Control of Working Temperature of Large Isothermal Magnetic Entropy Change in $\text{La}(\text{Fe}_x\text{TM}_y\text{Si}_{1-x-y})_{13}$ (TM = Cr, Mn, Ni) and $\text{La}_{1-z}\text{Ce}_z(\text{Fe}_x\text{Mn}_y\text{Si}_{1-x-y})_{13}$

Shun Fujieda¹, Naoyuki Kawamoto², Asaya Fujita¹ and Kazuaki Fukamichi²

¹Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

The Curie temperature T_C of $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ is increased by a partial substitution of Ni for Fe. On the contrary, T_C is decreased by a partial substitution of Cr or Mn. In addition, a partial substitution of Ce for La in $\text{La}(\text{Fe}_x\text{Mn}_y\text{Si}_{1-x-y})_{13}$ causes the further decrease of T_C . As a result, $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ exhibits a thermal-induced first-order transition at $T_C = 60$ K. This result means that T_C of the $\text{La}_{1-z}\text{Ce}_z(\text{Fe}_x\text{Mn}_y\text{Si}_{1-x-y})_{13}$ is tunable in the temperature range between 60 and 180 K by adjusting composition with keeping the itinerant-electron metamagnetic transition. In the magnetic field change from 0 to 4 T in the vicinity of $T_C = 60$ K, the $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ shows the isothermal magnetic entropy change $\Delta S_m = -13 \text{ J kg}^{-1} \text{ K}^{-1}$ and the relative cooling power $RCP = 458 \text{ J kg}^{-1}$. Consequently, the $\text{La}_{1-z}\text{Ce}_z(\text{Fe}_x\text{Mn}_y\text{Si}_{1-x-y})_{13}$ compounds are useful for magnetic refrigerants working in a temperature range between 60 and 180 K.

(Received September 20, 2005; Accepted November 24, 2005; Published March 15, 2006)

Keywords: magnetocaloric effect, itinerant-electron metamagnetic transition, magnetic refrigeration, relative cooling power

1. Introduction

Magnetic refrigerations and magnetocaloric effects (MCEs) have been investigated extensively. Magnetic refrigerations are free from environmentally-unfriendly gases such as hydrochlorofluorocarbon and hydrofluorocarbon. In addition, it has been pointed out that the magnitude of energy loss incurred in the refrigeration cycle of magnetic refrigerators is smaller than that of vapor-cycle refrigerators.¹⁾ Therefore, magnetic refrigerations are expected to be useful for refrigeration technologies such as freezers and air-conditioners in the vicinity of room temperature and the liquefaction of gases at low temperatures. To realize such applications with high performance in various temperature ranges, the research and development of magnetic refrigerants are important.

Above the Curie temperature T_C , $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ compounds exhibit the itinerant-electron metamagnetic (IEM) transition²⁻⁴⁾ which is accompanied by a large isothermal magnetic entropy change ΔS_m ⁵⁻⁹⁾ as well as a large adiabatic temperature change ΔT_{ad} .⁶⁻¹⁰⁾ Such large MCEs are obtained in relatively low magnetic fields just above T_C , because the critical field of the IEM transition becomes smaller when the temperature comes close to T_C . The $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ compounds also exhibit large magnetovolume effects such as a remarkable pressure effect^{4,11)} and a large thermal expansion anomaly.⁴⁾ The value of T_C for the $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ decreases remarkably by applying hydrostatic pressure. On the contrary, the hydrogen absorption into the $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ causes a volume expansion of about 3%, resulting in the increase of T_C up to about 340 K.^{12,13)} Furthermore, the IEM transition is maintained after hydrogen absorption. As a result, by controlling hydrogen concentration, the $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}\text{H}_y$ compounds exhibit large MCEs in relatively low magnetic fields in a temperature range between about 180 and 340 K.⁶⁻¹⁰⁾ Therefore, the $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ and their hydrides are promising as magnetic refrigerants working between about 180 and 340 K.

