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Magnetocaloric effect in $LaMn_{2-x}Fe_xGe_2$ at near room temperature

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Abstract

$LaMn_{2-x}Fe_xGe_2$ ($x = 0.10$, 0.15, 0.20) alloys were prepared by arc-melt method, the crystal structure and magnetic properties have been investigated by XRD and vibrating sample magnetometer, respectively. The arc-melted $LaMn_{2-x}Fe_xGe_2$ alloys mainly crystallize in $LaMn_2Ge_2$ phase with $ThCr_2Si_2$-type tetragonal structure, the Curie temperature declines gradually from 310.7 K at $x = 0.10$ to 274.5 K at $x = 0.20$ with the increase of transition metal Fe content. The magnetic entropy changes of the series alloys, with the field change from 0 to 18 kOe, are obtained based on the magnetization isotherms at different temperature. The maximal magnetic entropy of $LaMn_{2-x}Fe_xGe_2$ decreases a little with increasing substitution of Fe for Mn and is about 1.02 J/(kg K) (0–18 kOe) at $x = 0.10$.

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Keywords: $LaMn_{2-x}Fe_xGe_2$; Magnetocaloric effect; Curie temperature

1. Introduction

In the past two decades, the ternary rare earth intermetallic compounds RT_2X_2, where R is rare earth, T is transition metal and X is Si or Ge, have been extensively studied due to their many interesting physical properties [1–6]. RT_2X_2 compounds crystallize in the $ThCr_2Si_2$-type body-centered tetragonal structure with space group I4/mmm and have R–X–T–X–R-stacked layers along the *c*-axis, the site occupancies of the R, T and X are 2a(0, 0, 0), 4d(0, 1/2, 1/4 and 1/2, 0, 1/4) and 4e(0, 0, z and $0, 0, -z$), respectively [7–9]. It is interesting to note that Mn is the only transition metal ion known to possess magnetic moment in the RT_2X_2 series compounds and the magnetic ordering apparently is sensitive to Mn–Mn distances [10,11]. If Mn is replaced by other 3d-elements in RMn_2Ge_2, the strong dependence of the *intralayer* Mn–Mn exchange interaction is loss in $RMn_{2-x}T_xGe_2$ [11]. Correspondingly, the substitution of Fe for Mn leads to the loss of interlayer ferromagnetic ordering and a decrease of Curie and Néel temperatures with the increasing content of transition metal as have been observed the RT_2X_2 alloys [2,4,5,11]. The metamagnetic transition from antiferromagnetic to ferromagnetic state induced by temperature or magnetic field [2–5], giant magnetoresistance [12,13], reentrant ferromagnetism [14] have been observed in this system. Recently, magnetocaloric effect in $SmMn_2Ge_2$ [6] has been investigated by Koyama et al. which shows the RT_2X_2 series alloys possess entropy change at near the temperature of magnetic phase transformation (lower than 150 K).

Since the discovery of the giant magnetocaloric effect (MCE) in $Gd_5Si_2Ge_2$ [15], magnetic refrigeration at near room temperature that based on the MCE of magnetic materials as an environmentally friendly alternative to conventional vapor-cycle refrigeration has attracted more attention in recent years. Especially in recent years, more efforts have been devoted to seek new refrigerant materials and various new materials with large magnetic entropy change have been reported (see [16] and references therein). When Mn is substituted by other 3d elements in RMn_2X_2 compounds, the Curie temperature associated with the Mn sublattice drops gradually with increasing transition metal content [2,4] and the transition temperature of

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RMn_2X_2 can be tuned to fulfill the application in magnetic refrigeration. In the present Letter, we report the results of a detailed study of MCE in $LaMn_{2-x}Fe_xGe_2$ at near room temperature.

2. Experimental details

Polycrystalline $LaMn_{2-x}Fe_xGe_2$ alloys, with $x = 0.10$, 0.15, 0.20, were prepared by arc-melting the corresponding mixtures of pure components in a water-cooled copper hearth under an argon atmosphere. The purities of La, Mn, Fe are all 99.8wt% and that of Ge is 99.99wt%. The mass of each alloy is about 10 g, each alloy was turned over and re-melted several times to insure the homogeneity.

