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GREAT MAGNETIC ENTROPY CHANGE IN La(Fe, M)$_{13}$ (M=Si, Al) WITH Co DOPING*

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Very large magnetic entropy change $\Delta S_{\rm M}$, which originates from a fully reversible second-order transition at Curie temperature $T_{\rm C}$, has been discovered in compounds La(Fe, Si)$_{13}$, La(Fe, Al)$_{13}$ and those with Co doping. The maximum change $\Delta S_{\rm M} \approx 19\,{\rm J\cdot kg^{-1}\cdot K^{-1}}$, achieved in $LaFe_{11.4}Si_{1.6}$ at 209K upon a 5T magnetic field change, exceeds that of Gd by more than a factor of 2. The $T_{\rm C}$ of the Co-doped compounds shifts to higher temperatures. $\Delta S_{\rm M}$ still has a considerable large magnitude near room temperature. The phenomena of very large $\Delta S_{\rm M}$, convenience of adjustment of $T_{\rm C}$, and also the superiority of low cost, strongly suggest that the compounds La(Fe, M)$_{13}$ (M=Si, Al) with Co doping are suitable candidates for magnetic refrigerants at high temperatures.

Keywords: $NaZn_{13}$-type compounds, magnetic entropy change
PACC: 7530S, 7550B, 6550

Magnetic refrigerators provide an alternative method for cooling and gas liquefaction in cases where conventional thermomechanical cooling techniques do not satisfy the increasing practical requirements of capacity, mass, and ecological cleanliness. The study of magnetocaloric effect (MCE) in various magnetic materials is gaining worldwide attention.[1−9] Recently, the interest in the research of MCE at high temperatures is considerably enhanced. Some interesting materials, such as superparamagnetic materials,[4−6] polycrystalline perovskite manganese oxides[7,8,10] etc., were found to show large MCE at high temperatures under appropriate fields. A more exciting discovery was the giant MCE in $Gd_5(Si_xGe_{1-x})_4$,[1,11] which makes the magnetic refrigerant technique potentially viable in a wide temperature range. However, the preparation of GdSiGe materials requires Gd with extremely high purity,[12] and this prevents them to become commercial magnetic refrigerants. Therefore, the search for other materials, especially those of low cost and exhibiting large magnetic entropy change at high temperatures, is of great interest and urgency.

Rare earth intermetallic compounds are promising materials for magnetic refrigeration at different temperatures. However, most intermetallic compounds, which will be in a magnetic order at high temperatures, show significantly lower MCE than Gd. For a long time Gd has been considered to be the most suitable magnetic refrigerant used near room temperature, the reported $|\Delta S|$ value of which was $\sim 13.7\,{\rm J\cdot kg^{-1}\cdot K^{-1}}$ under a magnetic field of 8T at $T_{\rm C}(\sim 293{\rm K})$.[13] Up to date there have been few reports of magnetic entropy change $|\Delta S|$ in the rare earth intermetallic compounds which exceeds that of Gd. In a study of magnetic properties of the $NaZn_{13}$-type rare earth transition metal intermetallic compounds, we discovered a very large magnetic entropy change in La(Fe, M)$_{13}$ (M = Si, Al) with Co doping.

The highest content of 3d metal in any known rare earth intermetallic compounds and their cubic symmetry structure make the $NaZn_{13}$-type intermetallic compounds show high magnetization and excellent soft ferromagnetic properties. Among the compounds with $NaZn_{13}$-type stucture, $LaFe_{13}$ or $LaNi_{13}$ does not exist due to the positive heat of formation for La and Fe or Ni, but a small addition of Si or Al can stabilize the compounds, resulting in the cubic $NaZn_{13}$ type pseudobinary La($T_{1-x}M_x$)$_{13}$ compounds, where T=Fe, Ni and M=Si, Al.[14] The compounds La($Fe_{1-x}Si_x$)$_{13}$, x=1.4–2.4, have a cubic $NaZn_{13}$-type structure and show isotropic Heisen-

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berg ferromagnetic behavior.[15,16] At low concentration of Si, they have high magnetic moment and the magnetization shows a sharp change at the Curie temperature.[16] La(Fe$_x$Al$_{1-x}$)$_{13}$ compounds exist for x=0.46–0.92, and for x from 0.88 to 0.92 they show weak antiferromagnetic coupling.[17] A small amount of Co addition can make its antiferromagnetic coupling collapse fully, resulting in a perfect ferromagnetic state with high magnetic moment. With Co doping the T_C of the two compounds shifts to higher temperatures. We discovered a very large magnetic entropy change in compounds La(Fe, Si)$_{13}$, La(Fe, Al)$_{13}$ and those with Co doping in a wide range of high temperatures. This letter reports the typical results obtained in compounds $LaFe_{11.4}Si_{1.6}$, $LaFe_{10.98}Co_{0.22}Si_{1.8}$, and $LaFe_{11.12}Co_{0.71}Al_{1.17}$, with T_C at 209K, 242K, and 279K, respectively.

