Magnetocaloric effect in Sm-$Co_{2-x}Fe_x$ alloys

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Abstract

$SmCo_2$ and $SmFe_2$ magnetic cubic Laves phases have Curie temperatures of 220 and 669 K, respectively. Aiming to increase the Curie temperature of $SmCo_2$ for potential room temperature magnetic refrigeration Co was partially replaced by Fe. The fundamental magnetic entropy change of the $SmCo_2$ compound, ΔS_M = 3.61 J/kg·K, for an applied magnetic field of $\mu_o H$ = 1.5 T was observed at T_{SR}=175 K, where a spin reorientation transition occurs; furthermore a refrigerant capacity of 37 J/kg was calculated. Interestingly the addition of Fe practically suppressed the spin reorientation transition, shifting the magnetic entropy change maximum to the Curie temperature in the $SmCo_{1.8}Fe_{0.2}$ sample. The magnetic entropy change maximum at Curie temperature T_C=300 K and the refrigerant capacity for the doped compound decreased to ΔS_M=0.20 J/kg·K and 13.5 J/kg, respectively, for an applied magnetic field of $\mu_o H$=1.5 T. After an homogenization heat treatment at 773K during 50 h, the $SmCo_{1.8}Fe_{0.2}$ compound showed an increase of the maximum magnetic entropy change, ΔS_M=0.28 J/kg·K, and refrigerant capacity remains 13.5 J/kg, for an applied magnetic field of $\mu_o H$=1.5T.

Introduction

The magnetic ordering transitions in RCo_2 had been always classified as first-order transitions for R=Dy, Er, and Ho, and the rest as second-order transitions.[1,2] These first order transition materials are potential candidates for magnetic cooling in the

30–150K temperature range, limiting its applications as magnetic refrigerants.[1,3,4] A typical metallurgical strategy has been to combine the high Curie temperature of some members of the RCo_2 series ($GdCo_2$ with $T_c \approx 400$ K) with the very high entropy content of the first-order transition of other members (as $ErCo_2$) so as to tune the properties.[1,5] In this work, aiming to increase the Curie temperature of $SmCo_2$ for potential room temperature magnetic refrigeration, Co was partially replaced by Fe knowing that $SmCo_2$ and $SmFe_2$ compounds have Curie temperatures of 220 and 669 K, respectively.

Experimental

Polycrystalline samples of $SmCo_2$ and $SmCo_{1.8}Fe_{0.2}$ were prepared by arc melting method in a high purity argon atmosphere. The $SmCo_{1.8}Fe_{0.2}$ sample was homogenized at 773K during 50 h. X ray powder diffraction patterns were measured at room temperature in a Panalytical diffractometer model X'pert Pro-MPD with Cu Kα radiation (λ=1.5406 Å) and refined by the Rietveld method using the fullprof program for the determination of phases composition and lattice parameters. Bulk samples microstructure was observed in a scanning electron microscope JEOL model JSM-7401 F LV, and chemical composition elemental analysis with an energy-dispersive system (EDAX) Oxford model INCA Penta FETX3 was carried out. Sample powders were pressed into cylindrical shaped tablets for later measurement of Magnetic isotherms and thermomagnetic curves in a quantum design physical properties measurement system (PPMS).

Results and discussion

According to Fig. 1, for the $SmCo_2$ sample, the 1:2 main cubic Laves phase and a barely detected amount of 2:7 hexagonal secondary phase were identified, whereas for the $SmCo_{1.8}Fe_{0.2}$ and heat treated (HT) $SmCo_{1.8}Fe_{0.2}$ samples, the 1:2 main cubic Laves phase and the 5:2 hexagonal secondary phase were recognized. For the $SmCo_{1.8}Fe_{0.2}$ samples, the diffraction angles of the 1:2 main cubic Laves phase are shifted to minor angles compared to those reported in the crystallographic file (ICSD), which is related to the larger atomic radius of Fe compared to Co. A better defined pattern for the 1:2 main cubic Laves phase and angular displacements less than 1° are observed for the $SmCo_{1.8}Fe_{0.2}$ (HT) sample. Phase analyses, in wt. %, are shown in Table I. Calculated unit cell volume of 386.126 $Å^3$ and 386.605 $Å^3$ for the $SmCo_{1.8}Fe_{0.2}$ samples with and without heat treatment, respectively, are greater than the 382.82 $Å^3$ unit cell volume of nominal $SmCo_2$. The unit cell volume increase of the 1:2 compound determined by Rietveld method indicates the substitutional incorporation of Fe. A negligible volume increase of the 5:2 hexagonal secondary phase was noticed for the same samples.

