Magnetic entropy change and large refrigerant capacity of $Ce_6Ni_2Si_3$-type GdCoSiGe compound*

Shen Jun(沈 俊)[a)†], Zhang Hu(张 虎)[b)], and Wu Jian-Feng(吴剑峰)[a)]

[a)] *Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing* 100190, *China*

[b)] *State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*

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Magnetic entropy change ($\Delta S_{\rm M}$) and refrigerant capacity (RC) of $Ce_6Ni_2Si_3$-type $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compounds have been investigated. The $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ undergoes a reversible second-order phase transition at the Curie temperature $T_{\rm C} = 296$ K. The high saturation magnetization leads to a large $\Delta S_{\rm M}$ and the maximal value of $\Delta S_{\rm M}$ is found to be 5.9 J/kg·K around $T_{\rm C}$ for a field change of 0–5 T. A broad distribution of the $\Delta S_{\rm M}$ peak is observed and the full width at half maximum of the $\Delta S_{\rm M}$ peak is about 101 K under a magnetic field of 5 T. The large RC is found around $T_{\rm C}$ and its value is 424 J/kg.

Keywords: $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound, magnetocaloric effect, refrigerant capacity

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1. Introduction

In recent years, much attention has been paid to magnetic materials with the giant magnetocaloric effect (MCE) due to their potential application as magnetic refrigerants.[1−3] Large MCE around the transition temperatures has been found in many materials with a first-order phase transition, such as $Gd_5Si_2Ge_2$, $La(Fe, Si)_{13}$, $MnAs_{1-x}Sb_x$, $MnFeP_{1-x}As_x$, NiMnGa, etc.[4−10] Although, these materials have usually large magnetic entropy change ($\Delta S_{\rm M}$), magnetic hysteresis loss happens inevitably, which greatly reduce the actual refrigerant capacity (RC). Therefore, it is important to explore advanced magnetic refrigerant materials which possess not only large reversible $\Delta S_{\rm M}$ but also considerable RC. Recently, there has been a great deal of interest in the study of MCE of ferromagnetic materials that experience a second-order phase transition because of their high RC. Generally, heavy rare earth elements and their compounds are considered to be the best candidate materials for finding a large MCE due to their high magnetic moments. Gd metal has the highest MCE among the second-order phase transition materials and it shows a maximum $\Delta S_{\rm M}$ of 9.7 J/kg·K at $T_{\rm C} = 293$ K under a field change 0–5 T.[11,12] Recently, a ferromagnetic silicide $Gd_6Co_{1.67}Si_3$ derived from the $Ce_6Ni_2Si_3$-type structure was reported.[13,14] The compound exhibits a good MCE and a reversible second-order magnetic transition at room temperature.[15−17] In this paper, we study the magnetic properties and magnetocaloric effects of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound. Room-temperature maximum $\Delta S_{\rm M}$ of 5.9 J/kg·K and large RC of 424 J/kg are observed.

2. Experiments

Polycrystalline $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ was prepared by arc melting in a high-purity argon atmosphere. The purities of starting materials were better than 99.9%. The sample was turned over and remelted several times to ensure its homogeneity. Ingot obtained by arc melting was subsequently wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 1073 K for 30 days and then quenched to room temperature. The crystal structure of the samples was characterized using power x-ray diffraction (XRD) with Cu Kα radiation. Magnetizations were measured as functions of both temperature and

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†Corresponding author. E-mail: jshen@mail.ipc.ac.cn

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magnetic field by using a superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

Figure 1 displays the room-temperature powder XRD pattern of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$. All the diffraction peaks can be indexed in a hexagonal $Ce_6Ni_2Si_3$-type crystal structure (space group $P6_3/m$) except some smaller peaks (centred at about 23.98°, 25.02° and 36.40°) that indicate the existence of a minor phase other than the $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound. The lattice parameters are determined to be a = 1.1761(9) nm and c = 0.4161(3) nm by using the Rietveld refinement method, which are slightly larger than those of $Gd_6Co_{1.67}Si_3$[15] because of the atomic radius of Ge is larger than that of Si.