The ingots of the samples studied were prepared by repeatedly arc-melting the appropriate amount of the starting materials with purity of 99.9% and subsequent homogenization by annealing at 1273K for 50 days. X-ray powder diffraction (XRD) confirmed that all samples crystallized in a nearly single phase of the cubic $NaZn_{13}$ type structure, except that a small amount of impurity is α-Fe.

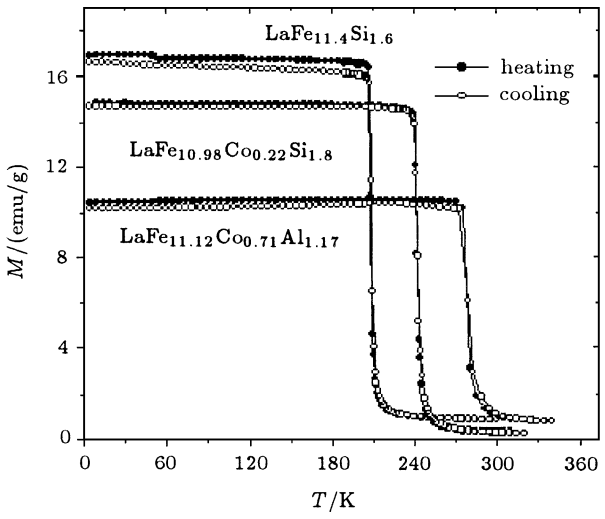


Fig.1. Temperature dependence of magnetization upon heating and cooling under 0.01T.

All magnetic measurements were performed using a Quantum Design SQUID magnetometer (MPMS-5S). Figure 1 shows the temperature dependence of magnetization upon heating and cooling under a field of 0.01T, showing sharp changes at T_C. The samples were cooled under zero field to 5K first. No temperature hysteresis is shown between the transitions on heating and cooling for any sample, indicating that the transition is of second-order in nature. The T_C's are found to be 209K, 242K, and 279K for $LaFe_{11.4}Si_{1.6}$, $LaFe_{10.98}Co_{0.22}Si_{1.8}$, and $LaFe_{11.12}Co_{0.71}Al_{1.17}$, respectively. We also performed the magnetic hysteresis loop measurements at low temperature (5K) in order to examine the magnetic hardness. The fact of non-hysteretic $M(H)$ curve and very low saturation magnetic field suggests that these materials are magnetically very soft.

We measured the magnetization isotherms of sample $LaFe_{11.4}Si_{1.6}$ under increasing and decreasing field in a wide temperature range. In the vicinity of the Curie temperature from 200 to 230K the temperature step of 2K is chosen, and for the far away regions 165–200K and 230–265K a step of 5K is chosen. With increasing temperature the usual nonlinearity of the M-H plots at low fields, typical for a ferromagnet, slowly diminishes, and above T_C all of them exhibit linear behavior. The existence of a very little nonlinearity above T_C at low field is due to the small amount of impurity of α-Fe. Every M-H plot shows a completely reversible behavior during the field increase and decrease, this is characteristic of a soft ferromagnet. One knows that a complete reversibility of the MCE requires that no hysteresis of both the temperature and magnetic field appear in the vicinity of a magnetic-ordering temperature. This is easily achievable for a soft ferromagnetic material. The samples of the present study are just the case.

From thermodynamical theory, the magnetic entropy change $\Delta S(T,\ H)$ is given by the Maxwell relation,[1,8,18]

$$\Delta S(T,H) = S(T,H) - S(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H.$$

The calculated ΔS during field increase is equal to that during field decrease. Figure 2 shows the $|\Delta S|$ curves of $LaFe_{11.4}Si_{1.6}$ under different fields of 2 and 5T. The peak values of 10.5, 14.3, and 19.3 J·kg^{-1}·K^{-1} are obtained under fields of 1T, 2T, and 5T, respectively. For comparison, we also measured the magnetic entropy change of Gd (Fig.2), and obtained $|\Delta S|$ ~2.9, 5.0, and 9.7 J·kg^{-1}·K^{-1} at T_C under the same fields; the measured values agree with those of early reports.[1,13,18] The maximum $|\Delta S|$ value of $LaFe_{11.4}Si_{1.6}$ exceeds that of Gd by more than a factor

of 2. The value under a field of 1T is of the same magnitude as that of Gd under 5T, comparing the peak values, without consideration of the temperature difference. The reported giant magnetic entropy change in $Gd_5Ge_2Si_2$[1] is of approximately the same order of magnitude as observed in $LaFe_{11.4}Si_{1.6}$. However, due to the nature of first order transition in $Gd_5Ge_2Si_2$, a little thermal hysteresis still appears between the transitions on warming and cooling. Using Maxwell relation to calculate ΔS can accurately screen the intrinsic nature of the magnetic refrigerant materials, especially for the materials with second-order transition. This indirect method of measuring MCE has long been suggested rightfully according to Landau theory, and successfully verified as a reliable way to evaluate candidate materials for magnetic refrigeration.[18]