Dendritic-like microstructures observed for bulk $SmCo_{1.8}Fe_{0.2}$ and heat treated $SmCo_{1.8}Fe_{0.2}$ by scanning electron microscopy are shown in Fig. 2. The darker zones correspond to the 1:2 main cubic Laves phase, and the lighter zones correspond to the 5:2 hexagonal secondary phase, according to semiquantitative chemical analysis (EDAX).

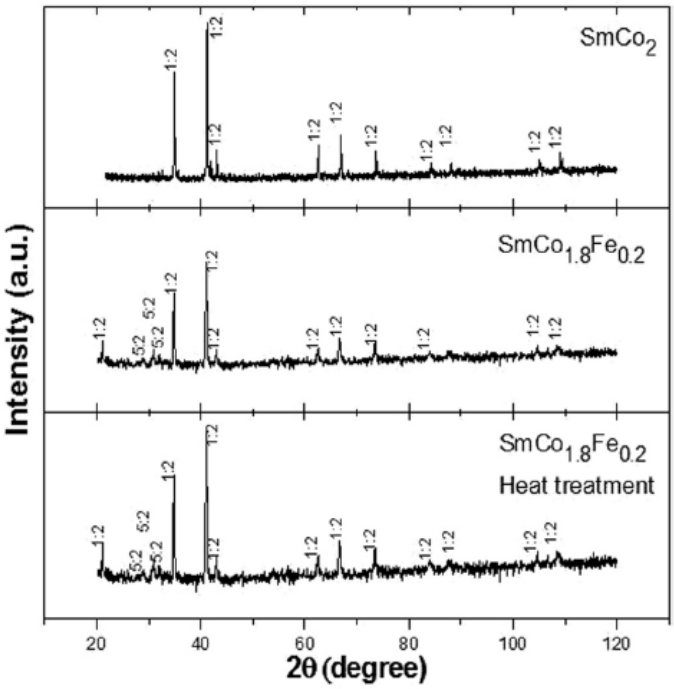


FIG. 1. X ray diffraction patterns for powders samples $SmCo_2$, $SmCo_{1.8}Fe_{0.2}$, and $SmCo_{1.8}Fe_{0.2}$ HT.

As shown in Fig. 3(a), two notable changes can be observed at 210 K and 175 K in the thermomagnetic curve of the $SmCo_2$ sample measured from 300 to 90 K under an applied magnetic field of $\mu_0 H = 0.02$ T. According to Ref. 6, the change at 210 K is a rhombohedral distortion of the $SmCo_2$ cubic crystal lattice, but the authors did not qualify the order of the structural transition. It would be important to do additional experiments on thermal hysteresis, field hysteresis, or neutron powder diffraction aiming to determine the order of this cubic to rhombohedral transition. The change at 175 K is accredited to a spin reorientation transition similarly observed in other laves phases like $SmFe_2$, where spin orientation changes from the [011] to [111] direction when the temperature is higher than 175 K.7 The ferromagnetic to paramagnetic Curie temperature was determined at 220 K.

In Fig. 3(b) is observed the ferromagnetic to paramagnetic transition at Curie temperatures of 300 and 290 K for the $SmCo_{1.8}Fe_{0.2}$ sample with and without heat treatment, respectively; these thermomagnetic curves were measured from 400 to 100K under an applied magnetic field of μ_oH=0.02 T. It can be noticed that the magnetization change at the Curie temperature is more abrupt in the heat treated sample, which is probably due to a more homogeneous distribution of Fe. Figure 4(a) shows isothermal magnetization curves for $SmCo_2$ pressed powders measured for temperatures between 100 and 280 K with applied magnetic fields from μ_oH=0 to 1.5 T.