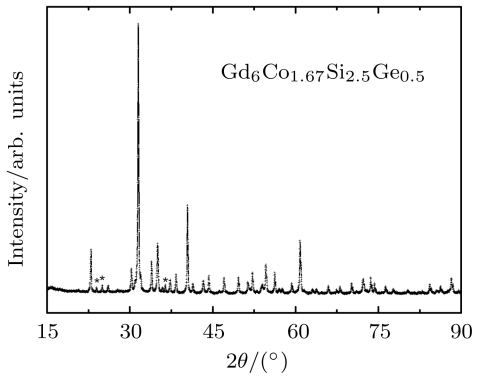


Fig. 1. Room-temperature powder XRD pattern of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$.

The temperature-dependent magnetization was measured in both zero field-cooled (ZFC) and field-cooled (FC) processes in order to determine the thermal hysteresis and the magnetic transition temperature. Figure 2(a) shows the thermomagnetic curves M–T of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ measured under an external magnetic field of 0.05 T. The sample was cooled down to 5 K in a zero field, the heating curve from 5 K to 300 K was measured first in a magnetic field of 0.05 T, then the cooling curve from 300 K to 5 K was measured in the same field. It is found that the M–T curves show a reversible behaviour in heating and cooling processes at the Curie temperature T_C, but without being accompanied by thermal hysteresis, indicating a nature of the second-order phase transition. It can be seen from Fig. 2(a) that $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ undergoes a magnetic transition from ferromagnetic (FM) to paramagnetic (PM) state, and its T_C is determined to be 296 K by evaluating the minimum value of the dM/dT on the ZFC M–T curve under a field of 0.05 T, which is nearly as large as that of pure Gd.[11,12] Figure 2(b) shows the temperature dependences of magnetization of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ in different magnetic fields. The magnetization exhibits a continuous change around T_C in different magnetic fields and T_C significantly increases with increasing magnetic field. The temperature dependence of the magnetization exhibits a rapid decrease at T_C, even at higher magnetic fields, therefore, a large ΔS_M may be expected of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$.

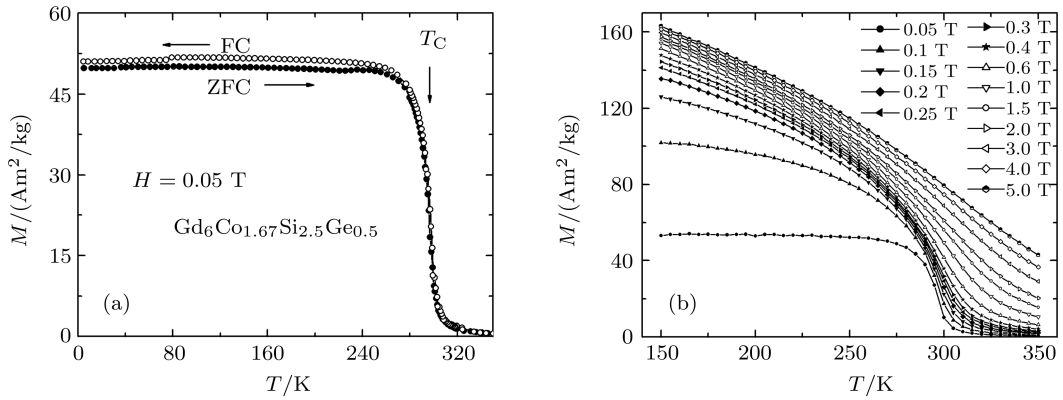


Fig. 2. Temperature-dependent magnetization of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ in both zero field-cooled (ZFC) and field-cooled (FC) processes under a magnetic field of 0.05 T (a), and thermomagnetic curves in different magnetic fields (b).

