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2000 J. Phys.: Condens. Matter 12 L691

(http://iopscience.iop.org/0953-8984/12/46/101)

J. Phys.: Condens. Matter **12** (2000) L691–L696. Printed in the UK PII: S0953-8984(00)18179-2

**LETTER TO THE EDITOR**

# Magnetic entropy change in $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$

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Received 20 October 2000

**Abstract.** Magnetization of compound $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ was measured carefully as functions of temperature and applied field around its Curie temperature of ∼198 K. Magnetic entropy change $|\Delta S|$, allowing estimation of the magnetocaloric effect (MCE), was determined based on thermodynamic Maxwell's relation. The achieved magnitude of $|\Delta S|$ reaches 10.6 J kg$^{-1}$ K$^{-1}$ under a field of 5 T. The considerable entropy change is believed to be due to the high magnetization and the sharp change in magnetization at $T_C$. It is found that the magnetic phase transition is completely reversible in temperature, indicating a nature of second-order phase transition.

Magnetic refrigeration is a promising technology for a broad range of applications [1–3]. Recently, interest in research into magnetocaloric effect (MCE) has been considerably enhanced owing to its potential impact on energy savings and environmental concerns [3–18]. Much effort has been dedicated to the search for suitable refrigerants. Some interesting materials, such as superparamagnetic materials [5, 6], polycrystalline perovskite manganese oxides [12–15] etc, have been discovered showing considerable magnetocaloric effect at relatively high temperatures. A variety of prototype materials and intermetallic compounds were studied in an attempt to achieve large MCE [17], of which GdSiGe alloys were recently discovered to exhibit great MCE in a very wide temperature range [16]. The compounds with cubic $NaZn_{13}$-type structure have not been studied in this way. They show excellent soft ferromagnetism with high saturation magnetization due to the high concentration of 3d metal and cubic symmetry structure. It is known that large MCE is expected in ferromagnets with high magnetization near their phase transition temperatures [3]. Therefore, the study of magnetic entropy change on the $NaZn_{13}$-type compounds is of significance and interest.

Among the compounds with $NaZn_{13}$-type structure, $LaCo_{13}$ is the only compound among the 45 binary systems consisting of one rare earth element and one of the metals Fe, Co, or Ni [19], but its $T_C$ is as high as 1318 K. $LaFe_{13}$ (or $LaNi_{13}$) does not exist due to its positive formation heat from La and Fe (or Ni); however, a small amount of Si or Al addition can stabilize the structure, resulting in pseudobinary $La(T_{1-x}M_x)_{13}$ compounds, where T = Fe, Ni and M = Si, Al [20]. Their $T_C$ or $T_N$ (Néel temperature) are below or near room temperature. Since the maximum magnetic entropy change of a ordered magnetic material occurs near the phase transition temperature upon an application of a magnetic field, these

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0953-8984/00/460691+06$30.00  

alloys would be suitable magnetic refrigerator materials at the corresponding temperatures, provided that they also exhibit the suitable entropy change. Previous investigations [21–23] indicate that $La(Fe_xAl_{1-x})_{13}$ compounds with $NaZn_{13}$-type structure exist in the range $0.46 \leqslant x \leqslant 0.92$ and display three different magnetic behaviour—mictomagnetism, ferromagnetism, and antiferromagnetism with the variation of iron concentration. At $0.88 \leqslant x \leqslant 0.92$ they show weak antiferromagnetic coupling, which can be overcome by applying a small field of a few Teslas and cause the spin–flip transitions to the fully saturated ferromagnetic state [22]. Our experiments confirm that the sample $LaFe_{11.7}Al_{1.3}$ (corresponding $x = 0.90$) shows antiferromagnetism, and further reveals that a small doping of Co can make its antiferromagnetic coupling collapse completely, resulting in a whole ferromagnetic state. In this letter, we report the investigation of magnetic entropy change, $|\Delta S|$, in compound $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$.