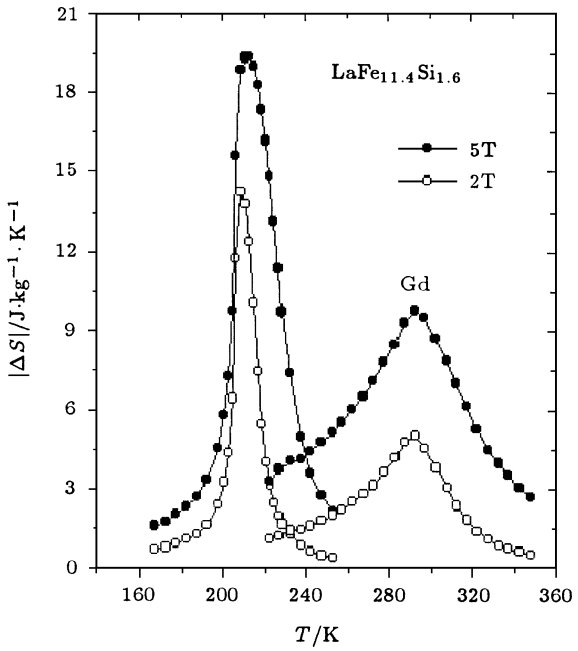


Fig.2. $|\Delta S|$ vs T curves of $LaFe_{11.4}Si_{1.6}$ and Gd under fields of 2 and 5T.

Figure 3 shows the obtained $|\Delta S|$ of other two samples, the magnitude of which is lower than that given above but still larger than or comparable to that of Gd. The obtained values of ΔS are 6.3 and 4.6 $J \cdot kg^{-1} \cdot K^{-1}$ under fields of 2T, and 11.5 and 9.1 $J \cdot kg^{-1} \cdot K^{-1}$ under 5T at T_C for $LaFe_{10.98}Co_{0.22}Si_{1.8}$, and $LaFe_{11.12}Co_{0.71}Al_{1.17}$, respectively. It is obvious that the T_C of Co-doped samples is obtained at higher temperatures.

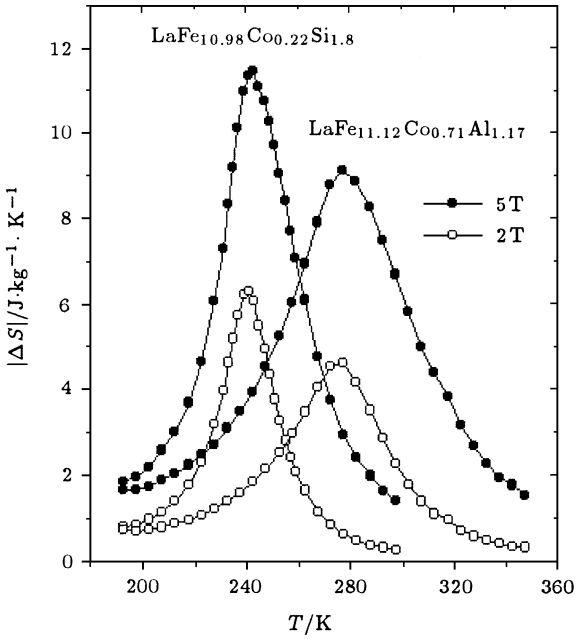


Fig.3. $|\Delta S|$ vs T curves of $LaFe_{10.98}Co_{0.22}Si_{1.8}$ and $LaFe_{11.12}Co_{0.71}Al_{1.17}$ under fields of 2 and 5T.

The origin of the large magnetic entropy change in compounds La(Fe, M)$_{13}$ (M=Si, Al) with Co doping should be ascribed to their high magnetic moment and the rapid change of magnetization at T_C. As was explained in Ref.[16], the extremely sharp transition at T_C, especially in the sample of $LaFe_{11.4}Si_{1.6}$, is just the same as that of ideal ferromagnets. The bulk magnetization of these compounds originates from Fe and Co atoms and thus the high content of Fe is the origin of the high magnetization. In their $NaZn_{13}$-type structure, the two different Zn sites are occupied by Fe in a ratio of 1:12, and each Fe^1 atom is surrounded by an icosahedron of Fe^2 atoms. While Si or Al atoms are substituted for Fe^2 atoms. In the past, MCE in 4f alloys was studied much more extensively than that in 3d alloys simply because 4f metals and their alloys have high angular momentum quantum number J.[19] In 3d alloys, due to the variation of local environment of 3d atoms, there exists a distribution of exchange fields. Their relative high moment and strong exchange interaction suggest that 3d alloys are also ideal materials showing large MCE, as evidenced now by our experiments. Usually, in 3d alloys a stronger exchange interaction is shown and thus their magnetization at T_C changes more rapidly compared with that in 4f alloys. Generally, 4f atoms have a higher moment than 3d atoms but show weak RKKY exchange interaction.