Figure 3(a) shows the magnetic hysteresis loop at 5 K. One can see from the figure that the hysteresis loop of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ exhibits a soft magnetic behaviour, because Gd has no orbital momentum with relatively small magnetocrystalline anisotropy. Figure 3(b) shows the field dependence of magnetization of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ at 5 K. The magnetic moment per f.u. in an external field of 13 T is found to be 42.3 μ_B. Thus, the magnetic moment of Gd atom is 7.06 μ_B, which is very close to the value of a free Gd^{3+} ion (7 μ_B).

These results mean that the Co atoms are non-magnetic in the $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound as observed in $R_6Co_{1.67}Si_3$ (R = Nd and Tb).[14]

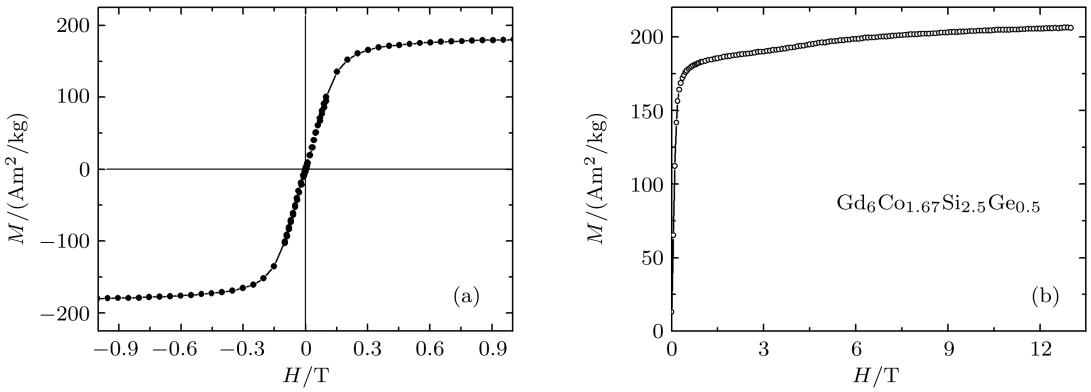


Fig. 3. Magnetic hysteresis loop (a), and field dependence of magnetization (b) of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ at 5 K.

The isothermal magnetization curves of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ were measured from 0 T up to 5 T around T_C in order to determine the ΔS_M. The sweep rate of the field was quite slow to ensure that the M–H curves could be recorded in an isothermal process. Figure 4(a) shows the magnetization isotherms of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ around T_C in a temperature range of 150–350 K with a temperature step of 5 K. It can be seen from Fig. 4(a) that the magnetization is smoothly saturated and its magnitude gradually decreases with the increase of temperature below T_C, exhibiting typical FM nature. For temperatures much higher than the T_C, the field dependence of the magnetization has a linear relation, indicating typical PM nature. Moreover, neither inflection nor negative slope in the Arrott plots of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ as shown in Fig. 4(b) indicates a characteristic of second-order FM-to-PM transition. It can also be seen from Fig. 4(a) that the isothermal magnetization curves obtained well above T_C show strong curvatures at low fields. Similar results have been observed in some other intermetallic compounds.[18−20] This may result from the existence of short-range ferromagnetic correlations in the PM state. To investigate the reversibility of the magnetic transitions in $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$, the M–H curves were measured respectively in field increasing and decreasing modes around T_C. There is no magnetic hysteresis in each curve shown, indicating the perfect magnetic reversibility of the magnetic transitions in $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$.