The crystal structure of the series alloys have been investigated by means of X-ray powder diffraction (XRD). Diffraction data were collected on a DX-2000 diffractometer with Cu Kα radiation and a graphite monochromater, the voltage and anode current were 40 kV and 30 mA, respectively. Measurements of temperature dependence of magnetization (M–T) and magnetization isotherms (M–H) were performed on a vibrating sample magnetometer (VSM). The isothermal magnetic entropy change ($|\Delta S_M|$), which is a measure of the MCE, is related to the change of the bulk magnetization M as a function of temperature and magnetic field at constant pressure, was calculated from magnetization data using the well-known Maxwell equation [15,16].

3. Results and discussion

Fig. 1 shows the temperature dependence of the magnetization at 0.2 kOe. The thermomagnetic curves confirm the ferromagnetic behavior with the literature [2], the Curie temperature is determined by the maximum in $|dM/dT|$ and a demonstration is given as the inset in Fig. 1 and it decreases gradually with increasing content of transition metal Fe (see the inset in Fig. 1). At near room temperature, the paramagnetic–ferromagnetic transition for all the $LaMn_{2-x}Fe_xGe_2$ alloys is observed, the magnetization changes rapidly at near Curie temperature and the series alloys have relatively large $|dM/dT|$ which is favorable for the magnetic entropy change of the material. In addition, the magnetic phase transition temperature declines gradually with the increase of Fe. According to

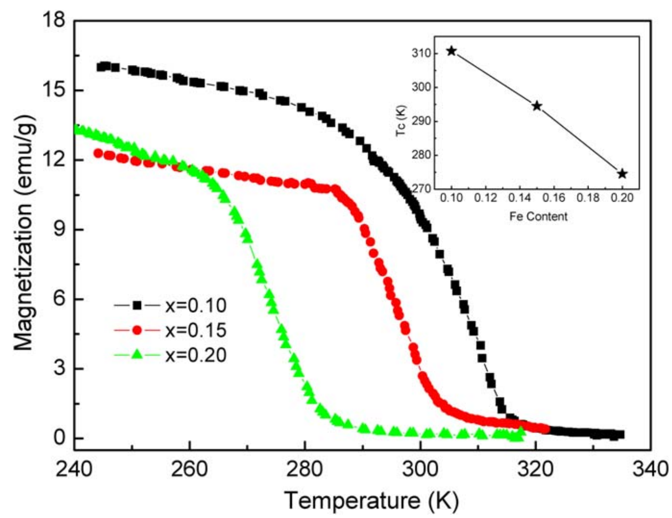


Fig. 1. Temperature-dependence of magnetization of the $LaMn_{2-x}Fe_xGe_2$ (0.10, 0.15, 0.20) measured at 0.2 kOe and the inset shows T_C as a function of Fe content.