The ingots of the present sample were prepared by repeatedly arc-melting the appropriate amount of the starting materials with purity of 99.9wt% and subsequently homogenizing by annealing at 1273 K for 30 days. The ingots were then quenched in liquid nitrogen. Figure 1 is the x-ray powder diffraction (XRD) pattern, which shows that the sample crystallized in a nearly single phase of the cubic $NaZn_{13}$-type structure. Marked by * in the pattern is the impurity of $\alpha$-Fe, the amount of which is estimated to be 8wt% based on the Rietveld refinement of x-ray diffraction data.

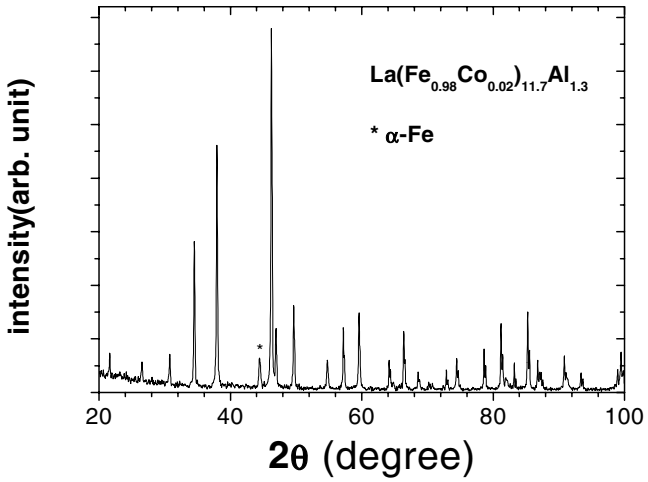


**Figure 1.** x-ray powder diffraction(XRD) pattern of $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$.

All magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer. The low-magnetic-field temperature-dependent magnetization has been measured in the zero-field-cooled (ZFC) and field-cooled (FC) process in order to determine the transition temperature and the nature of the transition [24]. The samples were first cooled in zero-field to 5 K, then a small field was applied to the sample, after that the magnetization was measured in the warming process up to 300 K, thus the ZFC magnetization curve was obtained. The FC magnetization was measured in the cooling process to 5 K with the same field. Figure 2 presents the ZFC-FC magnetization of $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ obtained under a magnetic field of 0.02 T. The Curie temperature $T_C$ is determined as $\sim$198 K. It is evident that the present sample exhibits a completely reversible temperature dependence of magnetization at $T_C$, thus the reversible magnetic entropy change

on temperature is expected. The magnetization changes sharply at $T_C$ even in a high magnetic field of 1 T, inset of figure 2 (this field is much higher than the saturation field). One should note that such a sharp change of magnetization suggests a large magnetic entropy change. The temperature behaviour of magnetization, shown in figure 2, indicates a nature of a second order phase transition in a simple ferromagnetic material. We also performed the magnetic hysteresis loop measurements at 5 K in order to examine the magnetic hardness. The facts of the small coercive fields less than 20 Oe and the small ratio of the remnant magnetization to saturation magnetization ($< 1\%$) suggest that our material is magnetically very soft.

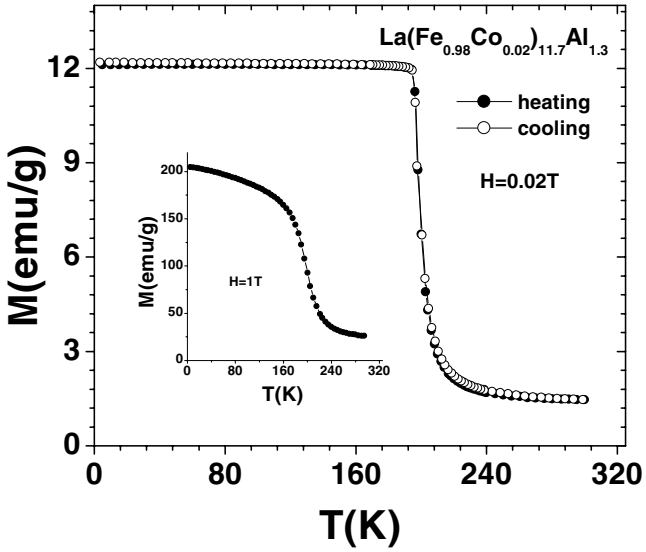


**Figure 2.** Temperature dependence of magnetization M–T of $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ measured under a field of 0.02 T. Inset shows M–T obtained under 1 T.

