Large magnetic entropy change in $La(Fe,Co)_{11.83}Al_{1.17}$

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Large magnetic entropy change with comparable magnitude to that of pure Gd has been observed in compounds $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x=0.06,0.08$) at their Curie temperatures of ~273 K and ~303 K, respectively. These compounds are of a cubic $NaZn_{13}$-type structure with soft ferromagnetism. The magnetic entropy change is reversible in the whole experimental temperature range from ~230 to ~330 K. The most interesting feature is that the Curie temperature can be easily tuned by adjusting the substitution of Co for Fe. It is suggested that the present compounds are suitable candidates for magnetic refrigerants in a wide range near room temperature. The calculated ΔS curve in the molecular field approximation is in a satisfactory agreement with the experimental one.

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As an alternative technology for cooling and gas liquefaction, magnetic refrigeration has attracted more and more attention for its advantages in capacity, mass and ecological cleanness in comparison with the conventional thermomechanical cooling techniques.[1–19] The research on the room-temperature magnetic refrigerant is of special interest for its widely practical application. Much effort has been dedicated to the search for suitable refrigerants. Some interesting materials, such as superparamagnetic materials,[3–5] polycrystalline perovskite manganese oxides,[7–10] etc., were discovered showing considerable magnetocaloric effect (MCE). A variety of prototype materials, intermetallic compounds and alloys of rare earths were studied in an attempt to achieve large magnetocaloric effect, of which GdSiGe alloys were recently discovered exhibiting great MCE in a very wide temperature range.[11,12] Near room temperature they show higher MCE than that of Gd which was thought to be the most suitable refrigerant near room temperature for a long time. However, 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 their high concentration of $3d$ metal and the cubic symmetry structure. One knows that large MCE is expected in magnetic materials with high magnetization.[18] Therefore, the study of magnetic entropy change on the $NaZn_{13}$-type compounds is of significance and interest.

The previous studies revealed that the $NaZn_{13}$-type compound $LaCo_{13}$, with T_C as high as 1318 K, is the only stable alloy among the RT_{13} alloys (R=rare earth elements, T =transition elements).[20] However, stable pseudobinary compounds $La(T,M)_{13}$ can be formed with a small amount of M, where T is Fe or Ni and M is Si or Al.[21] The Curie temperature T_C or Néel temperature T_N of those $La(T,M)_{13}$ alloys can be easily tuned in a wide temperature range near room temperature. Since the maximum magnetic entropy change of an ordered magnetic material occurs at the phase transition temperature upon an application of a magnetic field, these alloys would be good room-temperature magnetic refrigerator materials, provided that they also exhibit suitable entropy change. The magnetic properties and structures of these compounds have been carefully studied before.[22–25] The results indicate that $La(Fe_yAl_{1-y})_{13}$ compounds exist in the range of $0.46 \leqslant y \leqslant 0.92$ and display three different magnetic behavior—mictomagnetism, ferromagnetism, and antiferromagnetism with the variation of iron concentration. At the range of $0.88 \leqslant y \leqslant 0.92$ they show weak antiferromagnetic coupling, which can be overcome even by applying a small field of a few T and cause the spin-flip transitions to the fully saturated ferromagnetic state.[24]

In this paper, we report the observation of large magnetic entropy change $|\Delta S|$ in $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x=0.06,0.08$) alloys. These alloys appear to be very attractive candidates for magnetic refrigerants near room temperature for the following advantages: (a) showing a large magnetic entropy change $|\Delta S|$, which is comparable with that of Gd; (b) reversible in field and temperature; (c) easily tunable T_C near room temperature; and (d) much cheaper raw materials (even with relatively low purity) than the rare earth elements (Gd, Dy).

Our experiments confirm that the sample $LaFe_{11.83}Al_{1.17}$ ($y=0.91$) shows antiferromagnetism, and further reveal that a small doping of Co can make its antiferromagnetic coupling collapse completely, resulting in a whole ferromagnetic state. The T_C shifts to high temperature with the increase of Co doping. We chose samples of $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x=0.06,0.08$) with T_C around room temperature and found both of them show large magnetic entropy change.

The ingots of the present samples were prepared by repeatedly arc melting the appropriate amount of the starting materials with purity of 99.9 wt. % and subsequently homogenizing by annealing at 1273 K for 50 days. The ingots were then quenched in liquid nitrogen. Figure 1 is the x-ray powder diffraction (XRD) patterns, which shows that the samples crystallized in a single phase of the cubic $NaZn_{13}$-type structure. All magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer. The inset of Fig. 1 is the temperature dependency of the ac susceptibility χ on heating and cooling, which exhibits sharp changes at magnetic transition points. It is evident that both samples exhibit a completely reversible tem-