In summary, we have discovered a very large entropy change in compounds La(Fe, M)$_{13}$ (M=Si, Al)

with Co doping in a wide temperature range at high temperatures. This discovery is expected to make active magnetic regenerator (AMR) and magnetic refrigeration (MR) become a viable technology. To our knowledge, so large a magnetic entropy change involving second-order transition at high temperatures is reported for the first time. The excellent soft magnetic properties of our materials would be much beneficial to the magnetic cooling efficiency. The continuous variation of T_C with the increase of Co content makes it easy to get a constant ΔS at a wide temperature span. More exciting and important superiority is that our compounds are easier to fabricate and much cheaper as compared with the previously reported materials, such as FeRh, Gd, and GdSiGe etc. In La(Fe, M)$_{13}$ (M=Si, Al) with Co doping the main content is the richest metal of Fe. In short, the advantages of large magnetic entropy change, easy preparation, low cost and the convenience in controlling transition temperature strongly suggest that the compounds La(Fe, M)$_{13}$ (M=Si, Al) with Co doping are suitable candidates for AMR and MR.

REFERENCES

[1] V. K. Pecharsky, K. A. Gschneidner, Jr., *Phys. Rev. Lett.*, **78**(1997),4494.

[2] K. A. Gschneidner, Jr., H. Takeya, J.O. Moorman, V. K. Pecharsky, *Appl. Phys. Lett.*, **64**(1994),253.

[3] X. Y. liu, J. A. Barclay, B. R. Gopal, M. Foldeaki, R. Chahine, T. K. Bose, P. J. Schurer, J. L. LaCombe, *J. Appl. Phys.*, **79**(1996),1630.

[4] Y. Z. Shao, J. Zhang, J. K. L. Lai, C. H. Shek, *J. Appl. Phys.*, **80**(1996),76.

[5] R. D. McMichael, R. D. Shull, L. J. Swartzendruber, L. H. bennett, R. E. Watson, *J. Magn. Magn. Mater.*, **111**(1992),29.

[6] R. D. Shull, L. H. Bennett, L. J. Swartzendruber, "Nanocomposite Material for Magnetic Refrigeration and Superparamagnetic Systems Using the Same", US Patent #5381664(1995).

[7] X. X. Zhang, J. Tajada, Y. Xin, G. F. Sunm, K. W. Wong, X. Bohigas, *Appl. Phys. Lett.*, **69**(1996),3596.

[8] Z. B. Guo, Y. W. Du, J. S. Zhu, H. Huang, W. P. Ding, D. Feng, *Phys. Rev. Lett.*, **78**(1997),1142.

[9] F. X. Hu, B. G. Shen, J. R. Sun, *Appl. Phys. Lett.*, **76**(2000),3460.

[10] Z. B. Guo, J. R. Zhang, H. Huang, W. P. Ding, Y. W. Du, *Appl. Phys. Lett.*, **70**(1997),904.

[11] V. K. Pecharsky, K. A. Gschneidner, Jr., *Appl. Phys. Lett.*, **70**(1997),3299.

[12] K. A. Gschneidner, Jr., V. K. Pecharsky, *J. Appl. Phys.*, **85**(1999),5365.

[13] T. Hashimoto, T. Numasawa, M. Shino, T. Okada, *Cryogenics*, **21**(1981),647.

[14] P. I. Kripyakevich, O. S. Zarechnyuk, E. I. Gladyshevsky, O. I. Bodak, *Z. Anorg, Chem.*, **358**(1968),90.

[15] W. H. Tang, J. K. Liang, G. H. Rao, X. H. Yan, *Phys. Stat. Sol. (A)*, **141**(1994),217.

[16] T. T. M. Palstra, J. A. Mydosh, G. J. Nieuwenhuys, A. M. van der Kraan, K. H. J. Buschow, *J. Magn. Magn. Mater.*, **36**(1983),290.

[17] T. T. M. Palstra, G. J. Nieuwenhuys, J. A. Mydosh, K. H. J. Buschow, *Phys. Rev.*, **B31**(1985),4622.

[18] M. Foldeaki, R. Chahine, T. K. Bose, *J. Appl. Phys.*, **77**(1995),3528.

[19] V. K. Pecharsky, K. A. Gschneidner, *J. Magn. Magn. Mater.*, **200**(1999),44.