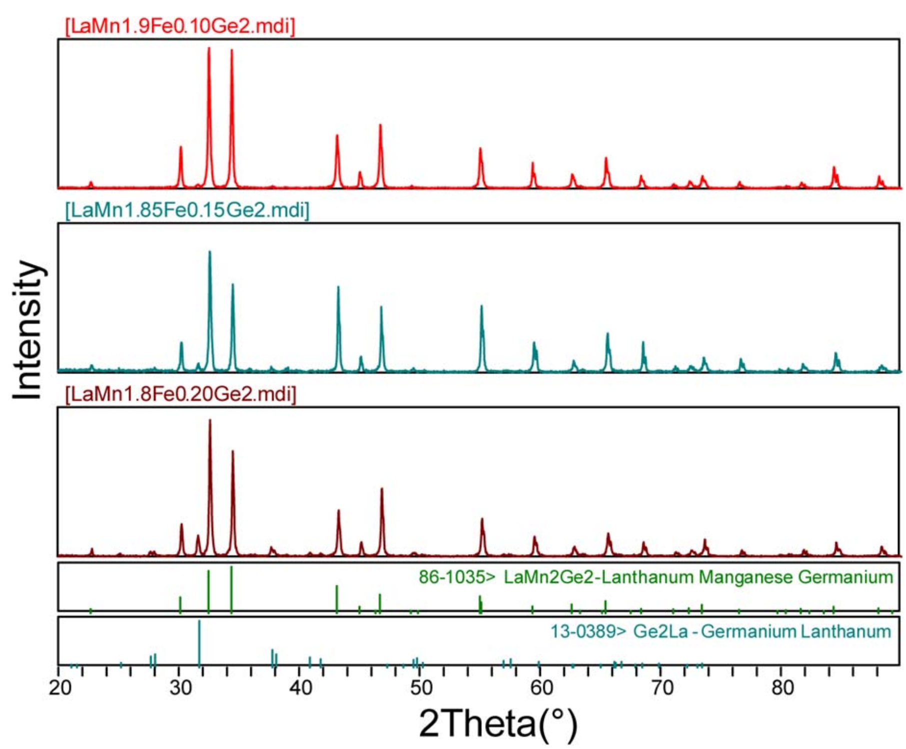


Fig. 2. X-ray powder diffraction pattern of $LaMn_{2-x}Fe_xGe_2$ ($x = 0$, 0.10, 0.20) compounds.

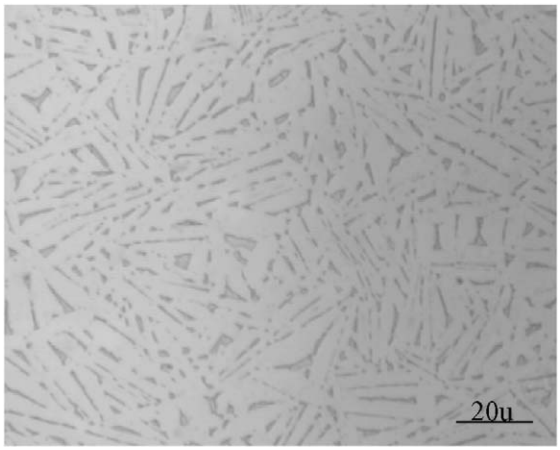


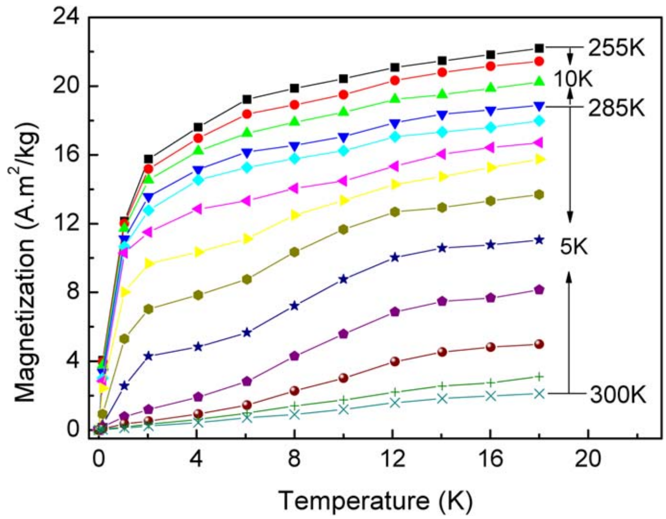
Fig. 3. The optical metallograph of the $LaMn_{1.8}Fe_{0.2}Ge_2$ compound.

molecular field approximation, the substitution of Fe for Mn weakens the strength of the molecular field acting on the Mn layers though the alloys crystallize in the same structure, yielding a decrease of the Curie temperature with increasing Fe content [5].

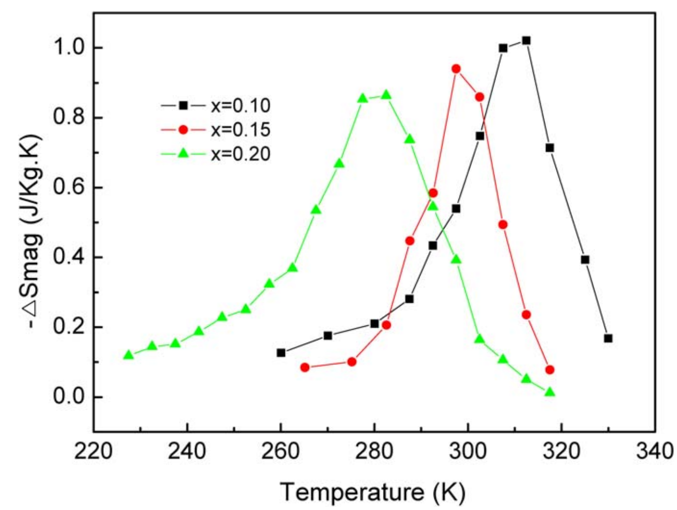
The X-ray diffraction patterns of $LaMn_{2-x}Fe_xGe_2$ ($x = 0.10, 0.15, 0.20$) at room temperature are displayed in Fig. 2. The XRD results show that $LaMn_{2-x}Fe_xGe_2$ compounds mainly adopt in $LaMn_2Ge_2$ phase with $ThCr_2Si_2$-type crystal structure (space group I4/mmm). Due to the mass loss of Mn during the arc-melting process, a small quantity of $LaGe_2$ phase was founded in each $LaMn_{2-x}Fe_xGe_2$ alloy. The refined lattice parameters of the main phase decline gradually with the increase of Fe and coincide with the literatures [2,5], which is mainly attributed to the 3.5% larger atomic radius of Mn compared with that of Fe. Fig. 3 is the metallograph of $LaMn_{1.8}Fe_{0.2}Ge_2$ in acid etched condition. Optical metallographic examination confirms the results of powder XRD, and the $LaGe_2$ secondary phase is also observed. The microstructure of other $LaMn_{2-x}Fe_xGe_2$ alloys, which is not shown here, has a similar feature to that of the $LaMn_{1.8}Fe_{0.2}Ge_2$ and the XRD conducted on them yielded the same results.