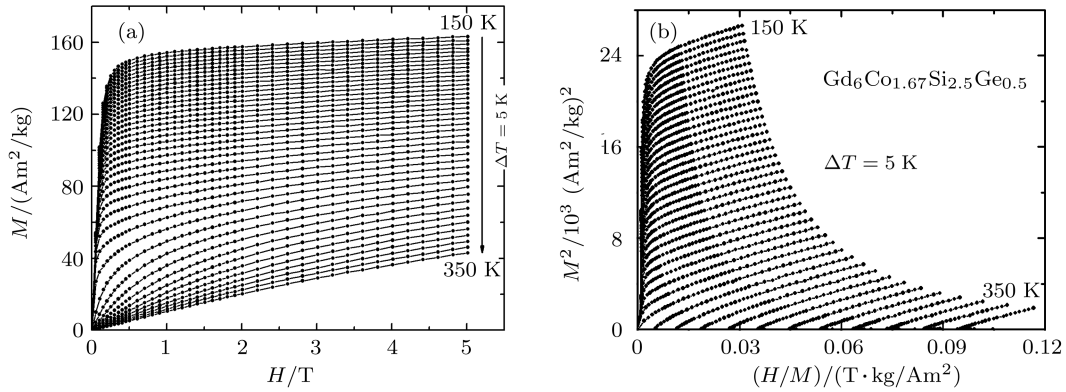


Fig. 4. Isothermal magnetization curves (a), and Arrott plot (b) of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ in a temperature range of 150–350 K with a temperature step of 5 K.

The ΔS_M of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ has been calculated from isothermal magnetization data by using the Maxwell relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H \mathrm{d}H$. Figure 5 shows the ΔS_M as a function of temperature and magnetic field. One can see from Fig. 5 that both the peak and the width of ΔS_M depend on the applied

magnetic field, and increase obviously with increasing field. No change in peak temperature of $\Delta S_{\rm M}$ is observed and the $\Delta S_{\rm M}$ shape shows a "λ"-type one as is usually seen in magnetic materials with a second-order magnetic transition. The maximal values of $\Delta S_{\rm M}$ for $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ are found to be 3.1 J/kg·K and 5.9 J/kg·K at 297.5 K for a field change of 0–2 T and 0–5 T, respectively, which are smaller than those of pure Gd,[12] but are comparable with those of $Gd_6Co_{1.67}Si_3$,[15–17] $Gd_6Ni_{1.67}Si_3$,[16] Gd_7Pd_3,[21] $Gd_5Si_2Ge_2$ compound prepared with low purity (99%) commercial Gd metal,[22] and $Mn_5Ge_{2.1}Ga_{0.9}$.[23] The large value of $\Delta S_{\rm M}$ is due to the high saturation magnetization in $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$.

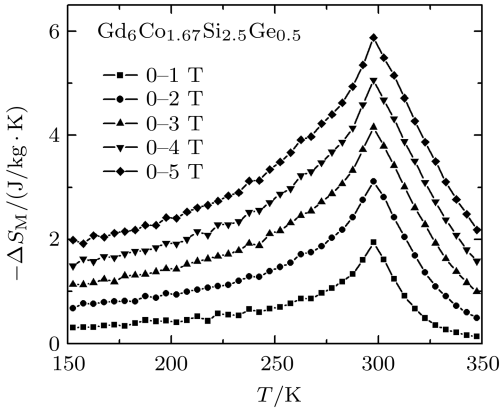


Fig. 5. Temperature dependence of magnetic entropy change $-\Delta S_{\rm M}$ for $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound for different magnetic field changes.

