CHIN. PHYS. LETT. Vol. 37, No. 1 (2020) 017501

# Table-Like Large Magnetocaloric Effect in the Misch Metal *R*Si Compound *

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(Received 16 July 2019)

*Magnetic properties and the magnetocaloric effect (MCE) of the RSi ($R$ = Ce, Pr, Nd) compounds made of Misch metal (MM) are investigated. Two transitions are found at 12 K and 38 K. Field variation generated large MCE and two peaks are found in the magnetic entropy change ($\Delta S$) curves, which correspond to the two transition temperatures. The maximum values of the magnetic entropy changes ($\Delta S$) are found to be $-5.1$ J/(kg·K) and $-9.3$ J/(kg·K) for the field ranges of 0–2 T and 0–5 T, respectively. The large $\Delta S$ as well as ultra-low price of MM make (MM)Si a competitive magnetic refrigerant candidate for low temperature in Eriksson cycle.*

*PACS:* 75.30.Sg, 75.50.Cc, 75.60.Ej DOI: 10.1088/0256-307X/37/1/017501

The magnetocaloric effect (MCE) was considered as one of the most important fundamental thermodynamic effects, which could induce temperature changes of magnetic material by exposing the material to a changing magnetic field.[1–3] Magnetocaloric effect technology has the outstanding merits of being highly energy-efficient and eco-friendly compared with traditional vapor compression refrigeration, which promotes it to play an important role in the refrigeration area.[1–5] Nowadays, $La(Fe,Si)_{13}$,[6] $MnAs_{1-x}Sb_x$,[7] $MnFeP_{1-x}As_x$[8] and Ni-Mn based Heusler alloys[9] have the potential application of working at room temperature, which were extensively reported one after the other, but only the paramagnetic salts such as $Gd_3Ga_5O_{12}$, $GdLiF_4$ or $GdF_3$ have been commercially used in the low temperature refrigeration area.[10,11] Rare earth base materials with low transition temperatures also exhibit bright application prospects in the low temperature refrigeration area. Lots of materials were reported, among which $(ErAl_2)_{0.312}(HoAl_2)_{0.198}(Ho_{0.5}Dy_{0.5}Al_2)_{0.490}$ and $RCo_2$ were highly concerned.[12,13] The Eriksson cycle was considered as the most suitable mode for the magnetic refrigeration machine, for which materials with table-like MCE property and wide refrigeration temperature range were desired.[12] $(ErAl_2)_{0.312}(HoAl_2)_{0.198}$ $(Ho_{0.5}Dy_{0.5}Al_2)_{0.490}$ was designed and used for the Eriksson cycle, and considerable effort was obtained.[12] Except for this, great effort has been devoted to investigate the table-like MCE materials. In general, the maximum values of magnetic entropy changes ($\Delta S$) correspond to the transition temperatures. Multiple transitions could generate several magnetic entropy change peaks, and a table-like MCE phenomenon would be observed. The table-like MCE was pivotal to the Eriksson cycle used in the magnetic refrigeration machine. It is difficult to get multiple transitions in a pure phase material, and many researchers have found ways to acquire this. In our previous works, $R$Si ($R$ = Ce, Pr, Nd) with low cost and excellent MCE performance has been generally studied.[13–15] After that, we also devoted energy to improve the MCE performance of these materials to give impetus to their application. The MM is mainly composed by La, Ce, Pr, Nd rare earth and some trace elements, as list in Table 1. The price of the MM is much lower than the rare earth sample substance. Depending on this, we expect to make an $R$Si sample using the Misch metal that can exhibit multiple phases with different transition temperatures, which could generate the table-like MCE phenomenon.

For generality, the magnitude of MCE is characterized by the isothermal magnetic entropy change or the adiabatic temperature change under the variation of the magnetic field.[1–9] In this work, (MM)Si is prepared and MCE is characterized by the isothermal magnetic entropy changes. Two peaks are found in the magnetic entropy change curves and table-like MCE property is discovered, which indicates its potential applications in the near future.

Taking into consideration of the comparison between the MM and rare earth sample substance, three samples were prepared by the arc melting method and named as S1, S2 and S3. The specific compositions of the three samples are listed in Table 1. Except for the Misch metal, the purity of all the constituent materials is better than 99.9 wt%. Stoichiometric starting raw materials were weighted and the ingots were obtained on a water-cooled copper crucible under protection of high-purity argon atmosphere. There was 3 wt% excessive rare earth added to make up the weight loss during the arc melting. The samples were turned over and re-melted six times to ensure homogeneity. The

*Supported by the National Natural Science Foundation of China under Grant Nos. 51701130, 51571146, and 51771124.
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as-cast ingots were sealed in a quartz tube filled with high-purity argon atmosphere and then annealed at 1073 K for four weeks.