Figure 3 displays the magnetization isotherms of $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ measured in a wide temperature range covering the Curie temperature with temperature steps of 5 K. The sweep rate of field is slow enough to ensure that M–H curves are recorded in an isothermal process. With increasing temperature the typical relations of M–H for a soft ferromagnet change to the ones for a paramagnetic material. As is well known, at $T \gg T_C$ the M–H has a linear dependence for not very large field. At temperatures much higher than the $T_C$, a slight nonlinearity in M–H curves in the low fields is found, which may be ascribed to the existence of the impurity of $\alpha$-Fe phase. Moreover, the M–H curves on field increase and decrease show a completely reversible behaviour at different temperatures (not shown), which is the characteristic of a soft ferromagnet. It is well known that a completely reversible MCE requires that there is no hysteresis existing in the magnetization as a function of both temperature and magnetic field. This is easily achievable for a soft ferromagnetic material. The present sample is just such a case.

According to the thermodynamical theory, the magnetic entropy change $\Delta S(T, H)$ is given by the Maxwell relation [25–27]

$$\Delta S(T, H) = S(T, H) - S(T, 0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \tag{1}$$

It has been suggested experimentally that, the entropy change $\Delta S(T, H)$ can be obtained approximately from the isothermal magnetization measured at the discrete temperatures with

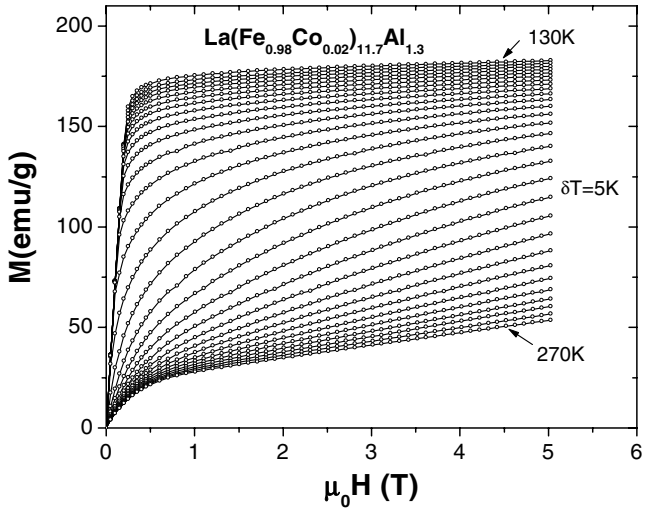


**Figure 3.** Isothermal M–H curves of $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ measured at different temperatures from 130 K to 270 K. The temperature step is 5 K.

the numerical formula

$$-\Delta S_M = \sum_i \frac{1}{T_{i+1} - T_i}(M_i - M_{i+1})\Delta H_i \tag{2}$$

where $M_i$ and $M_{i+1}$ are the magnetization values measured at temperatures $T_i$ and $T_{i+1}$ in a field H, respectively [12, 25]. It is an indirect, fast measurement of the MCE, but it gives the crucial information for determining the quality of a magnetic refrigerator material [25–27]. The accuracy of the calculated $\Delta S$ depends on the accuracy of the measurements of magnetic moment, temperature, and magnetic field. The estimated accuracy of $\Delta S$ obtained using above technique is in the range of 3–10% [26].

Figure 4 shows the calculated $\Delta S(H, T)$ of $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ as a function of temperature for different magnetic fields, noting that $|\Delta S|$ has an extremely large magnitude. The contribution of the minor phase $\alpha$-Fe to the $|\Delta S|$ should be negligibly small, because the very high Curie temperature $T_C$ (∼1040 K) of $\alpha$-Fe leads to a small $(\partial M_{Fe}/\partial T)_H$ at temperatures near the $T_C$ (∼198 K) of $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$. The $|\Delta S|$ peak values of the present sample under applied fields of 2 T and 5 T are 5.9 and 10.6 J $kg^{-1}$ $K^{-1}$, respectively. Such a high magnitude of $|\Delta S|$ involving a second-order transition was rarely observed in 3d alloys at the corresponding temperature range. This observation may be also of some theoretical interest. It is well known that pure Gd and some of its alloys are suitable magnetic refrigerants at high temperatures near room temperature. The magnetic entropy change of pure Gd, also shown in figure 4, has values of 5.0 and 9.7 J $kg^{-1}$ $K^{-1}$ at its $T_C$ (∼293 K) under 2 T and 5 T, respectively.

