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The refrigerant capacity (*RC*) of magnetocaloric materials can be enhanced using multiphase materials or composites, which expand the temperature range over which a significant magnetic entropy change can be obtained. Numerical simulations show that by controlling the parameters of the composite (the fraction of the different phases and their Curie temperatures) improvements of *RC* of ~83% are possible. The maximum applied field plays a crucial, nonmonotonic, role in the optimization. As a proof of concept, it is shown that the combination of two $Fe_{88-2x}Co_xNi_xZr_7B_4Cu_1$ alloys produces an enhancement in *RC* of ~37%, making it ~92% larger than that of $Gd_5Si_2Ge_{1.9}Fe_{0.1}$. © *2011 American Institute of Physics.* [doi:10.1063/1.3560445]

Ambient temperature magnetic refrigeration based on the magnetocaloric effect (MCE) has the potential for significantly improved energy efficiency compared with conventional refrigeration techniques based the compression/expansion of gases.[1] The MCE arises from the reversible temperature change associated with the application or removal of an applied magnetic field, H, under adiabatic conditions[2] which is accompanied by a change in magnetic entropy, ΔS_M, leading to a refrigerant capacity, RC, defined as:

$$RC(\delta T, H_{max}) = \int_{T_{cold}}^{T_{hot}} \Delta S_M(T, H_{max}) dT, \quad (1)$$

where $\delta T = T_{hot} - T_{cold}$ is the temperature span of the thermodynamic cycle and H_{max} is the maximum value of the applied field. There are three principle figures of merit used to evaluate potential refrigerant materials: the magnitude of RC, the peak magnetic entropy change (ΔS_M^{pk}), and the adiabatic temperature change (ΔT_{ad}). RC is frequently determined over the temperature range corresponding to the full width at half maximum of the $\Delta S_M(T)$ curve, δT_{FWHM}, and may be estimated (RC_{AREA}) as the numerical integration of Eq. (1) over δT_{FWHM}.[3]

Optimizing RC involves increasing the magnitude of ΔS_M^{pk} and broadening the temperature span, δT, thereby increasing the integrated value of ΔS_M. The maximum ΔT_{ad} experienced by the refrigerant material should not, however, exceed the working temperature span δT_{FWHM} of the cycle since, outside of this temperature range, $\Delta S_M(T)$ vanishes and there is little additional contribution to RC.[4] For this reason, magnetic materials with tall and narrow $\Delta S_M(T)$ peaks are generally not optimal magnetic refrigerants.

Single-phase materials exhibiting large RC values are rare, and there is considerable research toward expanding δT through various methods, including amorphization by ball milling,[5] modifying the structure by microalloying[6] and annealing,[7,8] nanostructuring,[9] developing composites[10,11] and nanocomposites,[12–14] and employing multilayered materials.[15,16] All of these methods involve either the existence of a Curie temperature distribution in the magnetic material, or the presence of several phases that contribute to the total ΔS_M.

The aim of this work is to study the enhancement of RC in multiphase magnetic systems with different Curie temperatures and analyze the conditions (i.e., fraction of each phase x, the difference in Curie temperature ΔT_C, and the applied field H) under which the RC can be optimized. It will be shown that optimum values of these parameters can be found, which maximize the increment of RC (denoted as RCI) with respect to the pure constituent phases. Also, contrary to general assumptions, there is an optimum value of H that produces the largest RCI, above which RCI diminishes. Numerical simulations will show that $RCIs$ of ~83% are possible. As a proof of concept, a simulated two-phase magnetic material based on experimentally measured properties of two constituent $Fe_{88-2x}Co_xNi_xZr_7B_4Cu_1$ amorphous alloys produces an $RCI \sim 37\%$. These values are validated by experimental measurements of a mixture of both phases.