**Table 1.** Compositions of *R*Si series samples.

| Element | S1(wt%) | S2(wt%) | S3(wt%) |
|---|---|---|---|
| La | 28.27 | 28.27 | |
| Ce | 50.46 | 50.46 | 50.46 |
| Pr | 5.22 | 5.22 | 5.22 |
| Nd | 15.66 | 15.66 | 15.66 |
| Sm | 0.05 | | |
| Fe | 0.037 | | |
| Mg | 0.057 | | |
| Si | 0.016 | | |
| Zn | 0.01 | | |
| W | 0.01 | | |
| C | 0.01 | | |
| Cu | 0.01 | | |
| Ti | 0.01 | | |
| Ga | 0.01 | | |
| Pb | 0.01 | | |
| Mo | 0.007 | | |
| Cr | 0.03 | | |

D8 x-ray diffractometer(XRD) from Bruker Inc by using Cu $K\alpha$ radiation was employed to determine the lattice parameter and phase composition. The ingots were milled to powder before the measurement. The DC magnetization as functions of temperature and magnetic field was measured on a small piece of the sample using the commercial superconducting quantum interference device magnetometer (SQUID, Quantum Design).

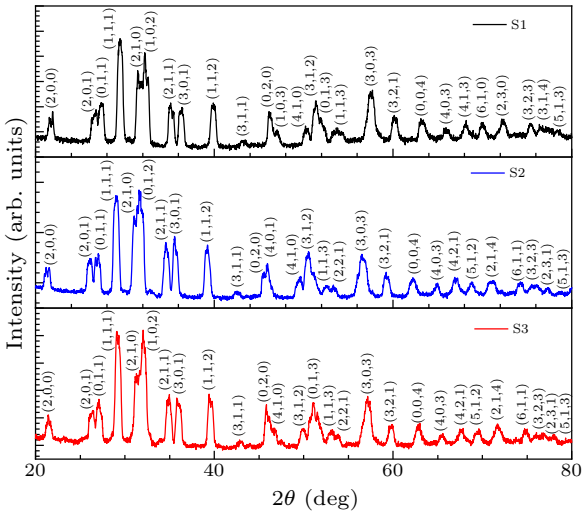


**Fig. 1.** XRD patterns of *R*Si series compounds at room temperature.

Figure 1 shows the standard $\theta$–$2\theta$ powder x-ray diffraction patterns for S1, S2 and S3 samples collected at room temperature. The black, blue and red patterns correspond to the S1, S2 and S3 samples, respectively. It is revealed that the three patterns are almost the same and all the peaks could be indexed, indicating that all the samples crystallized in an orthorhombic FeB-type structure (space group: *Pnma*, No. 62) as reported before.[16,17]

Figure 2 shows the temperature dependence of magnetization ($M$–$T$) both under zero-field cooling (ZFC) and field-cooling (FC) modes with a magnetic field of 0.01 T, in order to determine the transition temperatures of the three samples. The S1 sample as seen in Fig. 2(a) shows two phase transitions at 12 K and 46 K, respectively. However, S2 and S3 prepared by the rare earth sample substance only show one phase transition temperature at 12 K and 38 K, respectively, as shown in Figs. 2(b) and 2(c). As is expected, multiple transitions appear in the (MM)Si samples. For the S2 and S3 samples, single pure phase as (La, Ce, Pr, Nd)Si and (Ce, Pr, Nd)Si may be obtained. It is interesting that S1 and S2 almost have the same compositions, but with such different properties. A similar result was reported in ($MM_{0.3}Nd_{0.7}$)–Fe–B sintered magnets.[18] The reason was also not declared in that work. To our knowledge, the reason may be attributed to the existence of the trace elements and the symbiosis nature of the MM. In addition, more detail and deeper analysis will be required to figure out how the Misch metal worked in the (MM)Si sample. Considering the XRD patterns shown in Fig. 1, there may be two explanations for the two transitions in S1. First, there may exist several phases with different transition temperatures in the (MM)Si sample, which induces multiple transitions in the $M$–$T$ curve. The existing phases in S1 all crystallized in a pure FeB-type structure with almost the same patterns, so that it is difficult to distinguish them from the XRD data. For the second explanation, there may be only one pure phase in the (MM)Si sample, which shows two transitions. The fact that several transitions exist in one pure phase has been reported in other rare earth alloys.[19,20]