The origin of the large magnetic entropy change in compound $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ should be attributed to the high magnetic moment and the rapid change of magnetization at $T_C$. The bulk magnetization of compound $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ originates from Fe and Co atoms [23] and thus the high content of Fe is the origin of high saturation magnetization. From M–H curves at 5 K the saturation magnetization was determined as 2.0 $\mu_B$/(Fe,Co) after deducting the contribution of $\alpha$-Fe phase. The observation of such a large magnetic entropy change in a 3d alloy is of significance for both practical application and basic research. In the past, 4f

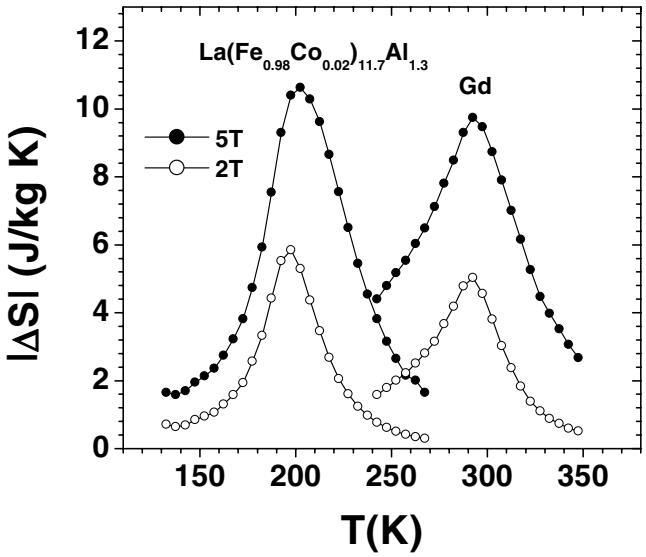


**Figure 4.** Magnetic entropy change of $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ and Gd for the magnetic field changes of 0 to 2 and 0 to 5 T, respectively.

alloys were studied much more intensively for MCE than the 3d alloys mainly because the 4f metals and their alloys have high angular momentum quantum number $J$ [17]. It is well known that the strong exchange interactions between 3d atoms lead to a perfect long-range magnetic order below $T_C$ in a 3d alloy, which implies a sharper transition at $T_C$ in comparison with that in the 4f metals or their alloys. Although the 4f atoms have higher moment than the 3d atoms, the interactions between them is usually the weak RKKY interaction. It was theoretically found that the variation of the exchange energy upon the application of a magnetic field provides a significant contribution to entropy change [28]. The exchange interaction in our sample is probably more sensitive to applied filed than 4f-alloys. This, as well as its relatively high moment, may be the reason for the large magnetic entropy change in $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$, as observed in this work.

In summary, a considerable magnetic entropy change was observed in cubic $NaZn_{13}$-type compound $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$. The reversible behaviour of the second-order transition makes the design and construction of a refrigerator become simple. A further exciting and important improvement is that the compound is much cheaper than the materials previously reported, such as FeRh [7], Gd, GdSiGe [16, 29] etc. In short, the compound $La(Fe_{0.98}Co_{0.02})_{11.7}Al_{1.3}$ appears to be an attractive candidate for a magnetic refrigerant due to its low cost and extremely large entropy change.

This work was supported by the State Key Project of Fundamental Research and the National Natural Science Foundation of China. This work was also supported partially by Hong Kong RGC grants (DAG99/00-SC35, HKUST6157/00E). The author would also like to thank Dr J Wang for his help.