The relation between magnetization, M, field, H, and temperature, T, of a second-order magnetic phase transition near T_C is given by the Arrott–Noakes equation of state (AN-EOS)[17] $(H/M)^{1/\gamma} = a(T - T_C) + bM^{1/\beta}$, where a and b are characteristic parameters of the material and β and γ are the critical exponents. The T and Hdependence of the magnetic entropy change in such a material can be calculated as:[18]

$$\Delta S_M(T, H_{max}) = -\int_{M_s}^{M_{max}} a\gamma M(a(T - T_C) + bM^{1/\beta})^{\gamma-1} dM, \quad (2)$$

where $M_s(T, H=0)$ is the spontaneous magnetization and $M_{max}(T, H=H_{max})$ is the magnetization at H_{max}.

For multiphase materials, Eq. (2) cannot be used since there is no analytical expression for the EOS of the composite. The magnetocaloric response can be calculated numerically, however, based on the magnetization behavior of each constituent material. We assume that the magnetic phases present in the multiphase composite are noninteracting, which allows the total magnetic entropy change to be expressed as a rule-of-mixtures sum of the entropy change in
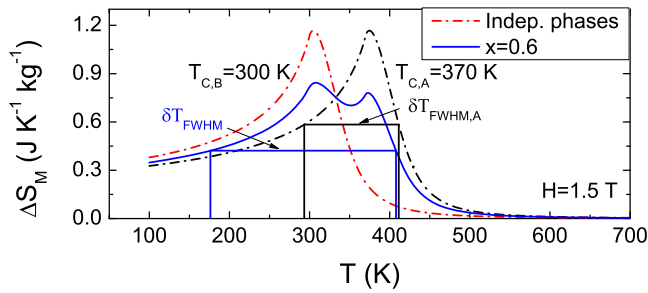
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FIG. 1. (Color online) Temperature dependence of the magnetic entropy change of the two independent phases (dashed lines), and of the biphasic system with fraction $x=0.6$ (solid line).

the constituent materials. For a two-phase composite (containing phases A and B), the entropy change is: $\Delta S_M(x,T,H_{max})=x\Delta S_{M,A}+(1-x)\Delta S_{M,B}$, where x is the fraction of constituent A.

We initially consider a composite composed of two phases with the same AN parameters and critical exponents but with different Curie temperatures. We suppose a typical soft magnetic amorphous alloy, $Fe_{77}Cr_8B_{15}$, where $a=1.228$ K^{-1}, $b=0.0077$ $(emu\ cm^{-3})^{-1/\beta}$, $\beta=0.4579$, and $\gamma=1.5593$.[19] The Curie temperature of phase A is $T_{C,A}=370$ K and that of phase B is variable, with $T_{C,B}<T_{C,A}$. The field and temperature ranges used in the numerical calculation are analogous to those explored experimentally (up to 6 T, in 50 mT increments and from 100 to 700 K, in 1 K increments). The entire phase fraction range, $0\le x\le 1$, has been examined in increments of 0.01.

RCI is defined as the percentage difference of the refrigerant capacity of the composite with respect to the majority phase (either $x=0$ or $x=1$):

$$RCI(x,\Delta T_C,H_{max})$$
$$=\begin{cases} \dfrac{RC(x)-RC(x=1)}{RC(x=1)}100, & if\ x>0.5 \\[2ex] \dfrac{RC(x,\Delta T_C)-RC(x=0)}{RC(x=0)}100, & if\ x<0.5 \end{cases} \quad (3)$$

For the constituents chosen presently (a, b, and the critical exponents are the same for both phases), both expressions in Eq. (3) give the same result. An alternative definition would be to compare with the phase with the largest RC; however, due to the phases chosen in this work, the results would not differ from those presented here.

Figure 1 shows $\Delta S_M(T)$ curves of phases A and B that make up the composite (with $T_{C,A}=370$ K and $T_{C,B}=300$ K), along with entropy change in the composite ($x=0.6$). The increased temperature span δT_{FWHM} of the composite is also shown, as compared with that of the pure constituent phases.

