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Influence of Co and Ni addition on the magnetocaloric effect in Fe_{88-2x}Co_xNi_xZr_B_Cu_1 soft magnetic amorphous alloys

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We have studied the magnetocaloric effect in a series of Fe_{88-2x}Co_xNi_xZr_B_Cu_1 alloys. The partial substitution of Fe by Co and Ni leads to a monotonic increase in the Curie temperature (Tc) of the alloys from 287 K for x=0 to 626 K for x=11. The maximum magnetic entropy change (ΔS_M^k) at an applied field of 1.5 T, shows a value of 1.98 J K^{-1} kg^{-1} for x=8.25. The refrigerant capacity (RC) has maximum values near 166 J kg^{-1} (for x=0 and 2.75). These values place the present series of alloys among the best magnetic refrigerant materials, with an RC ~40% larger than GdSi_2Ge_1.9Fe_0.1 and ~15% larger than Fe-based amorphous alloys. © 2010 American Institute of Physics. [doi:10.1063/1.3427439]

Ambient-temperature solid-state magnetic refrigeration employing the magnetocaloric effect (MCE) is a field of active research.\textsuperscript{1–3} Compared with conventional gas compression-expansion refrigeration, magnetic refrigeration based on MCE offers improved energy efficiency and reduced environmental impact.\textsuperscript{4} In magnetic materials, the change in magnetic entropy caused by a variation in magnetic transition temperatures by alloying,\textsuperscript{16} and slow kinetics of the first order transitions\textsuperscript{18} which can limit the performance of a refrigerator employing MCE, and

\[ \Delta S_M = \frac{\mu_0}{2} \int_{H_0}^{H_f} \frac{dM(T,H)}{dT} \, dH, \]  

(1)

where \( \Delta S = MS \) is the magnetic field change, \( \mu_0 \) is the magnetic permeability of vacuum, and \( M(T,H) \) is the magnetization of the material. The field and temperature dependence of \( M(T,H) \) was measured (up to \( \mu_0H_{max}=1.5 \) T in 10 mT increments and from 100 to 713 K in 10 K increments) by vibrating sample magnetometry. Figure 1 shows the corresponding temperature dependence of \( \Delta S_M \) at a maximum applied field of 1.5 T for the alloys studied. The curves have a caret-like shape, characteristic of a second order phase transition, which becomes sharper with increasing CoNi content.

RC may be calculated from \( \Delta S_M \) according to...
\[ RC(\Delta H) = \int_{T_{cold}}^{T_{hot}} \Delta S_M(T, \Delta H) dT. \]  

(2)

From the experimental data, this integral may be evaluated by a number of methods. RC\text{AREA} is calculated by integrating \( \Delta S_M \) across the temperature range spanning the half-maximum of the entropy change. RC\text{FWHM} approximates the integral as the product of \( \Delta S_M \) with the same full width at half maximum (FWHM) temperature range. According to Wood and Potter, RC\text{FWHM} is taken as the area of the largest rectangle which can be inscribed inside the \( \Delta S_M(T) \) curve. In this work all three definitions are used, to facilitate comparison with prior studies.

The compositional dependence of RC, \( \Delta S_M^{pk} \), and \( T_c \) is shown in Fig. 2 for the alloys studied. The values of \( T_c \) have been obtained from the inflection point of the experimental magnetization data at low field (\( \mu_0 H_{\text{max}} = 10 \) mT). There is a monotonic increase in \( T_c \) from 287 K for \( x = 0 \) to 626 K for \( x = 11 \), which follows a power law defined as \( T_c(x) \propto x^{0.81} \) (\( r^2 = 0.999 \)). This empirically obtained power law can be used to fine tune the composition of the alloy for a desired \( T_c \). The temperature at which \( \Delta S_M^{pk} \) occurs (Fig. 1) correlates well to the value of \( T_c \) for each alloy. The compositional evolution of \( \Delta S_M^{pk} \), however, does not show a power law behavior. For the extreme compositions of the series, \( \Delta S_M^{pk} \) passes from 1.32 J K\(^{-1}\) kg\(^{-1}\) for \( x = 0 \) to 1.81 J K\(^{-1}\) kg\(^{-1}\) for \( x = 11 \), and is maximized for \( x = 8.25 \) with a value of 1.98 J K\(^{-1}\) kg\(^{-1}\).