To evaluate applicability of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ as a room-temperature magnetic refrigerant material, its *RC* values have been estimated by using the approach suggested by Gschneidner *et al.*[24] The refrigerant capacity is defined as $RC = \int_{T_1}^{T_2} |\Delta S_{\rm M}| {\rm d}T$, where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of $-\Delta S_{\rm M}$ peak. Calculations show that the maximal value of *RC* for $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ is 424 J/kg for a field change of 0–5 T, which is comparable to or much larger than those of some magnetocaloric materials with a second-order magnetic transition, such as $LaFe_{11.2}Co_{0.7}Si_{1.1}$ (∼420 J/kg at 274 K),[25] $La(Fe_{0.92}Co_{0.08})_{11.83}Al_{1.17}$ (∼415 J/kg at 303 K),[26] $LaFe_{11.0}Co_{0.9}Si_{1.1}$ (∼275 J/kg at 294 K),[27] and $LaFe_{11.2}Co_{0.7}Si_{1.1}C_{0.1}$ (∼320 J/kg at 290 K),[28] but their $\Delta S_{\rm M}$ is larger than that of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$. Although some Gd- and Mn-based magnetocaloric materials with a first-order magnetic transition have a large $\Delta S_{\rm M}$, but their *RC* values are much smaller than that of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ in a similar temperature range for a field change of 0–5 T, such as $Gd_5Ge_2Si_2$ (305 J/kg at 276 K),[29] $Gd_5Ge_{18}Si_{18}Sn_{04}$ (366 J/kg at 278 K),[30] $MnFeP_{0.5}As_{0.5}$ (∼359 J/kg at 282 K),[31] $MnFeP_{0.45}As_{0.55}$ (∼356 J/kg at 308 K),[31] where the *RC* values are estimated from the temperature dependence of $\Delta S_{\rm M}$ in the literature. It can also be observed that both the values of $\Delta S_{\rm M}$ and *RC* for $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ are comparable to those of $Gd_6Co_{1.67}Si_3$,[15,17] and its *RC* value is larger than those of $Gd_5Ge_{1.9}Si_2Fe_{0.1}$[29] and the melt-spun $Gd_5Si_{18}Ge_{18}Sn_{04}$ ribbons prepared at 30 m/s,[30] and they have values of $\Delta S_{\rm M}$ close to each other (see Table 1). The present study shows that large *RC* and zero magnetic hysteresis are simultaneously achieved in $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound.

Table 1. Curie temperature $T_{\rm C}$, magnetic entropy change $\Delta S_{\rm M}$, and refrigerant capacity *RC* at $T_{\rm C}$ for a magnetic field change of 0–5 T for pure Gd and some Gd-based magnetocaloric materials.

materials	$T_{\rm C}$/K	$-\Delta S_{\rm M}$/(J/kg·K)	*RC*/(J/kg)	Refs.
Gd	293	9.7	556	[12]
$Gd_6Co_2Si_3$	295	6.3	503	[12]
$Gd_6Co_{1.67}Si_3$	298	5.2	440	[15]
$Gd_6Co_{1.67}Si_3$	300	5.8	426	[17]
$Gd_5Ge_{1.9}Si_2Fe_{0.1}$	276	7.0	360	[29]
$Gd_5Si_{18}Ge_{18}Sn_{04}$	278	6.5	335	[30]
$Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$	296	5.9	424	this work

4. Conclusion

In conclusion, the $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound with a hexagonal $Ce_6Ni_2Si_3$-type structure undergoes a ferromagnetic ordering below the Curie temperature $T_{\rm C} = 296$ K. A good magnetocaloric property is observed.

The maximal value of $\Delta S_{\rm M}$ is 5.9 J/kg $\cdot$ K for a magnetic field change of 0–5 T, which originates from a reversible second-order magnetic transition. The peak of the $\Delta S_{\rm M}$–T curve shows a broad distribution and the full width at half maximum of the $\Delta S_{\rm M}$ peak is about 101 K under a magnetic field of 5 T. The value of RC for a field change from 0 to 5 T is found to be 424 J/kg. Good magnetocaloric properties and especially considerable value of RC indicate that the $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound is a suitable candidate as magnetic refrigerants in the room temperature range.

References

[1] Gschneidner K A Jr, Pecharsky V K and Tsokol A O 2005 *Rep. Prog. Phys.* **68** 1479

[2] Brück E 2008 in *Handbook of Magnetic Materials* ed. Buschow K H J (Amsterdam: Elsevier) Vol. 17, pp. 235

[3] