for their utilization in room temperature magnetic refrigerators is a very active field of research due to its lower energy consumption and environmental friendly character.[1] The ideal Ericsson cycle (two isothermal and two isomagnetic field processes) is optimal for room temperature, RT, applications.[2] Its maximum efficiency is reached when the MCE exhibits a constant temperature dependence of the isothermal magnetic entropy change, $\Delta S_M(T)$, within the operating temperature range.[3] This condition is difficult to be accomplished by a single material, but a composite made of two ferromagnetic materials may fulfill it provided that the difference between their Curie points, T_C, is customized.[4] However, sintered mixtures of compounds are not well suited because they behave as a material with a single T_C.[5] Instead of that, the design of specific composites[6–8] can lead to an enlargement of the MCE temperature span and an almost constant $\Delta S_M(T)$ curve. The efficiency of the magnetic material in terms of the energy transfer between the cold (T_{cold}) and hot (T_{hot}) reservoirs is quantified by its refrigerant capacity, *RC*, an important figure of merit that characterizes the magneto-caloric material[9,10]

$$RC(H) = \int_{T_{cold}(H)}^{T_{hot}(H)} [\Delta S_M(T)]_H dT, \qquad (1)$$

where T_{cold} and T_{hot} are commonly selected as the temperatures corresponding to the full width at half maximum of $\Delta S_M(T)$. In order to attain large *RC* values, a large magnetic entropy change over a wide temperature range is desirable. However, it has been shown that although the maximum value of ΔS_M decreases, a large broadening of the $\Delta S_M(T)$ curves can overcompensate such decrease, giving rise to a significant *RC* enhancement.[7,10] In turn, numerical calculations and their proof-of-principle in real systems show that the design and practical realization of multiphase or composite magneto-caloric materials with optimized *RC* and $\Delta S_M(T)$ curves are not a simple task.[4–6] For a two-phase composite, the magnetic field variation of the *RC* is complex and depends on several factors such as ΔT_C and the shape, width, and peak value of $\Delta S_M(T)$ curve of the two constituents.[6]

In this letter, we report on the MCE in a two-ribbon composite showing a larger *RC* with respect to that of each individual ribbon and a flattened $\Delta S_M(T)$ curve. The composite is formed by two Fe-rich FeZrB(Cu) amorphous ribbons. These alloys, which were extensively studied due to their re-entrant spin-glass[11] and invar behaviors,[12] are particularly appropriate since, depending on the Fe content, the T_C is tunable between 200 and 400 K.[13,14] FeZrB(Cu) alloys exhibit broad $\Delta S_M(T)$ curves with moderate peak values, ΔS_M^{peak} ($\approx 1.5\ \mathrm{J\ kg^{-1}\ K^{-1}}$ for a magnetic field change of $\mu_o \Delta H = 2.0$ T);[6,15,16] thus offering the possibility of mixing two alloys with the appropriate ΔT_C difference.

Amorphous ribbons with nominal composition $Fe_{87}Zr_6B_6Cu_1$ (A) and $Fe_{90}Zr_8B_2$ (B) were produced by melt-spinning. The composite consists of two ribbons with approximate dimensions of 1 cm (long) × 1 mm (wide) × 25 μm (thick) glued together with a Kapton® film. Magnetization measurements were performed using a vibrating sample magnetometer (Quantum Design). A set of $M(H)$ curves was measured from 100 to 400 K each 10 K up to $\mu_o H = 5.0$ T for each material, with the magnetic field applied parallel to the ribbon largest length (1 cm) in order to minimize the demagnetizing factor. The temperature dependence of ΔS_M was calculated by numerical integration of the adequate Maxwell relation.[9] The total magnetic entropy change for the two-ribbon composite, $\Delta S_{comp}(T)$, can be calculated from the individual $\Delta S(T)$ curves[17]

$$\Delta S_{comp}(T,H,x) = x\Delta S_A(T,H) + (1-x)\Delta S_B(T,H), \qquad (2)$$

where x and $(1-x)$ are the weight amount of ribbons A and B, respectively, in the composite system $x\mathrm{A} + (1-x)\mathrm{B}$.

For $\mu_o \Delta H = 2.0$ T, $x \approx 0.5$ maximizes the *RC* value and $\Delta S_{comp}(T)$ exhibits a flattened region or table-like behavior. For these reasons, a combination with $x = 0.5$ was selected to compare the $\Delta S_{comp}(T)$ curves with those obtained from A

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and/or B ribbons [$\Delta S_A(T)$, $\Delta S_B(T)$ or $0.5\Delta S_A(T)+ 0.5\Delta S_B(T)$ curves].