TABLE I. Rietveld analysis for phase quantification results (% wt)

Phase	$SmCo_2$	Sm_2Co_7	Sm_5Co_2
ICSD	625219	2054	327
$SmCo_2$	86.7%	13.3%	-
$SmCo_{1.8}Fe_{0.2}$	72.24%	-	27.76%
$SmCo_{1.8}Fe_{0.2}$ HT	72.65%	-	27.35%

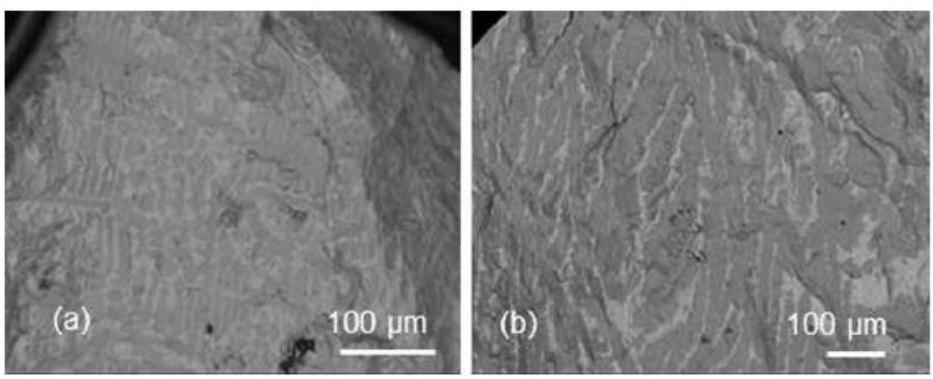
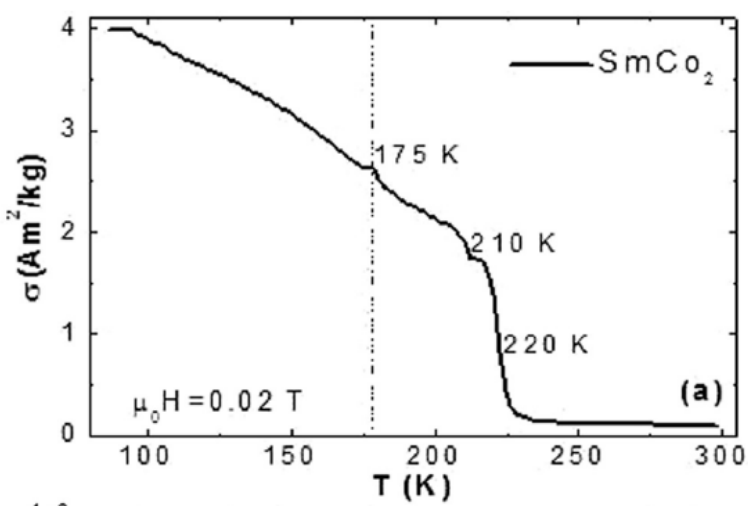


FIG. 2. (a) $SmCo_{1.8}Fe_{0.2}$ alloy micrograph. (b) $SmCo_{1.8}Fe_{0.2}$ HT alloy micrograph.

Figure 4(b) shows the magnetic entropy change curve calculated from these magnetization isotherms. The maximum magnetic entropy change, ΔS_M = 3.61 J/kg·K, occurs at the spin reorientation temperature of 175 K, and it is greater than the magnetic entropy change at the Curie temperature of 220 K. Calculated refrigerant capacity (RC) is 37 J/kg.

Isothermal magnetization curves for pressed powders of $SmCo_{1.8}Fe_{0.2}$ samples thermally untreated and treated from 100 to 395 K with applied magnetic fields from μ_oH = 0-5.0 T were measured (not shown here). Figures 5(a) and 5(b) show the corresponding calculated magnetic entropy change curves where it can be observed that the magnetocaloric effect is proportional to the maximum applied magnetic field. The maximum magnetic entropy change of the thermally untreated $SmCo_{1.8}Fe_{0.2}$ sample is ΔS_M J/kg·K at 300 K for μ_oH = 1.5 T, and the calculated refrigerant capacity (RC) is 13.5 J/kg.