The magnetic refrigeration below 180 K is also important. For example, new electronics devices for high-transition temperature (T_C) superconductor such as noise filters and high sensitive antennas can be operated in these temperatures. The transition temperature of high- T_C superconductors is located lower than about 140 K.¹⁴⁾ Therefore, high-performance of magnetic refrigerants working below the temperature mentioned above is necessary in the field of superconducting technologies. However, development research of magnetic refrigerants around such temperature ranges have not been so active, in comparison with that around room temperature range.¹⁵⁾ Therefore, we try to reduce T_C below 180 K for $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$. It is considered two kinds of feasible methods to decrease of T_C . The onset of the IEM transition means that magnetic free energy has two minima in the paramagnetic and ferromagnetic states. On the basis of the Landau–Ginzburg theory, such magnetic free energy has been discussed by using the Landau coefficients associated with the density of state (DOS) around the Fermi level.¹⁶⁾ Since T_C is influenced by the balance between two minima in the paramagnetic and ferromagnetic states, T_C is correlated with the Landau coefficients.¹⁶⁾ It is expected that T_C can be controlled by a partial substitution of 3d elements for Fe, because the Landau coefficients are changed by the shift of the Fermi level. Already, it has been reported that T_C is increased by a partial substitution of Co¹⁷⁾ and a partial substitution of Mn causes the decrease of T_C .¹⁸⁾ The other method is a partial substitution of rare earth elements for La, because the lanthanoid contraction decreases volume. We have reported that a partial substitution of Ce for La causes the decrease of T_C , which mainly attributes to the volume contraction.¹⁹⁻²¹⁾ Therefore, the investigation of the effect of the partial substitution on T_C is useful to control the working temperature range. In the present study, to obtain large MCEs in lower temperature ranges, we try to control T_C and ΔS_m for in $\text{La}(\text{Fe}_x\text{TM}_y\text{Si}_{1-x-y})_{13}$ (TM = Cr, Mn, Ni) and $\text{La}_{1-z}\text{Ce}_z(\text{Fe}_x\text{Mn}_y\text{Si}_{1-x-y})_{13}$ compounds adjusting the partial substitution rate.

2. Experiments

Several kinds of compounds of $\text{La}(\text{Fe}_{0.88-y}\text{TM}_y\text{Si}_{0.12})_{13}$ ($\text{TM} = \text{Cr}, \text{Mn}$), $\text{La}(\text{Fe}_{0.87-y}\text{TM}_y\text{Si}_{0.13})_{13}$ ($\text{TM} = \text{Ni}$) and $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ were arc-melted in an argon gas atmosphere. The subsequent heat-treatments were carried out in vacuum quartz tubes. The annealing temperature and duration were 1323 K and 10 days for the $\text{La}(\text{Fe}_{0.88-y}\text{TM}_y\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.87-y}\text{TM}_y\text{Si}_{0.13})_{13}$ compounds and 1423 K and 14 days for the $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ compound. The crystal structure was confirmed by x-ray powder diffraction with $\text{Cu K}\alpha$ radiation. The magnetization was measured with a superconducting quantum interference device (SQUID) magnetometer. The isothermal magnetic entropy change ΔS_m was obtained from the Maxwell relation.

3. Results and Discussion

The occurrence of the IEM transition of the $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ is limited in the concentration range $x \geq 0.86$, and the transition characteristics is very sensitive to the composition.⁴⁾ Therefore, the important point of investigation for the influence of the partial substitution is to prepare compositionally homogeneous specimens. The $\text{La}(\text{Fe}_{0.88-y}\text{Cr}_y\text{Si}_{0.12})_{13}$ with $y \leq 0.2$, $\text{La}(\text{Fe}_{0.88-y}\text{Mn}_y\text{Si}_{0.12})_{13}$ with $y \leq 0.3$ and $\text{La}(\text{Fe}_{0.87-y}\text{Ni}_y\text{Si}_{0.13})_{13}$ with $y \leq 0.2$ are identified as the single phase of a cubic NaZn_{13} -type structure with $Fm\bar{3}c$ space group. Figure 1 shows the concentration y dependence of the Curie temperature T_C for $\text{La}(\text{Fe}_{0.88-y}\text{Cr}_y\text{Si}_{0.12})_{13}$, $\text{La}(\text{Fe}_{0.88-y}\text{Mn}_y\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.87-y}\text{Ni}_y\text{Si}_{0.13})_{13}$. The value of T_C was determined from the thermomagnetization curve of heating process in a magnetic field of 0.01 T. The value of T_C is increased by the partial substitution of Ni for Fe. Contrary, T_C is decreased by the partial substitution of Cr or Mn. The influence of the partial substitution of Mn on the decrease of T_C is much larger than that of Cr. To be more

Fig. 1 Concentration y dependence of the Curie temperature T_C for $\text{La}(\text{Fe}_{0.88-y}\text{Cr}_y\text{Si}_{0.12})_{13}$, $\text{La}(\text{Fe}_{0.88-y}\text{Mn}_y\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.87-y}\text{Ni}_y\text{Si}_{0.13})_{13}$.