Three independent parameters (x, H_{max}, and ΔT_C) determine RCI. Figure 2(a) displays the surface $RCI(x,\Delta T_C)$ for a maximum applied field of 1.5 T, while Fig. 2(b) shows the surface $RCI(x,H_{max})$ for $\Delta T_C=130$ K. For a given value of H_{max} [Fig. 2(a)], there exist optimum values x_{opt} (for each ΔT_C) and ΔT_C^{opt} (for each x) which maximize RCI. These values are indicated by the line overlaid on the surface in Fig. 2(a). Note that maximum RCI is always obtained for $x>0.5$, indicating that the minority phase should have a lower T_C than that of the majority phase in order to maximize the RC of the composite. RCI is negative for large ΔT_C, indicat-
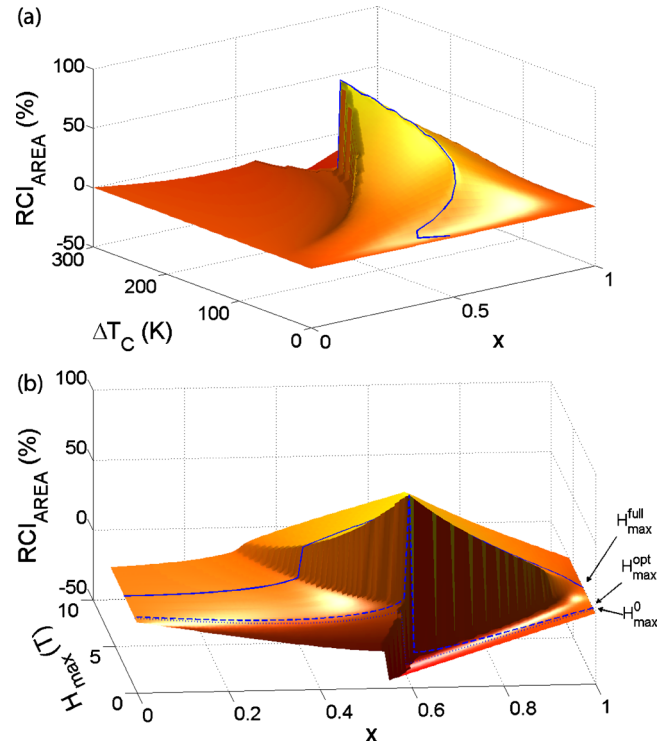

FIG. 2. (Color online) Influence of x, ΔT_C and H_{max} on RCI. (a) $RCI_{AREA}(x,\Delta T_C)$ surface for a maximum magnetic field of 1.5 T. For each ΔT_C value, the maximum RCI is connected through the solid line. (b) $RCI_{AREA}(x,H_{max})$ surface for $\Delta T_C=130$ K. The characteristic field values H_{max}^0, H_{max}^{opt}, and H_{max}^{full} are marked.

ing that RC cannot be improved with a composite whose constituents have too dissimilar T_C values. The physical reason for this effect is the so-called "sum rule," which predicts smaller RC values when the $\Delta S_M(T)$ of the two constituents are widely displaced.[20] The decrease in RCI for large ΔT_C explained the fact that the partial nanocrystallization of a Finemet-type alloy[21] did not produce an increase in RC with respect to the amorphous precursor (the majority phase has the lower T_C and ΔT_C is too large, so that the nanocrystalline phase hardly contributes to MCE). It should be noted that, for the parameters used in the simulation, an improvement of RC near 83% can be obtained. For $H_{max}=1.5$ T, $x_{opt}=0.6$ and $\Delta T_C^{opt}=195$ K. For different values of H_{max}, the peak in Fig. 2(a) occurs at different ($\Delta T_C^{opt},x_{opt}$) coordinates. The general rule, however, is that ΔT_C^{opt} increases with increasing H_{max}, and the peak value of RCI does not change.