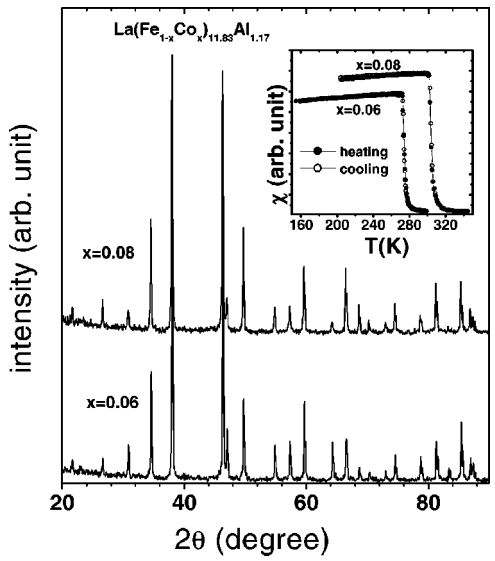

FIG. 1. X-ray diffraction (XRD) patterns of $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x=0.06,0.08$), showing that the samples crystallize in a single phase of the cubic $NaZn_{13}$-type structure. The inset is the temperature dependence of ac susceptibility χ upon heating and cooling for both samples, which show fully reversible behavior between the transition on heating and cooling.

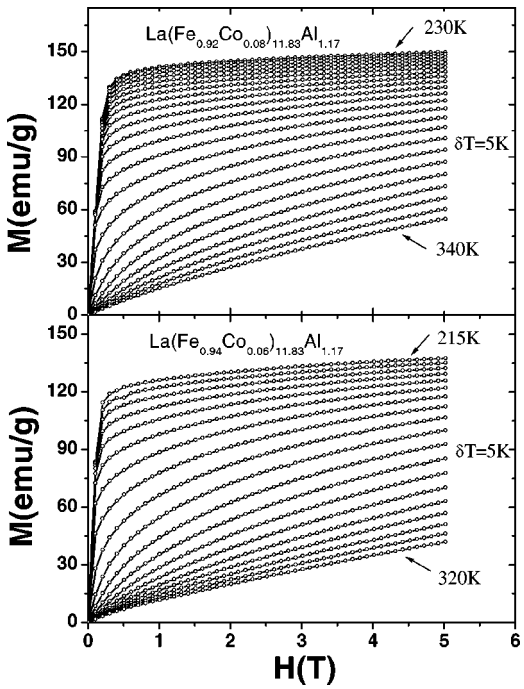

FIG. 2. Magnetization isotherms of $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x=0.06,0.08$). The temperature step is 5 K.

perature dependence of ac susceptibility at the transition points, which is a characteristic of a second-order magnetic transition. Thus the reversible magnetic entropy change on temperature can be expected. The Curie temperatures for $La[(Fe_{1-y}Co_y)_{0.91}Al_{0.09}]_{13}$ ($y=0.06,0.08$) are determined as ~ 273 K and ~ 303 K, respectively, from the inset of Fig. 1. We also performed the magnetic hysteresis loop measurements at 5 K in order to examine the magnetic hardness. The fact that the small coercive fields less than 20 Oe and the small ratio of the remanent magnetization to saturation one ($<1\%$) suggests that our materials are magnetically very soft.

Figure 2 presents the isothermal magnetization of the two samples measured at different temperatures in a wide temperature range covering T_C. The temperature increment is 5 K. The sweep rate of field is slow enough to ensure that M-H curves are recorded in an isothermal process. The M-H curves on field increase and decrease (not shown) at different temperatures show completely reversible behavior, which is expected for a very soft ferromagnet. It is well known that a complete reversibility of MCE requires that no hysteresis of both the temperature and the magnetic field appear in the vicinity of a magnetic ordering temperature. This is easily achievable for a soft ferromagnetic material. Our samples are just the case.

According to the thermodynamical theory, the magnetic entropy change $\Delta S(T,H)$ is given by the Maxwell relation[9,11,26,27]

$$\Delta S(T,H) = S(T,H) - S(T,0) = \int_0^H (\partial M/\partial T)_H dH. \quad (1)$$

Using Maxwell relation to calculate magnetic entropy change can accurately screen the intrinsic nature of the magnetic refrigerant materials, especially for the materials with a second order transition. This indirect method of measuring MCE has been rightfully suggested according to Landau theory,[26] and successfully verified as a reliable way to evaluate candidate materials for magnetic refrigeration.[11,27] The accuracy of the calculated ΔS depends on the accuracy of the measurements of magnetic moment, temperature, and magnetic field. The reported accuracy of ΔS is in the range of 3–10%.[16]

Figure 3 shows the $|\Delta S|$ of $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x=0.06,0.08$) determined by above equation as a function of temperature under different fields. The maximum $|\Delta S|$ under applied fields of 2 T and 5 T are 4.8 and 9.5 J/kg K for the

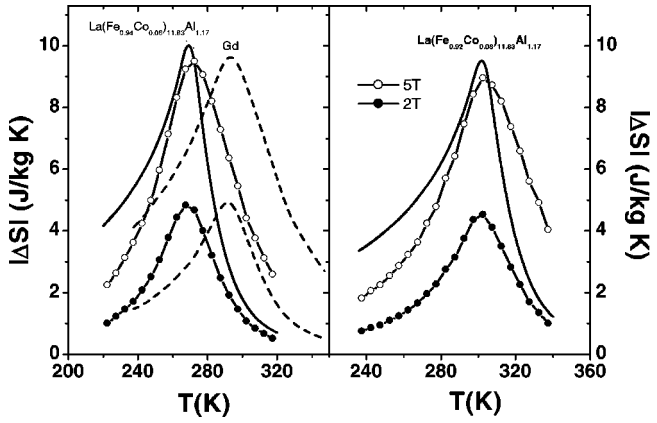

FIG. 3. Magnetic entropy change $|\Delta S|$ of $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x=0.06,0.08$), compared with that of Gd for the magnetic field changes of 0 to 2 and 0 to 5 T. Solid lines: theoretical results calculated in the molecular field approximation for a field of 5 T.