The RC\text{FWHM} and RC\text{AREA} have a stepwise behavior due to the much narrower peak widths of the alloys with \( x \approx 5.5 \). RC\text{FWHM} varies abruptly from \(-166 \) J kg\(^{-1}\) (\( x = 0 \) and 2.75) to 130 J kg\(^{-1}\) (\( x = 5.5, 8.25, \) and 11). This is due to the different shapes of the low temperature tails of the \( \Delta S_M(T) \) curves presented in Fig. 1. RC\text{FWHM}, however, decreases monotonically from \(-95 \) J kg\(^{-1}\) for \( x = 0 \) to \(-73 \) J kg\(^{-1}\) for \( x = 11 \).

In order to compare these experimental values with those reported in the literature for other alloys, it would be necessary in most cases to formulate an expression to convert the values to an applied field of 5 T. It has been shown theoretically and experimentally that the field dependence of \( \Delta S_M \) can be represented as \( \Delta S_M(T, H) = c(T) H^p \). At \( T = T_c \) and \( T = T_{pk} \), the exponent \( n \) is field independent. At any other temperature, \( n \) is a function of the applied magnetic field.\(^{25} \)

RC can also be expressed as a power law of the field:

\[ RC(H) = b H^{n'}. \]

By normalizing these expressions with the values corresponding to the maximum applied field, dimensionless relationships can be written for the different studied compositions

\[ \delta_S = \frac{\Delta S_M^{pk}(H, x)}{\Delta S_M^{pk}(H_{\text{max}}, x)} = \left( \frac{a(H)}{a(H_{\text{max}})} \right) = h^n, \]

\[ r_c = \frac{RC_{\text{FWHM}}(H, x)}{RC_{\text{FWHM}}(H_{\text{max}}, x)} = \left( \frac{b(H)}{b(H_{\text{max}})} \right) = h^{n'}, \]

where \( h = H / H_{\text{max}} \). In principle, the exponents \( n \) and \( n' \) could be composition dependent (i.e., dependent on \( x \)). However, when these power laws are plotted for the different alloys (Fig. 3) both power law exponents have very similar values for the full series of alloys.

The present alloys compare favorably with other magnetocaloric materials. Among crystalline compounds, Gd\(_3\)Si\(_2\)Ge\(_2\)Fe\(_{0.1}\) is one of the most prominent materials due to its reduced hysteresis. For an applied field of 5 T its RC\text{AREA} is 355 J kg\(^{-1}\); when the values of the studied alloys are calculated at 5 T based on the power law relationship in Fig. 3, the two alloys with the transition temperatures closest to room temperature (\( x = 0 \) and 2.75) have RC\text{AREA} \= 496 J kg\(^{-1}\), which is a \(-40\% \) increase. The values of \( \Delta S_M^{pk} \) for the present alloys, which extrapolate to 5.3 J kg\(^{-1}\) K\(^{-1}\) for an applied field of 5 T, is smaller than that of Gd\(_3\)Si\(_2\)Ge\(_2\)Fe\(_{0.1}\) (7 J kg\(^{-1}\) K\(^{-1}\)). The comparison with the
Fe_{83}Zr_6B_{10}Cu_1 amorphous alloy (the Fe-based amorphous alloy with largest RC reported to date) is also favorable.\textsuperscript{17} In that case, for an applied field of 1.5 T, $R_{\text{area}}=104\text{ J kg}^{-1}$, indicating that the series of alloys studied in this work give an increase of $\sim 15\%$. In addition to this enhancement, with the present alloy series we have been able to tune the Curie temperature down to room temperature, while Fe_{83}Zr_6B_{10}Cu_1 had a $T_c=398\text{ K}$. The values of the peak entropy change for Fe_{83}Zr_6B_{10}Cu_1 and for the present series are similar.

In summary, it has been shown that by the simultaneous addition of Co and Ni to Fe–Zr–B–Cu alloys, the Curie temperature of the alloys can be tuned in a range which includes room temperature. The RC of this family of alloys is enhanced in $\sim 40\%$ with respect to the crystalline Gd$_2$Si$_2$Ge$_4$Fe$_3$, and $\sim 15\%$ with respect to the best Fe-based amorphous alloy reported so far. This makes these alloys promising candidates to be used as room temperature magnetic refrigerants.

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