Figure 2(b) shows that, for a given pair of phases for which the optimization of RC is possible (a given value of ΔT_C which is not too large), the value of H_{max} plays an important role in the optimization. There are three characteristic values of H_{max}: H_{max}^0 is the minimum necessary field to obtain an enhancement in RC (for lower field values, the $\Delta S_M(T)$ curves of each phase are so narrow that the addition does not cause an enhancement of δT); H_{max}^{opt} corresponds to the field that produces the largest optimization in RC; H_{max}^{full} is the minimum field necessary to have a positive RCI for the whole compositional range. For $H_{max}>H_{max}^{opt}$ the maximum RCI decreases monotonically. This figure shows again the strong asymmetry of $RCI(x)$. This is primarily due to the asymmetry of the $\Delta S_M(T)$ curves of the constituent phases. Since $\Delta S_M(T)$ for each phase diminishes rapidly at high temperatures, a relatively large fraction of a second phase (with
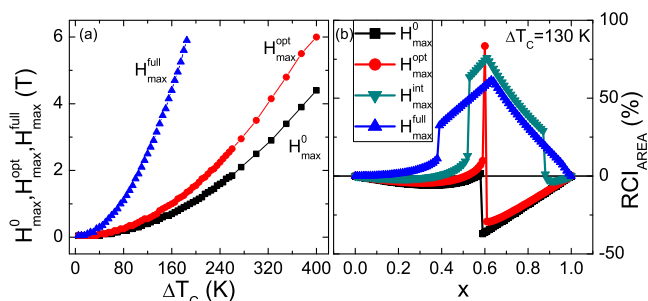
FIG. 3. (Color online) (a) Dependence of the characteristic field values with ΔT_C. (b) Evolution of RCI with the fraction of phase x at $\Delta T_C = 130$ K for the characteristic field values and for $H_{max}^{opt} < H_{max}^{int} < H_{max}^{full}$.

larger T_C) is necessary for a broad (ideally tablelike) $\Delta S_M(T)$ curve. Similar behavior has been found in these two surfaces when the critical exponents from the mean field and Heisenberg models are considered.

Figure 3(a) shows the variation in the three characteristic fields (H_{max}^0, H_{max}^{opt}, and H_{max}^{full}) with ΔT_C. H_{max}^0 and H_{max}^{opt} have a similar dependence, while H_{max}^{full} increases more rapidly with ΔT_C. For magnetic phases with similar T_C values, the small value of H_{max}^0 indicates that small fields are sufficient to produce an enhancement in RC, and the fact that H_{max}^{opt} and H_{max}^{full} have similar values indicates that the compositional range over which RC is increased grows quickly with H_{max}. However, the differences between these two characteristic fields increase rapidly with increasing ΔT_C. Figure 3(b) shows the variation in RCI with x for $\Delta T_C = 130$ K, for the three characteristic values of H, as well as for an intermediate field $H_{max}^{opt} < H_{max}^{int} < H_{max}^{full}$. Figure 3(b) clearly shows the decreasing value of the maximum RCI for $H_{max} > H_{max}^{opt}$.

These arguments can be used to understand the reason why the amorphous materials, usually with a Curie temperature distribution, typically have larger values of RC than crystalline phases (as shown above, a small ΔT_C produces an enhancement of RC for almost any fraction of phases), and why ball milled alloys,[5] manganite-based composites,[10,11] clathrates-EuO composites,[14] which involve a combination of phases with different Curie temperatures, may improve RC.

We now consider a two-phase magnetic composite based on $Fe_{88-x}Co_xNi_xZr_7B_4Cu_1$ amorphous alloys.[22,23] The two phases ($Fe_{66}Co_{11}Ni_{11}Zr_7B_4Cu_1$, phase A and $Fe_{71.5}Co_{8.25}Ni_{8.25}Zr_7B_4Cu_1$, phase B) have the following magnetocaloric properties under an applied magnetic field of 1.5 T: $T_{C,A} = 626$ K, $\delta T_{FWHM,A} = 74$ K, $RC_{AREA,A} = 97.7$ J kg^{-1} and $T_{C,B} = 558$ K, $\delta T_{FWHM,B} = 67$ K, $RC_{AREA,B} = 97.4$ J kg^{-1}.

Maximum performance is achieved for $x = 0.65$, where $\delta T_{FWHM} = 141$ K, $RC_{AREA} = 134$ J kg^{-1}, and $RCI_{AREA} = 37\%$. These calculated results were verified experimentally by preparing a laminate composite (layers of melt-spun ribbon pieces of the two compositions in intimate contact) corresponding to $x = 0.643$. The experimental RCI_{AREA} is 36%, in excellent agreement with the predictions based on the simulated composite.[24] This validates the assumption of noninteracting phases. These results represent an improved RC of $\sim 92\%$ as compared with $Gd_5Si_2Ge_{1.9}Fe_{0.1}$. Further studies to analyze the influence of magnetic interactions between the

constituent phases of the composite material are being undertaken, both experimentally and numerically.