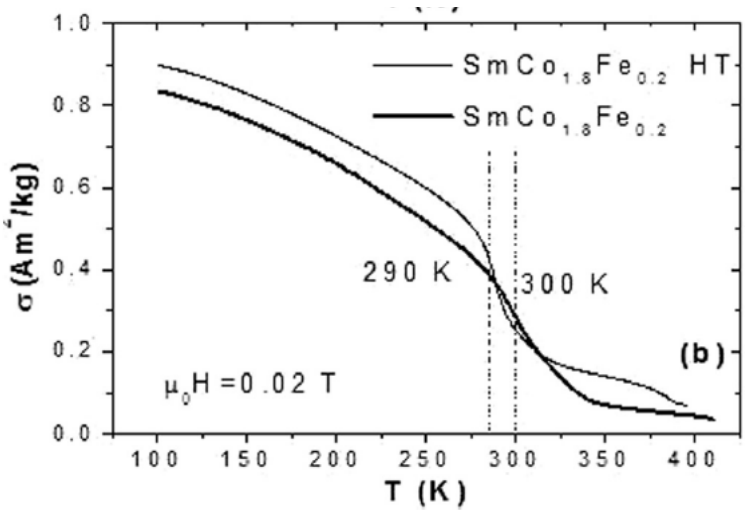


FIG. 3. Thermomagnetic curves for (a) $SmCo_2$, (b) $SmCo_{1.8}Fe_{0.2}$, and $SmCo_{1.8}Fe_{0.2}$ HT pressed powders.

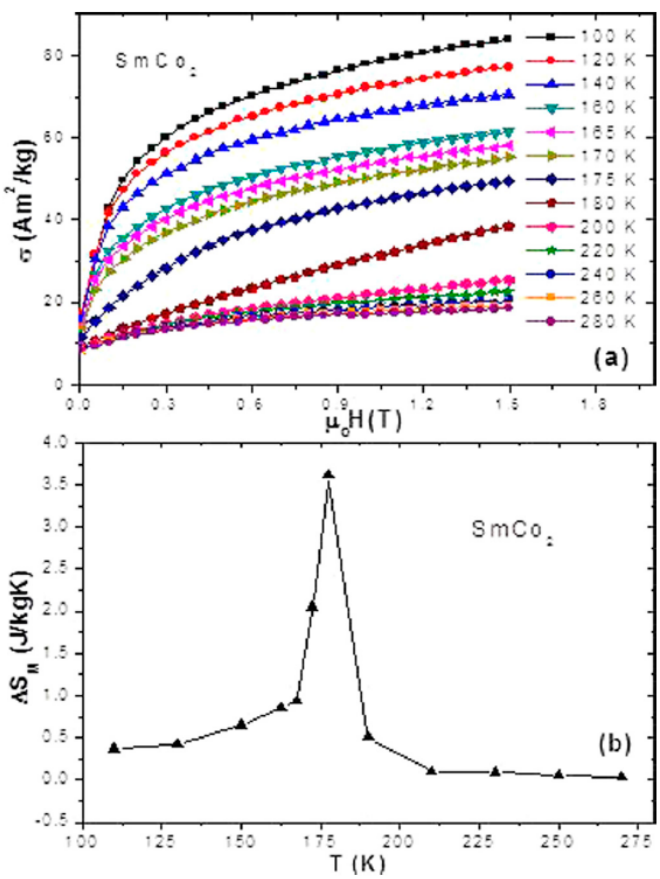


FIG. 4. (Color online) (a) Magnetization isotherms and (b) Magnetic entropy change for $SmCo_2$ pressed powders.

For the treated $SmCo_{1.8}Fe_{0.2}$ sample, the maximum magnetic entropy change is ΔS_M=0.28 J/kg·K at 290 K for $\mu_o H$=1.5 T, and the calculated refrigerant capacity (RC) is 13.5 J/kg. The heat treated sample shows a slight increase of the maximum value of magnetic entropy change, probably related to a more homogeneous distribution of Fe. The RC temperature range for Fe doped compounds is wider than $SmCo_2$, but the maximum magnetic entropy change is not enough to make a difference. The magnetic entropy change for $SmCo_2$ is several times higher than $SmCo_{1.8}Fe_{0.2}$, but the origin of each one is different. If the magnetic entropy change at T_C=220 K in $SmCo_2$ (ΔS_M=0.09 J/kg·K) is compared with those (T_C=300 and 290 K, respectively) of Fe doped compounds (ΔS_M=0.20 and 0.28 J/kg·K, respectively), the magnitude of each one is from the same order.

Conclusions

The replacement of 1/10 of Co atoms for Fe atoms in the $SmCo_2$ compound shifts the Curie temperature from 220 K to room temperature. The compound $SmCo_2$ shows a magnetic entropy change maximum, ΔS_M = 3.61 J/kg·K at the spin reorientation transition T_{SR}=175 K for an applied magnetic field of $\mu_o H$=1.5 T; this magnetic entropy change is greater than the magnetic entropy change at the ferromagnetic to paramagnetic transition temperature (T_C=220 K).

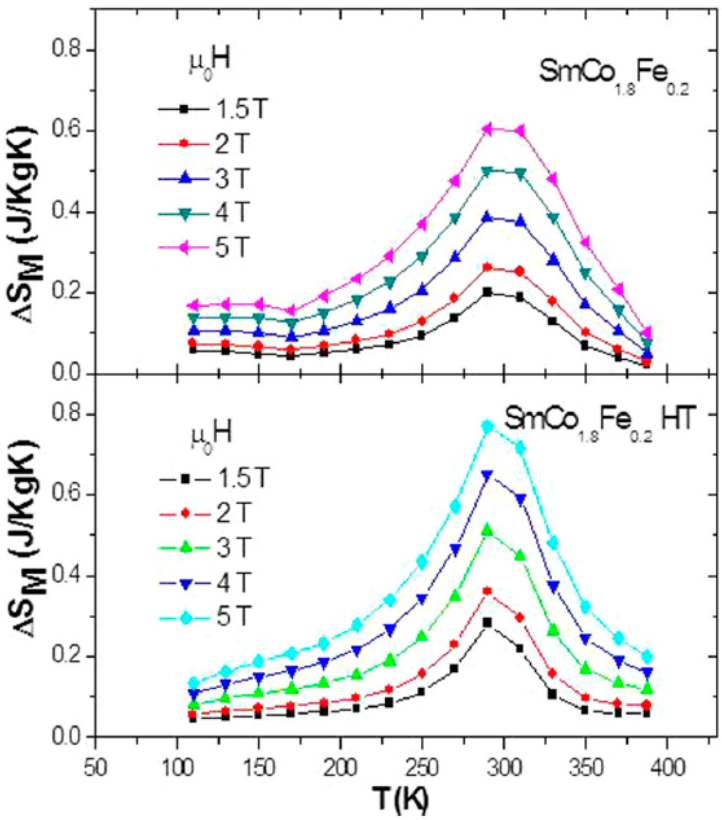


FIG. 5. (Color online) (a) Magnetic entropy change for $SmCo_{1.8}Fe_{0.2}$ and (b) $SmCo_{1.8}Fe_{0.2}$ HT at different applied magnetic fields.

The addition of Fe to the $SmCo_2$ compound practically suppresses the spin reorientation transition of the $SmCo_{1.8}Fe_{0.2}$ compounds, and the magnetic entropy change maximum appears at the Curie temperature. The magnetic entropy change at Curie temperature for all samples at μ_oH = 1.5 T maintains a close difference between each other, highlighting the role of the spin reorientation transition in obtaining a high entropy change in the $SmCo_2$ compound.

Acknowledgments

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References

1.- M. Parra-Borderíasa, F. Bartoloméa, J. Herrero-Albillos, and L. M. García, J. Alloys Compd. 481, 48 (2009).

2.- N. K. Singh, K. G. Suresh, A. K. Nigam, S. K. Malik, A. A. Coelho, and S. Gama, J. Magn. Magn. Mater. 317, 68 (2007).

3.- E. Gratz, and A. S. Markosyan, J. Phys.: Condens. Matter 13, R385 (2001).

4.- N. A. de Oliveira, P. J. Von Ranke, M. V. Tovar Costa, and A. Troper, Phys. Rev. B. 66, 094402 (2002).

5.- E. Brück, J. Phys. D 38, R381 (2005).

6.- Cz. Kapusta, I. S. Oliveira, P. C. Riedi, E. Gratz, G. Wiesinger, H. Figiel. and A. P. Guimaraes, J. Magn. Magn, Mater. 177, 1121 (1998).

7.- A. M. van Diepen, H. W. de Wijn, and K. H. J. Buschow, Phys. Rev. B. 8, 1125 (1973).