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 cleanliness in comparison with the conventional thermomechanical cooling techniques.\textsuperscript{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,\textsuperscript{3–5} polycrystalline perovskite manganese oxides,\textsuperscript{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.\textsuperscript{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.\textsuperscript{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).\textsuperscript{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.\textsuperscript{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.\textsuperscript{22–25} The results indicate that La(Fe_{1-x}Al_{x})_{13} compounds exist in the range of 0.46 ≤ y ≤ 0.92 and display three different magnetic behavior—mictomagnetism, ferromagnetism, and antiferromagnetism with the variation of iron concentration. At the range of 0.88 ≤ y ≤ 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.\textsuperscript{24}

In this paper, we report the observation of large magnetic entropy change |ΔS| 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 |ΔS|, 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_{1.83}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-
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$(Fe_{1-x}Co_x)_{11.83}Al_{1.17}$ ($x = 0.06, 0.08$) are determined as 273 K and 303 K, respectively, from the inset of Fig. 1. We also performed the magnetic hysteresis loop measurements 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 do not 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:

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

(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, and successfully verified as a reliable way to evaluate candidate materials for magnetic refrigeration. The accuracy of the calculated $\Delta S$ depends on the accuracy of the measurements of magnetic moment, temperature, and magnetic field. The reported accuracy of $\Delta S$ is in the range of $3-10\%$. 

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. 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 $\chi$ 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.

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.
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 $\Delta S_M$, 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 $\Delta S$ 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, Gd, GdSiGe, 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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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.