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Thermal transport properties of magnetic refrigerants $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ and their hydrides, and $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and MnAs

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$\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ and their hydrides exhibit large magnetocaloric effects due to the itinerant-electron metamagnetic transitions in a wide temperature range covering room temperature. Thermal conductivity and diffusivity of $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ have been investigated, together with those of other candidates for magnetic refrigerants working in the vicinity of room temperature such as Gd, $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and MnAs. The thermal conductivity in the vicinity of room temperature for $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ is larger than that for $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and MnAs, and almost identical to that for Gd. Furthermore, the thermal diffusivity in the vicinity of room temperature for $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ is as large as that for Gd and $\text{Gd}_5\text{Si}_2\text{Ge}_2$, and larger than that for MnAs. Consequently, $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ and their hydrides are promising as the magnetic refrigerants from the standpoint of thermal transport properties. © 2004 American Institute of Physics.
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I. INTRODUCTION

In the recent research and development of magnetic refrigerants, large magnetocaloric effects (MCEs) in the vicinity of room temperature have been reported in several materials.¹⁻⁴ For example, Gd metal exhibits the isothermal entropy change $\Delta S_m = -9$ J/kg K and the adiabatic temperature change $\Delta T_{\text{ad}} = 11.6$ K at the second-order magnetic transition temperature, 298 K, in the magnetic field change from 0 to 5 T.² The compounds having the first-order transition such as $\text{Gd}_5\text{Si}_2\text{Ge}_2$ (Ref. 3) and MnAs⁴ exhibit large MCEs in comparison with Gd metal. By changing the magnetic field from 0 to 5 T, ΔS_m and ΔT_{ad} for $\text{Gd}_5\text{Si}_2\text{Ge}_2$ are -18 J/kg K and 15.3 K, respectively at the first-order transition temperature, 278 K.³ Moreover, MnAs compound⁴ exhibits $\Delta S_m = -32$ J/kg K at the first-order transition temperature, 318 K, though $\Delta T_{\text{ad}} = 12.8$ K is smaller than that of $\text{Gd}_5\text{Si}_2\text{Ge}_2$.³

$\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ shows a first-order transition between the paramagnetic and the ferromagnetic states at the Curie temperature, $T_C = 195$ K.⁵⁻⁷ The first-order transition from the paramagnetic to the ferromagnetic state, that is, the itinerant-electron metamagnetic (IEM) transition, can be triggered by applying magnetic field.⁵⁻⁷ Recently, large values of ΔT_{ad} for $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ due to the IEM transition have been confirmed just above T_C .⁸⁻¹¹ In addition, T_C for $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ can be controlled up to about 330 K by hydrogen absorption, without vanishing the IEM transition.^{12,13} Therefore, $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ and their hydrides exhibit large MCEs due to the IEM transition in a wide temperature range covering room temperature.⁸⁻¹¹ For $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$, ΔS_m and ΔT_{ad} due to the IEM transition are -23 J/kg K and 11.1 K, respectively, at $T_C = 274$ K in the magnetic field

change from 0 to 5 T.⁸⁻¹⁰ Furthermore, $\text{La}(\text{Fe}_{0.90}\text{Si}_{0.10})_{13}\text{H}_{1.1}$ exhibits $\Delta S_m = -31$ J/kg K and $\Delta T_{\text{ad}} = 15.4$ K at $T_C = 287$ K in the magnetic field change from 0 to 5 T.^{10,11} The value of ΔS_m for $\text{La}(\text{Fe}_{0.90}\text{Si}_{0.10})_{13}\text{H}_{1.1}$ is larger than that for Gd² and $\text{Gd}_5\text{Si}_2\text{Ge}_2$,³ almost the same as that for MnAs.⁴ In addition, ΔT_{ad} for $\text{La}(\text{Fe}_{0.90}\text{Si}_{0.10})_{13}\text{H}_{1.1}$ is almost the same as that for $\text{Gd}_5\text{Si}_2\text{Ge}_2$,³ and larger than that for MnAs⁴ and Gd.² Accordingly, $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ and their hydrides are promising as the magnetic refrigerants working in a wide temperature range covering room temperature.⁸⁻¹¹

The active magnetic regenerator refrigerator (AMRR) with the Bryton cycle is practical in the vicinity of room temperature.¹⁴ The bed of magnetic materials in the AMRR acts as both magnetic refrigerants and regenerator materials. Therefore, the thermal conductivity of the bed along the heat transfer fluid flow direction should be small to keep the temperature gradient in the bed. Since the bed cools and heats the heat transfer fluid, excellent behavior of heat exchange between the bed and the heat transfer fluid is also necessary. In the AMRR, the bed should be composed porously of fine particles having excellent thermal transport properties, because the porous state restrains heat transfer between the hot and cold heat exchangers through the bed.^{15,16} Furthermore, its effective surface area is utilized for heat transfer with the heat transfer fluid.^{15,16} Therefore, to obtain the high performance of magnetic refrigeration, magnetic materials are claimed to have not only large MCEs but also excellent thermal transport properties.^{15,16} Several kinds of materials having large MCEs have been reported, but their thermal transport properties are still uncertain.