Fig. 2 Thermomagnetization curves in a magnetic field of 1 T for (a) $\text{La}(\text{Fe}_{0.88-y}\text{Cr}_y\text{Si}_{0.12})_{13}$ and (b) $\text{La}(\text{Fe}_{0.88-y}\text{Mn}_y\text{Si}_{0.12})_{13}$.

precise, T_C of the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ is decreased from 195 to 136 K by the substitution of $y = 0.03$ of Mn.

It is important to control the working temperature range with keeping large magnetocaloric effects (MCEs). Therefore, we should pay notice to the influence of partial substitution on not only T_C but also the magnetization change in the vicinity of T_C . According to the Maxwell relation, the isothermal magnetic entropy change ΔS_m is expressed by

$$\Delta S_m = \int_0^B \left(\frac{\partial M}{\partial T} \right)_B dB, \quad (1)$$

where M , T and B are the magnetization, temperature and magnetic field. Therefore, a large $\partial M / \partial T$ is important to obtain a large ΔS_m . Shown in Figs. 2(a) and (b) are the thermomagnetization curves in a magnetic field of 1 T for (a) $\text{La}(\text{Fe}_{0.88-y}\text{Cr}_y\text{Si}_{0.12})_{13}$ and (b) $\text{La}(\text{Fe}_{0.88-y}\text{Mn}_y\text{Si}_{0.12})_{13}$. All the curves were measured in both the heating and cooling processes. The thermomagnetization curve without TM for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ exhibits a remarkable change with hysteresis at T_C because of the thermal-induced first-order transition. Such behavior becomes obscure with increasing Cr or Mn concentration. In particular, by substituting Mn, the magnetization change at T_C remarkably becomes broader. Additionally, the thermal hysteresis at T_C disappears after the substitution of $y = 0.03$ of Mn. In other words, the magnetic transition at T_C changes from the first-order to the second-order, and the IEM transition above T_C disappears after the substitution of $y = 0.03$ of Mn.

Fig. 3 Temperature dependence of the isothermal magnetic entropy change ΔS_m in a magnetic field change from 0 to 4 T for $\text{La}(\text{Fe}_{0.88-y}\text{TM}_y\text{Si}_{0.12})_{13}$ (TM = Cr, Mn).

Figure 3 shows the temperature dependence of ΔS_m obtained by using eq. (1) in a magnetic field change from 0 to 4 T ($\Delta B = 4$ T) for the $\text{La}(\text{Fe}_{0.88-y}\text{TM}_y\text{Si}_{0.12})_{13}$ (TM = Cr, Mn). Since T_C decreases with increasing Cr or Mn concentration, the negative peak of ΔS_m for $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ is shifted toward a lower temperature range. In addition, the maximum value of ΔS_m , ΔS_m^{MAX} is decreased especially for the $\text{La}(\text{Fe}_{0.88-y}\text{Mn}_y\text{Si}_{0.12})_{13}$, whereas the full width of the half maximum δT becomes wider with increasing Mn concentration. Recently, it has been pointed out that the relative cooling power (RCP) is also important to magnetic refrigerants, because RCP is one of the measures of heat quantity transferred by magnetic refrigerants.²²⁾ The value of RCP is defined by the following expression:²²⁾

$$RCP = -\Delta S_m^{\text{MAX}} \times \delta T. \quad (2)$$

The values of RCP calculated from Fig. 3 for the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$, $\text{La}(\text{Fe}_{0.86}\text{Cr}_{0.02}\text{Si}_{0.12})_{13}$ and $\text{La}(\text{Fe}_{0.86}\text{Mn}_{0.02}\text{Si}_{0.12})_{13}$ are 370, 361 and 327 J kg^{-1} , respectively. Therefore, RCP is also decreased by the partial substitution of Mn or Cr. Accordingly, it is clear that the further decrease of T_C due to the partial substitution of Cr or Mn is undesirable from the practical viewpoint.