The magnetocaloric effect is a phenomenon of emitting or absorption of heat by a magnetic material under the action of a magnetic field, which can be evaluated as an isothermal magnetic entropy change (ΔS_{mag}) or an adiabatic temperature change (ΔT_{ad}) of a magnetic material upon the application of a magnetic field. In this Letter we estimated the MCE with ΔS_{mag}. The magnetic entropy change (ΔS_{mag}) can be obtained from the magnetization data by integrating Maxwell relation [15,16].

The magnetization isotherms (M–H) are obtained based on temperature dependence of magnetization (M–T) at different magnetic field. Fig. 4 displays the magnetic isothermal curves $LaMn_{2-x}Fe_xGe_2$ ($x = 0.10$) as a demonstration and the magnetic entropy change of $LaMn_{2-x}Fe_xGe_2$ ($x = 0.10, 0.15, 0.20$) at the magnetic field change of 0–18 kOe. From the figure, it is easy to see that the temperature point of maximal magnetic entropy change declines linearly with the increase of Fe content, this phenomenon coincides with that the Curie temperature determined by thermomagnetic curves ($|dM/dT|$). The maximal magnetic entropy change of $LaMn_{1.90}Fe_{0.10}Ge_2$ is about 1.02 J/(kg K) (0–18 kOe) and decreases a little, as the phenomenon of Curie temperature, with more Fe substitution for Mn. For $LaMn_{1.80}Fe_{0.20}Ge_2O$, the datum is about 0.9 J/(kg K) (0–18 kOe) at near room temperature. The MCE of $LaMn_{2-x}Fe_xGe_2$ can be mainly explained on the basis of the magnetic phase transformation at the corresponding Curie temperature. The little saturation moment of $LaMn_{2-x}Fe_xGe_2$, which is $\sim 2.4\ \mu_B$/mole for $x = 0.10$ and 0.20 [2], may also account for the small MCE.



(a)



(b)

Fig. 4. (a) The magnetization isotherms of $LaMn_{2-x}Fe_xGe_2$ ($x = 0.10$) in a 18 kOe magnetic field change; (b) magnetic entropy change for $LaMn_{2-x}Fe_xGe_2$ ($x = 0.10, 0.15, 0.20$) in a 18 kOe magnetic field change.

4. Conclusions

Optical microscopy and X-ray diffraction studies show $LaMn_{2-x}Fe_xGe_2$ ($x = 0.10, 0.15, 0.20$) alloys mainly adopt in $LaMn_2Ge_2$ phase with $ThCr_2Si_2$-type crystal structure, minor $LaGe_2$ phase is also observed in each alloy. Magnetic phase transition and magnetocaloric effect properties have been investigated using a vibrating sample magnetometer, Curie temperature declines gradually with the increase of Fe content. The maximal magnetic entropy change of $LaMn_{2-x}Fe_xGe_2$ with $x = 0.10$ is 1.02 J/(kg K) (0–18 kOe) at its corresponding Tc and the datum decreases a little with increasing Fe substitution for Mn. For practical use, the MCE of $LaMn_{2-x}Fe_xGe_2$ is small and need to be improved.

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