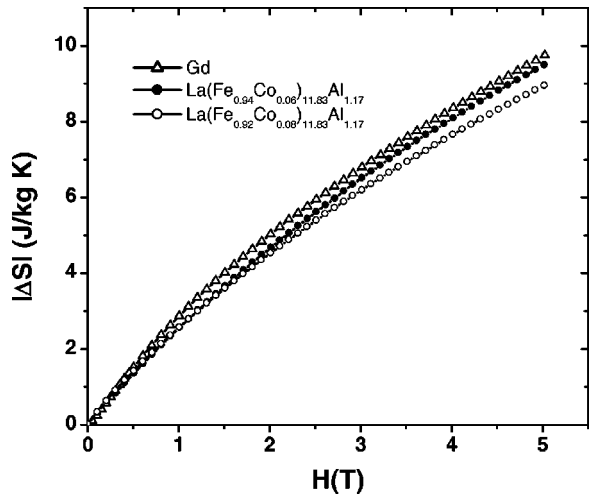

FIG. 4. Field dependence of $|\Delta S|$ for $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x=0.06,0.08$) at their T_C compared with that of Gd.

former ($T_C \sim 273$ K) and 4.5 and 9.0 J/kg K for the latter ($T_C \sim 303$ K), respectively. For comparison, we also measured the magnetic entropy change of Gd (Fig. 3), and obtained $|\Delta S| \sim 5.0$ and 9.7 J/kg K at T_C (293 K) under the corresponding fields, which agree with those reported earlier.[11,28] The field dependence of $|\Delta S|$ for $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x=0.06,0.08$) and Gd at their T_C is displayed in Fig. 4. It is evident that the $|\Delta S|$ of our compounds has nearly same magnitude as that of Gd in the whole field range from 0 to 5 T. Since the highest magnetocaloric effect involving a second order magnetic transition near room temperature is produced by Gd, and most intermetallic compounds which are ordered magnetically near or above room temperature show significantly lower $|\Delta S|$ than Gd,[16] obviously, our results are very attractive. Furthermore, the broad distribution of $|\Delta S|$ from ~ 230 to ~ 330 K for our two samples is very favorable to a room temperature Ericsson-cycle magnetic refrigerator.

The calculation of magnetic entropy change in the molecular field approximation is expected to describe the measured quantities qualitatively.[10] The calculated $\Delta S(H,T)$ as a function of temperature at a field of 5 T is also shown in Fig. 3 with solid lines. The qualitative agreement between theoretical and experimental curves is found. The discrepancies, especially for the peak shape of ΔS_M, are probably due to the roughness of the molecular field model, and also due to magnetic inhomogenization, lattice distortion, etc. in real ferromagnetic materials.

The high magnetization of $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ should be one reason of the large magnetic entropy change. Considering the fact that the magnetization of $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ originates from Fe and Co atoms, the values of 2.0 and $2.1\mu_B$/Fe, Co were determined for $La(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x=0.06,0.08$), respectively, from *M-H* curves measured at 5 K. It is also found from Figs. 3 and 4 that the maximum magnetic entropy change $|\Delta S|$ remains nearly constant at any field when the substitution of Co for Fe increases, which should be ascribed to the nearly same magnetization of the two samples. Usually, a small amount of Co substituting for Fe shifts T_C to higher temperatures in Fe-based intermetallic compounds, but it does not affect the saturation magnetization considerably due to the strong exchange interaction between Fe and Co atoms.

In summary, we discovered a large magnetic entropy change in compounds $La(Fe,Co)_{11.83}Al_{1.17}$ at room temperature range. Theoretical results of ΔS_M, calculated in the molecular field approximation, have been found to describe satisfactorily the ones determined from the magnetization measurements. The reversible behavior of the second order transition in our materials makes the design and construction of the refrigerator simple. The nearly unchanged $|\Delta S|$ and the variation of T_C with Co doping makes it easy to get a nearly constant ΔS in a wide temperature range, which is desired for application to Ericsson-type magnetic refrigerator. A further exciting and important superiority is that our compounds are much cheaper than the materials previously reported, such as FeRh,[6] Gd, GdSiGe,[11,12,19] etc. In other words, the large magnetic entropy change, low cost and the convenience of controlling transition temperature suggest that our materials are promising candidates for magnetic refrigerants.

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