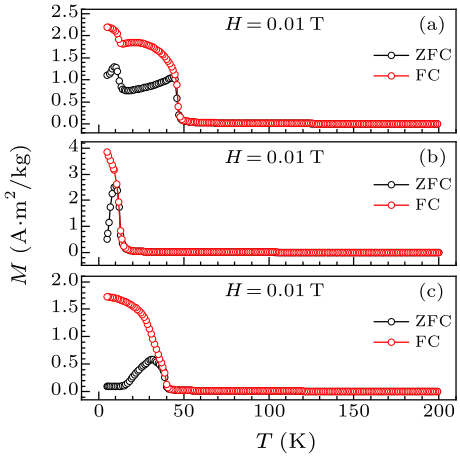


**Fig. 2.** The temperature dependence of magnetization curves of *R*Si series samples (a) S1, (b) S2, and (c) S3.

Figure 3 exhibits the initial magnetization curves ($M$–$H$) for the S1, S2 and S3 samples with magnetic fields up to 5 T, respectively. Figure 4 presents the Arrott plots ($M^2$ vs $H/M$) for the S1, S2 and S3 samples, which are derived from the $M$–$H$ data in Fig. 3. The positive slopes of the three samples in the Arrott plots confirm the occurrence of second-order phase transition in the three samples according to the Banerjee

criterion.[21]

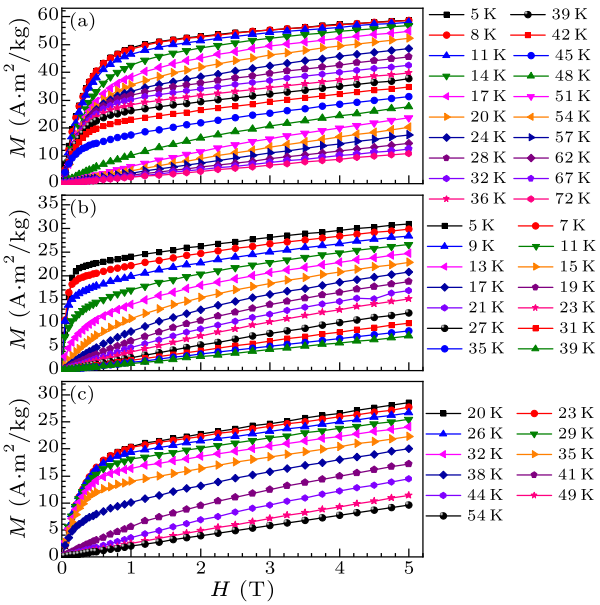


**Fig. 3.** Initial magnetization curves of *R*Si series samples (a) S1, (b) S2, and (c) S3.

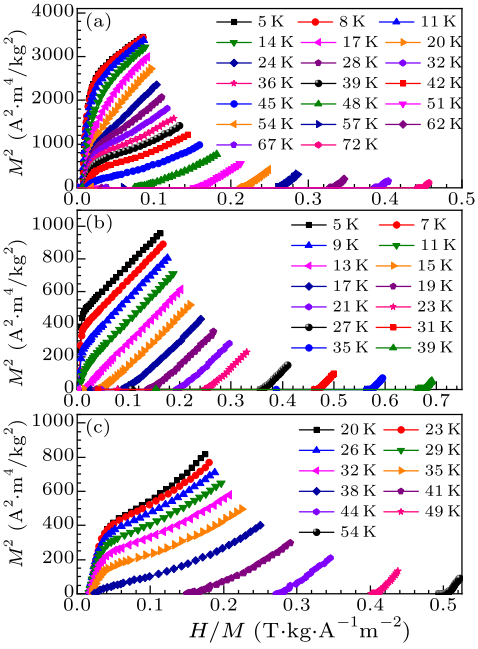


**Fig. 4.** Adiabatic magnetization curves and the corresponding Arrott plots of *R*Si series samples (a) S1, (b) S2, and (c) S3.