Figs. 1(a) and 1(b) show the low field $M(T)$ and the $\Delta S_M(T)$ curves (for $\mu_o\Delta H = 2.0$ T and 5.0 T) for A and B ribbons. The Curie temperatures are $T_{C,A} = 300(5)$ K and $T_{C,B} = 240(5)$ K, hence, $\Delta T_C = 60$ K.[13] The $\Delta S_{comp}(T)$ curves show a broad single-peak for all x [see Fig. 1(c)], however, for low values of $\mu_o\Delta H$ the $\Delta S_{comp}(T)$ curve exhibits a double peak shape [see inset of Fig. 2(a)] and RC_{comp} cannot be defined. Moreover, the central region of $\Delta S_M(T)$ becomes relatively flat and the maximum of δT_{FWHM} (full width at half maximum of the $\Delta S_M(T)$ curve) occurs for $x \approx 0.5$ [see inset of Fig. 2(b)].

For layered composite materials, the value of RC_{comp} and the attainment of a constant ΔS_M inside a certain temperature interval depend strongly on the applied magnetic field.[4,6] Fig. 2(a) depicts how RC_{comp} varies with x in our composite system for $\mu_o\Delta H = 2.0$ and 5.0 T. The maximum value of RC_{comp} corresponds to $x \approx 0.5$ and is larger than those RC values for either A or B (see upper right panel in Fig. 3). This RC enhancement is a consequence of the increase in δT_{FWHM}. Nevertheless, a compromise between the value of the δT_{FWHM} and the potential lost of efficiency of the machine (due to an increase of cycles in the heat exchange medium) is needed. In turns, the $\Delta S_{comp}(T)$ curves under low magnetic field changes ($\mu_o\Delta H < 0.4$ T) exhibit a double-peak profile [see inset of Fig. 2(a)], and the δT_{FWHM} cannot be properly defined.

Both, the enhancement of RC_{comp} and the flattening observed in the ΔS_{comp} curve stimulated us to measure the $M(H)$ curves for the two-ribbon composite. This is important in order to assess whether the shape of $M(H)$ curves is in some extend affected by dipolar interactions between the individual components A and B. In Fig. 3, the $\Delta S_{comp}(T)$ curves obtained from the $M(H)$ curves measured on the composite through numerical calculation of the Maxwell relation,[3,9] and by Eq. (2) using $\Delta S_M(T)$ of the individual constituents are compared. The excellent agreement between both curves suggest that the dipolar interaction between the ribbons can be neglected and validates the $\Delta S_{comp}(T)$ curves shown in Fig. 1(c).