In the present article, the temperature dependences of thermal conductivity and thermal diffusivity for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ have mainly been investigated. From the viewpoint of application in magnetic refrigeration, thermal conductivity and thermal diffusivity in the vicinity of room temperature for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$

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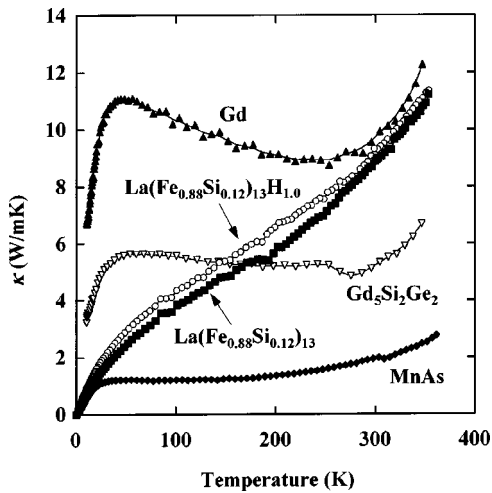


FIG. 1. Temperature dependence of the thermal conductivity κ for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$, together with that for the $\text{Gd}_5\text{Si}_2\text{Ge}_2$, Gd and MnAs. For the MnAs compound, κ for the specimen with the density of about 90% was corrected to the x-ray density value by using the equation for porous materials (see Ref. 18).

have been discussed by comparison with those of other candidates for magnetic refrigerants working in the vicinity of room temperature such as Gd, $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and MnAs.

II. EXPERIMENT

The $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{Gd}_5\text{Si}_2\text{Ge}_2$ were prepared by arc melting in an Ar gas atmosphere. The heat treatments for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{Gd}_5\text{Si}_2\text{Ge}_2$ were carried out in an evacuated quartz tube at 1323 K for ten days and at 1270 K for three days, respectively. The hydrogen absorption into the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ was carried out by annealing under hydrogen gas atmosphere. The MnAs compound was prepared by a solid–vapor reaction. Mn and As elements were sealed under vacuum in a quartz tube and annealed at 1073 K for seven days. Since the MnAs specimen becomes porous, it was compacted at 973 K under pressure 590 N and then sintered at 1073 K for three days under vacuum in a quartz tube. The bulk density of the MnAs specimen was about 90% of the x-ray density. A polycrystalline Gd metal with purity of 99.9 wt% was used as the Gd specimen. No extra phase in all the present specimens was detected by x-ray powder diffraction measurements. The specific heat measurements were carried out by a relaxation method, and the electrical resistivity was measured by a conventional four-probe method. The thermal conductivity was measured by a pulse method.¹⁷

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of thermal conductivity κ for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$, together with that for Gd, $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and MnAs. According to Schulz,¹⁸ the modified equation for porous materials is given by

$$\kappa = \kappa_p / (1 - P)^{3/2}, \quad (1)$$

where κ_p is the thermal conductivity of porous materials and P is the porosity. Following this expression, the value of the MnAs compound with the density of about 90% was corrected to the x-ray density value. For the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$, κ increases gradually with temperature and slightly decreases at $T_C = 195$ K. The value of κ is expressed as

$$\kappa = \kappa_e + \kappa_{ph}, \quad (2)$$

where κ_e and κ_{ph} are the electron and the phonon thermal conductivities, respectively. The contribution of κ_e is given by the following expression associated with the Wiedemann–Franz law

$$\kappa_e = LT / \rho, \quad (3)$$

where L is the Lorenz number, and ρ is the electrical resistivity. Above the Debye temperature Θ , L has the constant value of $L_0 = 2.45 \times 10^{-8} \text{ W}\Omega/\text{K}^2$, because the elastic scattering of electrons dominates in this temperature. By using the Debye function obtained from the specific heat data, Θ for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ is calculated to be about 350 K. From Eq. (3), $\kappa_e = 6.6 \text{ W/Km}$ for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ at 350 K is estimated by using $\rho = 1.3 \times 10^{-6} \Omega\text{m}$. This value is about 60% of κ for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$. Accordingly, κ_e in Eq. (2) for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ is dominant in the vicinity of 350 K. The behavior of κ for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ has analogy with that for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$. Therefore, κ for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ is hardly changed after hydrogen absorption.