Recently, it has been reported the partial substitution of Ce for La in the $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ brings about not only the decrease of T_C but also the significant enhancement of MCEs.^{19–21)} Therefore, both the further decrease of T_C and enhancement of ΔS_m for the $\text{La}(\text{Fe}_{0.86}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ are expected by the partial substitution of Ce for La. The thermomagnetization curves in a magnetic field of 1 T for the $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ are given in Fig. 4. The value of T_C is decreased from 136 to 60 K by the substitution of 35% Ce for La in $\text{La}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$. It should be noted that the thermomagnetization curve is accompanied by a hysteresis. The IEM transition at finite temperature has been discussed in the terms of the phenomenological Landau–Ginzburg theory with the magnetic free energy

Fig. 4 Thermomagnetization curves in a magnetic field of 1 T for $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$.

expanded up to the sixth order, by taking the renormalization effect of spin fluctuations on the Landau–Ginzburg coefficient and the magnetovolume effects into account.^{23,24)} According to the theoretical investigation, the negative sign of the forth order of the Landau–Ginzburg coefficient which means the negative mode–mode couplings among spin fluctuations is necessary to induce the IEM transition. In addition, it has been indicated that the magnetic transition at T_C of the itinerant-electron ferromagnets with negative mode–mode coupling among spin fluctuations changes from the second-order to the first-order by applying hydrostatic pressure and the IEM transition takes place above T_C of the first-order.^{23,24)} In fact, such behaviors were obtained for $\text{Co}(\text{Se}_x\text{Si}_{1-x})_2$ Ref. 25), $\text{Lu}(\text{Co}_x\text{Ga}_{1-x})_2$ and $\text{Lu}(\text{Co}_x\text{Al}_{1-x})_2$ Ref. 26) which show the IEM transition. Furthermore, the thermal-induced first-order transition of the $\text{La}_{1-z}\text{Ce}_z(\text{Fe}_x\text{Si}_{1-x})_{13}$ becomes clear with increasing Ce concentration because of the volume contraction.^{19–21)} Therefore, $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ exhibits clearly the thermal-induced first-order magnetic transition with the IEM transition, though the $\text{La}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ without Ce exhibits the second-order transition at T_C . Accordingly, T_C of the $\text{La}_{1-z}\text{Ce}_z(\text{Fe}_x\text{Si}_{1-x})_{13}$ is tunable in the temperature range between 60 and 180 K, with keeping the IEM transition by adjusting the composition.

The temperature dependence of ΔS_m in $\Delta B = 4$ T is given in Fig. 5 for $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$. The values of ΔS_m^{MAX} and RCP for $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ in $\Delta B = 4$ T are about $-13 \text{ J kg}^{-1} \text{ K}^{-1}$ and 458 J kg^{-1} , respectively. Therefore, the values of ΔS_m^{MAX} and RCP become larger by substituting Ce for La in the $\text{La}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$. In addition, the value of the RCP of the $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$ is much larger than that of the $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$, though ΔS_m^{MAX} of the former is smaller than that of the latter. This result means that such large values of ΔS_m and RCP are obtained in the temperature range between 60 and 180 K by adjusting the composition in

Fig. 5 Temperature dependence of the isothermal magnetic entropy change ΔS_m in a magnetic field change from 0 to 4 T for $\text{La}_{0.65}\text{Ce}_{0.35}(\text{Fe}_{0.85}\text{Mn}_{0.03}\text{Si}_{0.12})_{13}$.

$\text{La}_{1-z}\text{Ce}_z(\text{Fe}_x\text{Mn}_y\text{Si}_{1-x-y})_{13}$. Consequently, the $\text{La}_{1-z}\text{Ce}_z(\text{Fe}_x\text{Mn}_y\text{Si}_{1-x-y})_{13}$ compounds are promising as magnetic refrigerants working in the temperature range between 60 and 180 K.

4. Conclusion

To obtain large magnetocaloric effects (MCEs) in temperature ranges much lower than room temperature, we have investigated the change of T_C for the $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ by the partial substitution. The value of T_C for $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ is increased by the partial substitution of Ni for Fe and decreased by the partial substitution of Cr or Mn. In addition, the partial substitution of Ce for La in $\text{La}(\text{Fe}_x\text{Mn}_y\text{Si}_{1-x-y})_{13}$ causes the further decrease of T_C . As a result, a large isothermal entropy change is obtained in the temperature range between 60 and 180 K by adjusting the composition of $\text{La}_{1-z}\text{Ce}_z(\text{Fe}_x\text{Mn}_y\text{Si}_{1-x-y})_{13}$. Consequently, it is concluded that the $\text{La}_{1-z}\text{Ce}_z(\text{Fe}_x\text{Mn}_y\text{Si}_{1-x-y})_{13}$ compounds are promising as magnetic refrigerants working in the temperature range between 60 and 180 K.