The isothermal magnetic entropy changes are calculated from the isothermal magnetization data by employing Maxwell's relationship:

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

The $\Delta S$ for different magnetic field changes as a function of temperature ($\Delta S$–$T$) are shown in Fig. 5, under magnetic field changing in the range from 0 to 5 T with an increment of 1 T. It is apparent that the $\Delta S$–$T$ graph of the S1 sample show two peaks near the two phase-transition temperatures as expected, and the maximum $\Delta S$ under a 0–5 T magnetic field are $-5.1$ J/(kg·K) and $-9.3$ J/(kg·K), respectively. Different from the two peaks exhibited in the S1 sample, the $\Delta S$–$T$ plots of the S2 and S3 samples show only a single peak, with a value of $-6.4$ J/(kg·K) and $-5.9$ J/(kg·K) for magnetic changes of 0–5 T, respectively. It is worth noting that the two magnetic entropy peaks of S1 are significantly larger than that of S2 and S3 under the same magnetic field changes. In addition, the price of the Misch metal is one order of magnitude lower than that of rare earth sample substances, which is very beneficial to the large-scale commercial production of the (MM)Si magnetic refrigeration refrigerant in the future.

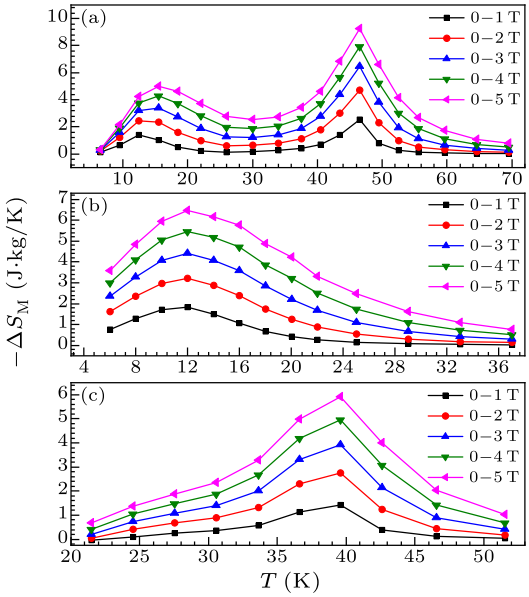


**Fig. 5.** The $\Delta S$ curves of the *R*Si series samples (a) S1, (b) S2, and (c) S3 versus temperature.

**Table 2.** Phase transition temperatures and magnetic entropy changes of the *R*Si series samples.

| Sample | Magnetic ground state | Phase transition temperature | $\Delta S$ (0–2 T) | $\Delta S$ (0–5 T) |
|---|---|---|---|---|
| CeSi | AFM | 6.1 K | −7.2 J/(kg·K) | −13.7 J/(kg·K) |
| NdSi | FM | 46 K | −6.8 J/(kg·K) | −12.4 J/(kg·K) |
| PrSi | FM | 52 K | −8.6 J/(kg·K) | −15.3 J/(kg·K) |
| S1 | | 12/46 K | 2.4/4.7 J/(kg·K) | 5.1/9.3 J/(kg·K) |
| S2 | | 12 K | 3.3 J/(kg·K) | 6.4 J/(kg·K) |
| S3 | | 38 K | 2.8 J/(kg·K) | 5.9 J/(kg·K) |

In summary, the magnetic and MCE properties of $R$Si series samples have been systematically studied. The three samples all crystallize in an orthorhombic FeB-type structure by arc melting and long-time annealing. The S1 sample made of the Misch metal shows two phase transitions and the corresponding magnetic entropy curves ($\Delta S$–$T$) show two peaks. The maximum $\Delta S$ of the S1 sample under 0–5 T magnetic field variation are $-5.1\,\mathrm{J/(kg{\cdot}K)}$ and $-9.3\,\mathrm{J/(kg{\cdot}K)}$, respectively. The single peaks of the S2 and S3 samples prepared with the rare earth sample substance under the same magnetic field change are $-6.4\,\mathrm{J/(kg{\cdot}K)}$ and $-5.9\,\mathrm{J/(kg{\cdot}K)}$, respectively. It is worth noting that the sample prepared by the Misch metal not only have two peaks of magnetic entropy change, but also its maximum value is larger than that of the samples prepared by the rare earth sample substance under the same magnetic field changes. A considerable MCE and one order of magnitude lower price make the Misch metal $R$Si a competitive candidate for low temperature magnetic refrigerant. All these characters of the Misch metal $R$Si are very beneficial to the large-scale commercial production as a magnetic refrigeration refrigerant in the future.

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