In conclusion, it has been shown that large enhancements of RC can be obtained by combining different phases in a composite. The parameters controlling this enhancement are the fraction of phases, the difference between their Curie temperatures, and, in contrast with what is usually assumed, the maximum magnetic field. A composite optimized for a particular field range might have diminished properties with respect to the constituent phases when operated at a different field. The increment of RC is asymmetric in the fraction of phases, being more beneficial to have a majority phase with the larger Curie temperature. Increments of RC as large as $\sim 83\%$ can be envisioned. Numerical calculations and experimental results for a combination of $Fe_{88-x}Co_xNi_xZr_7B_4Cu_1$ alloys support the validity of this approach.

[1] A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Applications*, 1st ed. (Institute of Physics, Bristol, Philadelphia, 2003), p. 475.
[2] K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[3] K. A. Gschneidner, Jr. and V. K. Pecharsky, Annu. Rev. Mater. Sci. **30**, 387 (2000).
[4] V. I. Zverev, A. M. Tishin, and M. D. Kuz'min, J. Appl. Phys. **107**, 043907 (2010).
[5] B. Chevalier, J.-L. Bobet, J. Sánchez Marcos, J. Rodriguez Fernandez, and J. C. Gómez Sal, Appl. Phys. A: Mater. Sci. Process. **80**, 601 (2005).
[6] W. H. Wang, Prog. Mater. Sci. **52**, 540 (2007).
[7] Q. Zhang, J. Du, Y. B. Li, N. K. Sun, W. B. Cui, D. Li, and Z. D. Zhang, J. Appl. Phys. **101**, 123911 (2007).
[8] D. Wang, K. Peng, B. Gu, Z. Han, S. Tang, W. Qin, and Y. Du, J. Alloys Compd. **358**, 312 (2003).
[9] 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).
[10] A. L. L. Sharma, P. A. Sharma, S. K. McCall, S. B. Kim, and S. W. Cheong, Appl. Phys. Lett. **95**, 092506 (2009).
[11] A. Biswas, T. Samanta, S. Banerjee, and I. Das, Appl. Phys. Lett. **92**, 012502 (2008).
[12] Y. Shao, J. Zhang, J. K. L. Lai, and C. H. Shek, J. Appl. Phys. **80**, 76 (1996).
[13] F. Shir, L. Yanik, L. H. Bennett, E. Della Torre, and R. D. Shull, J. Appl. Phys. **93**, 8295 (2003).
[14] M. H. Phan and H. Srikanth, private communication (17 November 2010).
[15] M. A. Richard, A. M. Rowe, and R. Chahine, J. Appl. Phys. **95**, 2146 (2004).
[16] C. E. Reid, J. A. Barclay, J. L. Hall, and S. Sarangi, J. Alloys Compd. **207–208**, 366 (1994).
[17] A. Arrott and J. E. Noakes, Phys. Rev. Lett. **19**, 786 (1967).
[18] V. Franco and A. Conde, Int. J. Refrig. **33**, 465 (2010).
[19] V. Franco, A. Conde, and L. F. Kiss, J. Appl. Phys. **104**, 033903 (2008).
[20] R. D. McMichael, R. D. Shull, L. J. Swartzendruber, L. H. Bennet, and R. E. Watson, J. Magn. Magn. Mater. **111**, 29 (1992).
[21] V. Franco, J. S. Blázquez, C. F. Conde, and A. Conde, Appl. Phys. Lett. **88**, 042505 (2006).
[22] K. E. Knipling, M. Daniil, and M. A. Willard, Appl. Phys. Lett. **95**, 222516 (2009).
[23] R. Caballero-Flores, V. Franco, A. Conde, K. E. Knipling, and M. A. Willard, Appl. Phys. Lett. **96**, 182506 (2010).
[24] See supplementary material at http://dx.doi.org/10.1063/1.3560445 for a figure including the comparison between model an experiment.