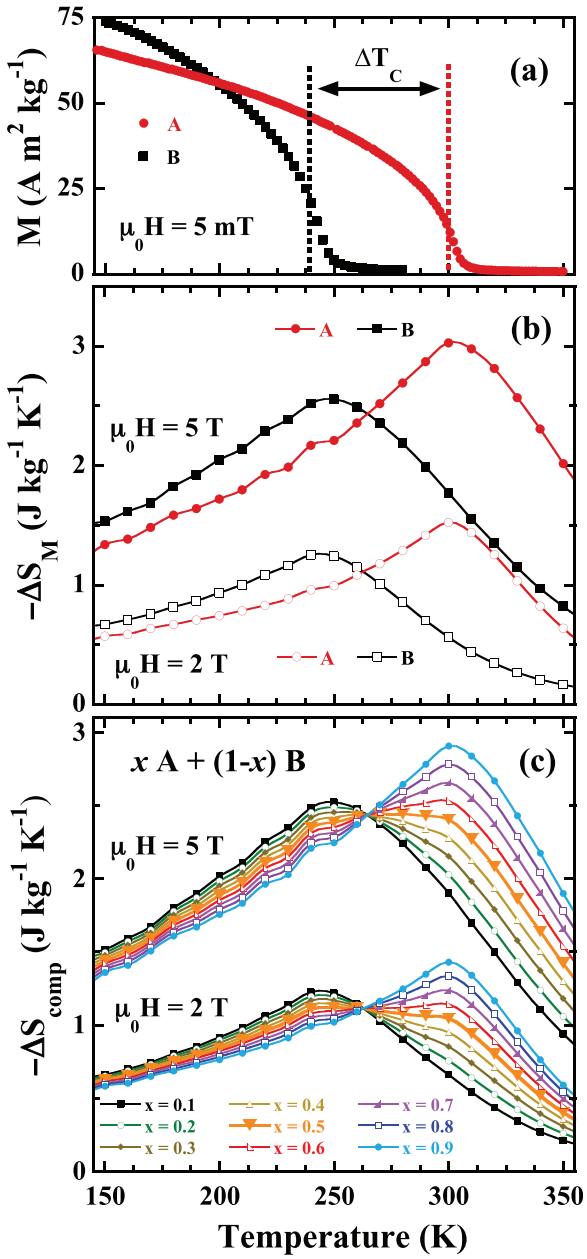

FIG. 1. (Color online) (a) Magnetization vs. temperature curves under $\mu_oH = 5$ mT. (b) $\Delta S_M(T)$ curves of samples A and B for $\mu_oH = 2$ and 5 T. (c) $\Delta S_{comp}(T)$ curves for the two-ribbon system calculated from the isothermal $M(H)$ curves measured independently for samples A and B for $\mu_oH = 2$ and 5 T.

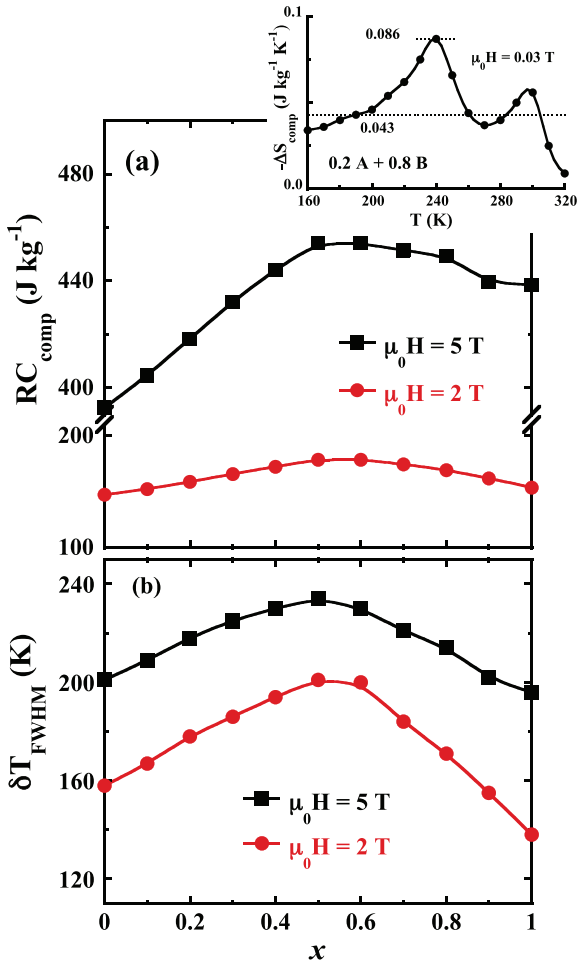

FIG. 2. (Color online) (a) RC_{comp} as a function of x for $\mu_oH = 2$ and 5 T. Inset: illustration of the difficulty encountered to define RC for a double-peak $\Delta S_{comp}(T)$ curve. (b) δT_{FWHM} vs. x for $\mu_oH = 2$ and 5 T.

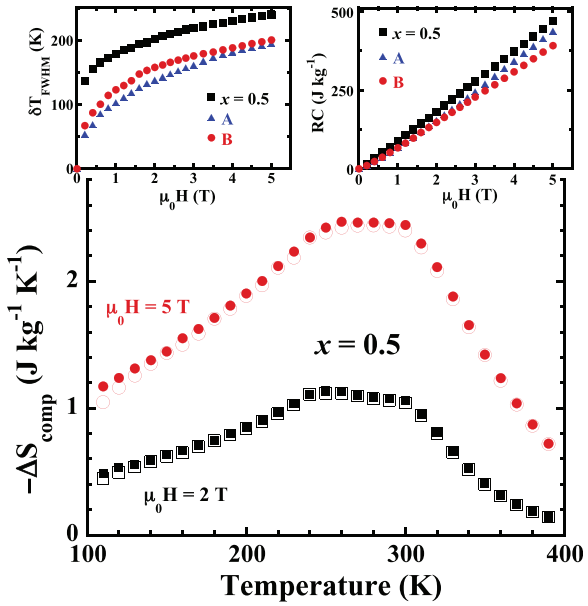

FIG. 3. (Color online) $\Delta S_{comp}(T)$ curves for the composite 0.5 A + 0.5B ($\mu_o H = 2$ and 5 T) obtained from the measured $M(H)$ curves of the composite (full symbols) and from Eq. (2) (open symbols). Left upper panel: Experimental magnetic field dependence of the δT_{FWHM} for the samples A, B, and the composite system. Right upper panel: RC vs. $\mu_o H$ for the samples A, B, and the composite.

On the other hand, the flattening, or temperature range where the ΔS_M remains almost constant, is an important attribute of the system if an ideal Ericsson refrigerant cycle is considered, since it avoids the generation of irreversible work.[3] Assuming a 10% difference with respect to $|\Delta S_{comp}^{peak}|$, the $\Delta S_{comp}(T)$ curve flattens in the intervals 220–300 K, and 230–320 K, for 2.0 and 5.0 T, respectively. Finally, the broadening of the $\Delta S_{comp}(T)$, due to the increase of the δT_{FWHM} in more than 30 K (see left upper panel in Fig. 3), gives rise to an improvement of the RC (see Fig. 3 upper right panel).

We have shown that the full-width at half maximum of the $\Delta S_M(T)$ curve in FeZrB amorphous alloys may be significantly increased via a layered composite made of two ribbons with different values of T_C. As a consequence, a significant improvement of the refrigerant capacity RC_{comp} can be obtained. For $\mu_o \Delta H = 2.0$ T, we found increments of 47% and 29% (18% and 23%) in δT_{FWHM} (RC_{comp}) compared with the individual A and B ribbons, respectively. In addition, $\Delta S_{comp}(T)$ showed a flattening over 80 K around room temperature, which is a key attribute that magnetic coolants must possess for its potential use in an Ericsson cycle. These findings path the way to an enhancement of the room temperature MCE through the adequate combination of materials with second order magnetic phase transitions. Therefore, we foresee that these results will attract the attention of researchers currently in charge of developing magnetic refrigeration devices that can exploit the present results.

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[1]O. Gutfleisch, M. A. Willard, E. Brück, C. H. Chen, S. G. Sankar, and J. P. Liu, Adv. Mater. **23**, 821 (2011).
[2]B. F. Yu, Q. Gao, B. Zhang, X. Z. Meng, and Z. Chen, Int. J. Refrig. **26**, 622 (2003).
[3]A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Applications* (IOP, Bristol, 2003).
[4]A. Smaïli and R. Chahine, J. Appl. Phys. **81**, 824 (1997).
[5]T. Hashimoto, T. Kuzuhara, M. Sahashi, K. Inomata, A. Tomokiyo, and H. Yayama, J. Appl. Phys. **62**, 3873 (1987).
[6]R. Caballero-Flores, V. Franco, A. Conde, K. E. Knipling, and M. A. Willard, Appl. Phys. Lett. **98**, 102505 (2011).
[7]A. Chaturvedi, S. Stefanoski, M. H. Phan, G. S. Nolas, and H. Srikanth, Appl. Phys. Lett. **99**, 162513 (2011).
[8]M.-A. Richard, A. M. Rowe, and R. Chahine, J. Appl. Phys. **95**, 2146 (2004).
[9]K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[10]P. Gorria, J. L. Sánchez Llamazares, P. Álvarez, M. J. Pérez, J. Sánchez Marcos, and J. A. Blanco, J. Phys. D: Appl. Phys. **41**, 192003 (2008).
[11]L. Fernández-Barquín, J. C. Gómez Sal, P. Gorria, J. S. Garitaonandia, and J. M. Barandiarán, Eur. Phys. J. B **35**, 3 (2003).
[12]J. M. Barandiarán, P. Gorria, I. Orue, M. L. Fdez-Gubieda, F. Plazaola, and A. Hernando, Phys. Rev. B **54**, 3026 (1996).
[13]J. M. Barandiarán, P. Gorria, J. C. Gómez Sal, L. Fernández-Barquín, and S. N. Kaul, IEEE Trans. Mag. **30**, 4776 (1994).
[14]J. M. Barandiarán, P. Gorria, I. Orue, M. L. Fernández-Gubieda, F. Plazaola, J. C. Gómez Sal, L. Fernández-Barquín, and L. Fournes, J. Phys.:Condens. Matter, **9**, 5671 (1997).
[15]P. Álvarez, P. Gorria, J. Sánchez Marcos, L. Fernández-Barquín, and J. A. Blanco, Intermetallics **19**, 982 (2010).
[16]P. Álvarez, J. Sánchez Marcos, P. Gorria, L. Fernández-Barquín, J. A. Blanco, J. Alloys Compd. **504S**, S150 (2010).
[17]A. Smaïli and R. Chahine Adv. Cryog. Eng. **42**, 445 (1996).