Acknowledgements

The present work has been supported by the Grant-in-Aids for Scientific Research (B) (No. 17360333) from the Japan

Society for Promotion of Science. The present authors wish to thank Mr. Y. Morita for his experimental support. One of the authors (S. Fujieda) acknowledges the support of the JSPS Research Fellowships for Young Scientists.

REFERENCES

- 1) C. Zimm, A. Jastrab, A. Sternberg, V. Pecharsky, K. Gschneidner, Jr., M. Osborne and I. Anderson: *Adv. Cryog. Eng.* **43** (1998) 1759–1766.
- 2) A. Fujita, Y. Akamatsu and K. Fukamichi: *J. Appl. Phys.* **85** (1999) 4756–4758.
- 3) K. Fukamichi and A. Fujita: *J. Mater. Sci. Technol.* **16** (2000) 167–171.
- 4) A. Fujita, S. Fujieda, K. Fukamichi, H. Mitamura and T. Goto: *Phys. Rev. B* **65** (2002) 014410, 1–6.
- 5) F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Cheng, G. H. Rao and X. X. Zhang: *Appl. Phys. Lett.* **78** (2001) 3675–3677.
- 6) A. Fujita, S. Fujieda, K. Fukamichi, Y. Yamazaki and Y. Iijima: *Mater. Trans.* **43** (2002) 1202–1204.
- 7) S. Fujieda, A. Fujita and K. Fukamichi: *Appl. Phys. Lett.* **81** (2002) 1276–1278.
- 8) A. Fujita, S. Fujieda, Y. Hasegawa and K. Fukamichi: *Phys. Rev. B* **67** (2003) 104416, 1–12.
- 9) S. Fujieda, A. Fujita and K. Fukamichi: *Sci. Tech. Adv. Mater.* **4** (2003) 339–346.
- 10) S. Fujieda, Y. Hasegawa, A. Fujita and K. Fukamichi: *J. Magn. Magn. Mater.* **272–276** (2004) 2365–2366.
- 11) A. Fujita, K. Fukamichi, M. Yamada and T. Goto: *J. Appl. Phys.* **93** (2003) 7263–7265.
- 12) A. Fujita, S. Fujieda, K. Fukamichi, Y. Yamazaki and Y. Iijima: *Trans. Mater. Res. Soc. Jpn.* **26** (2001) 219–222.
- 13) S. Fujieda, A. Fujita, K. Fukamichi, Y. Yamazaki and Y. Iijima: *Appl. Phys. Lett.* **79** (2001) 653–655.
- 14) A. Schilling, M. Cantoni, J. D. Guo and H. R. Ott: *Nature* **363** (1993) 56–58.
- 15) A. M. Tishin and Y. I. Spichkin: *The magnetocaloric effect and its applications* (Institute of Physics Publishing, London).
- 16) H. Yamada: *Physica B* **149** (1988) 390–402.
- 17) A. Fujita and K. Fukamichi: *IEEE Trans. Magn.* **35** (1999) 3796–3798.
- 18) F. Wang, Y. F. Chen, G. J. Wang and B. G. Shen: *J. Phys. D: Appl. Phys.* **36** (2003) 1–3.
- 19) S. Fujieda, A. Fujita and K. Fukamichi: *Mater. Trans.* **45** (2004) 3228–3231.
- 20) S. Fujieda, A. Fujita, K. Fukamichi, N. Hirano and S. Nagaya: *J. Alloys Compd.* **408–412** (2006) 1165–1168.
- 21) S. Fujieda, A. Fujita and K. Fukamichi: *IEEE Trans. Magn.* **41** (2005) 2787–2789.
- 22) K. A. Gschneidner, Jr. and V. K. Pecharsky: *Annu. Rev. Mater. Sci.* **30** (2000) 387–408.
- 23) H. Yamada and K. Terao: *J. Phys.: Condens. Matter* **6** (1994) 10805–10809.
- 24) H. Yamada, K. Fukamichi and T. Goto: *Phys. Rev. B* **65** (2001) 024413, 1–6.
- 25) T. Goto, Y. Shindo, H. Takahashi and S. Ogawa: *Phys. Rev. B* **56** (1997) 14019–14028.
- 26) K. Fukamichi, T. Yokoyama, H. Saito, T. Goto and H. Yamada: *Phys. Rev. B* **64** (2001) 134401, 1–8.