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Original Article

Saturated Magnetization in Sm and Tb Doped $La(Fe_{0.88}Si_{0.12})_{13}$

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Abstract : The saturated magnetization in 20% substituted $La_{0.8}R_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ (R = Sm, Tb) magneto-caloric alloys is discussed in this work. The measurements were taken up to 70 kOe (7 Tesla) to detect the saturation of magnetic moments. As reported recently [Mat. Trans. 59(7) (2018) 1068], these compounds show a large variation of magnetic entropies at low field variation (~ 1.5 T), which associate with the large relative cooling efficiency (RCP) of 52 (for Tb-doped) and 102 J/kg (for Sm-doped) even at low effective ΔH of ~ 15 kOe. We re-detected the effective range of field variation ΔH and recognized that the effective ΔH ~ 5 kOe which is much lower than the value of other magneto-caloric compounds and is excellent for application of Sm-doped compound in modern cooling devices.

Keywords: Magnetic, alloys, $LaFe_{13}$, phase transition, rare-earth.

1. Introduction

Magneto-caloric compounds are of great importance for application in modern environmental friendly gas-free cooling devices [1-4]. In our previous study [5], we reported on the magneto-caloric effects in 20% doped compounds $La_{0.8}R_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ (R=Sm, Tb) where large values of RCP were observed. But due to technical limitation the values of magnetization were only achieved at applied field up to 15 kOe, so the achieved RCP were reported for ΔH = 1.5 T, although there were signatures that the effective field variation may be significantly different. Even though, the RCP obtained for Sm, and Tb doped compounds are as good as comparable to that of the others, for examples, of the first-

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order phase transition Gd-based alloys $Gd_5(Si_{1-x}Ge_x)_4$ [1], or $NaZn_{13}$ type structured La-based alloys $La(Fe_{1-x}M_x)_{13}$ [2], or Mn-based alloys MnAs, $MnFe(P_{1-x}As_x)$ [3], and the Heusler Ni-Mn-Ga alloys [4] etc... As mentioned in the previous studies, the binary compounds $La(Fe_{1-x}M_x)_{13}$ (M=Si, Al) can exhibit a quasi-cubic form when partially substituted by Si, and/or Al, for Fe. Their magnetic properties depend strongly on substituted constituents and may vary from ferromagnetism to anti-ferromagnetism [2]. Recall that, the $La(Fe_xSi_{1-x})_{13}$ itself is ferromagnetic for a range of $0.62 \leq x \leq 0.89$ [6, 7]. Usually, the optimal content of Fe is around 88%, and we know that the increase of Fe content reduces the Curie temperature T_C and increases the saturated magnetization M_s. The itinerant electron metamagnetism, its relation to pressure and the magneto-volume effect, which are typical for $La(Fe_{1-x}M_x)_{13}$ compounds, are discussed in details by this same group of authors in ref. [8]. Here we are concerned with the saturation of magnetic moments in higher applied magnetic field (above 1.5T) to re-detect the effective field variation that can change RCP values. As reported in ref.[5] the magnetization does not seem to be saturated at 15 kOe, and the practical RCP-s may be achieved at higher field variation than 15 kOe, which lower the chance for application. For this purpose, we re-detect the saturated magnetization to shed light on to the application ability of Sm and Tb-doped compounds.

2. Experimental

The alloys of nominal composition $La_{0.8}R_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ (R = Sm, Tb) were fabricated by mean of arc-melting techique in Ar atmosphere at high vacuum ($P = 10^{-5}$ Torr) as presented in ref. [5]. We note that a surplus of 2% of the precursors La and R metals were added as these metals are easily evaporated during melting process. The structure analysis was reported in ref. [5], here we re-measured the magnetization by using the Superconducting Quantum Interference Device (SQUID) in a temperature range from 4 to 300 K and magnetic field up to 70 kOe, in the Japan Advanced Institute of Science and Technology (JAIST), Japan.

3. Results and discussion

Recall that the structure of Sm-doped compound is a single phase $NaZn_{13}$ type cubic *Fm-3c* but the one of Tb-doped compound is accompanied with a small amount of a secondary phase α-Fe. The obtained lattice parameters are: $a = b = 11.455(1)$ (Sm-doped) and 11.446(2) Å (Tb-doped); $c =$ 11.894(11) (Sm-doped) and 11.885(01) Å (Tb-doped), correspondingly. Thus, the unit cell of the Tb-doped compound appears visibly smaller than that of the Sm-doped one. This agrees with a smaller cationic size of Tb in comparison with that of Sm, as it is a heavier element (atomic mass of Tb is 159.92) than Sm (atomic mass is 150.36) in the lanthanide row (La < Ce < Pr < Nd < Pm < Sm < Eu < Gd < Tb < Dy < Ho < Er < Tm < Yb < Lu). Therefore, the partial substitutions of Sm and Tb lead to lowering of site symmetries, but the space group still remains as cubic *Fm-3c*. We also studied the cases of doping Ce, Pr, Nd, Ho, Er, and Yb for La (will be presented elsewhere) and revealed that the lattice parameters systematically reduced from Ce to Nd, Sm, Tb and Yb. The same trends can also be seen in the literature, *i.e.* in ref. [9-14]. Note that, the cationic sizes of all lanthanides are smaller than the one of La^{3+} (1.06 Å).

The magnetic properties of the alloys $La_{0.8}R_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ are characterized by magnetization measurements, such as $M(T)$ and $M(H)$. The $M(T)$ curves for the two cases of Sm and Tb-doped compounds were reported in ref. [5]. Here we show in Fig. 1 the re-measurement of $M(T)$ at the applied field of H=100 Oe, from the low temperature of 2 K until the room temperature (around 300

K). The result shows a clear ferro-to-paramagnetic phase transition with a mere increase of Curie temperature T_C for Sm doped compound. The particular values of T_C are listed in Table 1 with comparison with the values from the other cases.

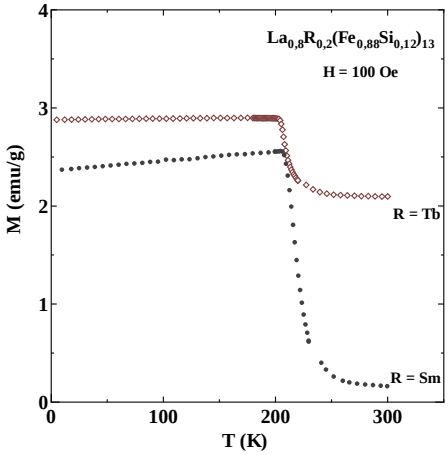

Fig. 1. The dependence of magnetization on temperature $M(T)$ in $La_{0.8}R_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ (R = Sm, Tb) at applied field H = 100 Oe.

Table 1. Variation of T_C and saturated magnetization M_s in $La_{0.8}R_{0.2}(Fe_{0.88}Si_{0.12})_{13}$

Substituted element *R*	T_C (K)	M_S (emu/g)	H (kOe)
La [11]	202 ± 1	170.5 ± 0,5	20
Ce [12]	186 ± 2	121.0 ± 0,5	20
Sm	225 ± 1	120.5 ± 0,5	8
Tb	219 ± 3	93.5 ± 1,5	5

As observed in Table 1, the substitution of Sm and Tb led to the increase of Curie temperature but reduces the saturated magnetization correspondingly. The Sm-doped compound shows both higher T_C and higher M_S. The variation of T_C due to replacement of lanthanium by other rare-earths may be explained by the change in magnetic exchange strength between the substituted rare-earth element and iron in the compounds $LaR(Fe,Si)_{13}$. With substitution of the rare-earths the ferromagnetism increases consequently in the lanthanides row, leading to the increase in exchange strength between the substituted sites and the neighboring Fe sites, whereas the ferromagnetic coupling between two Fe cations remains unchanged. According to the molecular field model, the field parameter may be estimated by the formula:

$$n_{Fe-Fe} = \frac{T_{Fe}}{C_{Fe}} \quad (1)$$

where C_{Fe} is a Curie constant of corresponding transition metal and is given as:

$$C_{Fe} = \frac{4N_{Fe}S^*\left(S^*+1\right)\mu_B^2}{3k_B} \quad (2)$$

in which, T_{Fe} is phase transition temperature of pure metal Fe (in this case is its T_C), k_B a Boltzmann constant, N_{Fe} number of Fe atoms per mole. The iron effective magnetic moment in paramagnetic state is determined equal to $2[S^*(S^*+1)]^{1/2} = 3.5\ \mu_B$. Therefore, with increasing substituted contents of the rare-earths, the disorders of sites increase correspondingly, leading to the

increase in exchange distances between two Fe- Fe sites. This finally increases $n_{\text{Fe-Fe}}$ and Curie temperature T_C. The dependence of T_C on atomic mass of rare-earths should be linear.

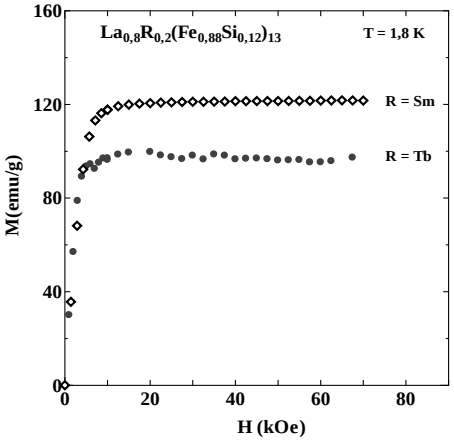

Fig. 2. Saturated magnetizations of $La_{0.8}R_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ (R = Sm, Tb) at 1.8 K.

The dependence of saturated magnetization on applied magnetic field $M(H)$ is studied at low temperature from 1.8 K until the room temperature and is given in Fig. 2. As seen, the magnetizations are saturated at quite low applied field around 5 kOe for Tb-doped compound, 8 kOe for Sm-doped and 9 kOe for un-doped compounds. For comparison, the saturated magnetization is achieved at H = 5 kOe for Ce-substituted compounds, 10 kOe for Yb-doped ones. The saturated magnetizations are listed in Table 1 together with the values of applied field at which the saturation was achieved. The obtained values of H are very interesting as they allow limiting the measurement of the entropy changes only to these maximum fields. Therefore, for the RCP reported in ref.[5] the practical field variations are restricted to below these maximum saturated fields. We now can claim that the corresponding RCPs are now 52 J/kg at ΔH = 5kOe for Tb-doped, and 102 J/kg at ΔH = 8 kOe for Sm-doped compound. For practical application, a much smaller applied field is of greater advantage.

The lanthanide row begins with La, which in its typical oxidation state La^{3+} has a blank *4f* shell ($4f^0$), and the next lanthanide in the row, Ce^{3+} has 1 electron in *4f* shell ($4f^1$). The number of electrons in 4*f* shell increases in the lanthanide row until $4f^{13}$ for Yb^{3+} and fully occupied ($4f^{14}$) for Lu^{3+}. Therefore we observe a systematic decrease of cationic size from Ce to Yb in our samples, in particular from 1.10 Å for Ce^{3+} to 0.94 Å for Yb^{3+}. Note that the *4f* electrons are highly locallized with strong spin-orbit coupling which in turn reduces the total magnetic moment in lighter rare-earths while increases it in the heavier elements. Therefore we can observe both increases of T_C and M_S upon substitution. The dependence is quite reasonable as the saturated magnetization is proportionate to magnetic susceptibility, which is on the other hand proportionate to the Curie temperature.

4. Conclusion

We successfully fabricated the Sm and Tb doped compound of the formula $La_{0.8}R_{0.2}(Fe_{0.88}Si_{0.12})_{13}$ (R = Sm, Tb) which appear to possess the single phase $NaZn_{13}$ type cubic structure with space group *Fm-3c*. The re-measurement of saturated magnetization shows that the saturated fields are much lower than that were used in the determination of RCP values reported in ref.[5], *i.e.* the saturated *H =5* and 8 kOe for Tb- and Sm-doped compounds correspondingly. This allows limiting the maximum field

variations to below 8 kOe in the practical refrigeration cycle using Sm-doped magneto-caloric compound.

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