## References

[1] Hashimoto T, Numasawa T, Shino M and Okada T 1981 *Cryogenics* **21** 647

[2] Zimm C B, Jastrab A G, Sternberg A A, Pecharsky V K, Gschneidner K A Jr, Osborn M Jr and Anderson I 1998 *Adv. Cryog. Eng.* **43** 1759
[3] Tishin A M 1999 *Handbook of Magnetic Materials* vol 12, ed K H J Bushow (Amsterdam: Elsevier) pp 395–524
[4] Gschneidner K A Jr, Takeya H, Moorman J O and Pecharsky V K 1994 *Appl. Phys. Lett.* **64** 253
[5] Shao Y Z, Zhang J, Lai J K L and Shek C H 1996 *J. Appl. Phys.* **80** 76
[6] McMichael R D, Shull R D, Swartzendruber L J, Bennett L H and Watson R E 1992 *J. Magn. Magn. Mater.* **111** 29
[7] Annaorazov M P, Nikitin S A, Tyurin A L, Asatryan K A and Dovletov A Kh 1996 *J. Appl. Phys.* **79** 1689
[8] Dankov S Yu, Tishin A M, Pecharsky V K and Gschneidner K A Jr 1998 *Phys. Rev.* B **57** 3478
[9] Canepa F, Napoletano M, Palenzona A, Merlo F and Clrafici S 1999 *J. Phys. D: Appl. Phys.* **32** 2721
[10] Wada H, Tanabe Y, Hagiwara K and Shiga M 2000 *J. Magn. Magn. Mater.* **218** 203
[11] Sampathkumaran E V, Das I, Rawat R and Majumdar S 2000 *Appl. Phys. Lett.* **77** 418
[12] Zhang X X, Tajada J, Xin Y, Sunm G F, Wong K W and Bohigas X 1996 *Appl. Phys. Lett.* **69** 3596
[13] Guo Z B, Du Y W, Zhu J S, Huang H, Ding W P and Feng D 1997 *Phys. Rev. Lett.* **78** 1142
[14] Chaudhary S, Sunil Kumar V, Roy S B, Chaddah P, Krishnakumar S R, Sathe V G, Kumar A and Sarma D D 1999 *J. Magn. Magn. Mater.* **202** 47
[15] Szewczyk A, Szymczak H, Wisniewski A, Piotrowski K and Kartaszynski R 2000 *Appl. Phys. Lett.* **77** 1026
[16] Pecharsky V K and Gschneidner K A Jr 1997 *Appl. Phys. Lett.* 70 3299
[17] Pecharsky V K and Gschneidner K A Jr 1999 *J. Magn. Magn. Mater.* **200** 44
[18] Hu F X, Shen B G and Sun J R 2000 *Appl. Phys. Lett.* **76** 3460
[19] Buschow K H J 1977 *Rep. Prog. Phys.* **40** 1179
[20] Kripyakevich P I, Zarechnyuk O S, Gladyshevsky E I and Bodak O I 1968 *Z. Anorg. Chem.* **358** 90
[21] Tang W H, Liang J K, Rao G H and Yan X H 1994 *Phys. Status Solidi* A **141** 217
[22] Palstra T T M, Nieuwenhuys G J, Mydosh J A and Buschow K H J 1985 *Phys. Rev.* B **31** 4622
[23] Helmholdt R B, Palstra T T M, Nieuwenhuys G J, Mydosh J A, ven der Kraan A M and Buschow K H J 1986 *Phys. Rev.* B **34** 169
[24] Zhang X X, Hernandez J M, Tejada J and Ziolo R F 1996 *Phys. Rev.* B **54** 4101
[25] Foldeaki M, Chahine R and Bose T K 1995 *J. Appl. Phys.* **77** 3528
[26] Pecharsky V K and Gschneidner K A Jr 1999 *J. Appl. Phys.* **86** 565
[27] Sun J R, Hu F X and Shen B G 2000 *Phys. Rev. Lett.* at press
[28] Tishin A M 1997 *J. Alloys Compounds* **250** 635
[29] Gschneidner K A Jr and Pecharsky V K 1999 *J. Appl. Phys.* **85** 5365