The value of κ for the Gd metal exhibits a peak in a low temperature range, and increases with temperature above room temperature. The value of κ for the Gd metal resembles the previous data.¹⁹ Similar behavior is also observed in the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and MnAs as seen from the figure. The value of κ for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ is larger than that for the MnAs compound. In a low temperature range, κ for the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and Gd is larger than that for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$. However, it should be pointed out that κ of the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ is larger than that of the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and almost the same value as that of the Gd metal in the vicinity of room temperature.

When the temperature gradient in magnetic refrigerants is constant, the steady heat transfer is expressed by the following expression by using κ :

$$U = -\kappa \text{ grad } T, \quad (4)$$

where U is the density of heat flow. Accordingly, under the steady heat transfer condition, the thermal conductive property of the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ in the vicinity of room temperature is superior to that of the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and MnAs, almost the same as that of the Gd metal. The magnetic refrigeration requires the process of temperature change in the magnetic materials. Therefore, the time dependence of temperature gradient in the magnetic refrigerants should be taken into consideration. Such nonsteady heat transfer can be discussed by the following equation:

$$\partial T / \partial t = \alpha \nabla^2 T, \quad (5)$$

where t is the time, and the thermal diffusivity α is given as

$$\alpha = \kappa / dC_p, \quad (6)$$

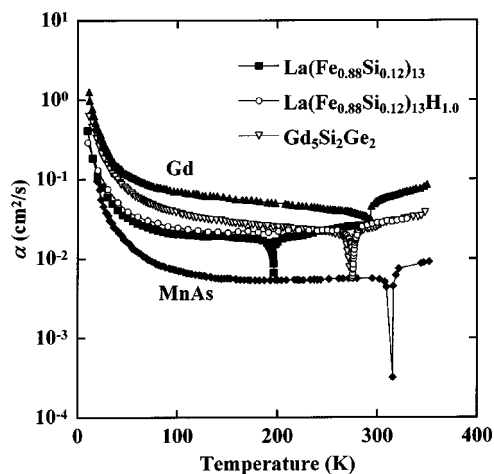


FIG. 2. Temperature dependence of the thermal diffusivity α for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$, together with that for $\text{Gd}_5\text{Si}_2\text{Ge}_2$, Gd and MnAs.

where d is the density, and C_p is the specific heat at constant pressure. From Eq. (5), it is clear that α is the important characteristic measure for the nonsteady heat transfer in the magnetic refrigerants.

Shown in Fig. 2 is the temperature dependence of thermal diffusivity for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$, together with that for the $\text{Gd}_5\text{Si}_2\text{Ge}_2$, Gd and MnAs. The value of α is evaluated from Eq. (6) by using available data of heat capacity^{2,3,20} and the x-ray density at room temperature. The value of α for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ increases with temperature. The value of κ first increases gradually with temperature and then slightly decreases at $T_C = 195$ K as seen in Fig. 1. Additionally, it is well known that C_p at the thermal-induced first-order transition temperature diverges because of the latent heat, although the divergence of C_p at T_C for the presented compounds cannot be obtained completely from the heat capacity measurements. Therefore, α exhibits a small minimum at $T_C = 195$ K because of the first-order transition. The value of C_p for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ is gradually saturated as the temperature comes close to Θ of about 350 K, and hence α becomes larger with increasing temperature. Similar temperature dependence of α is observed in the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$, Gd, $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and MnAs, though the change at T_C for the Gd metal is relatively small because of the second-order transition. The value of α for the Gd metal is almost the same as that of the previous data.¹⁹ The value of α in the vicinity of room temperature for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ is as large as that for the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and Gd, and larger than that for the MnAs compound. Therefore, under the nonsteady heat transfer condition, the thermal diffusive property in the vicinity of room temperature for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ is superior to that for the MnAs compound, and almost the same as that for the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and Gd.

IV. SUMMARY

The thermal transport properties such as thermal conductivity κ and thermal diffusivity α for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ have been discussed by comparison with those for other candidates as the magnetic refrigerants working in the vicinity of room temperature such as $\text{Gd}_5\text{Si}_2\text{Ge}_2$, Gd and MnAs. The value of κ for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ is larger than that for the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and MnAs compounds, and almost the same value as that for the Gd metal in the vicinity of room temperature. Furthermore, α in the vicinity of room temperature for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}\text{H}_{1.0}$ is almost the same order as that of the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and Gd, and larger than that of the MnAs compound. The $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}\text{H}_y$ with the different compositions of Fe and H also exhibit almost the same results. For example, the values of κ and α at 300 K for the $\text{La}(\text{Fe}_{0.90}\text{Si}_{0.10})_{13}\text{H}_{1.1}$ are 8.7 W/mK and 0.027 cm^2/s , respectively. Consequently, it is concluded that the $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ and their hydrides are promising as magnetic refrigerants from the standpoint of the thermal transport properties.

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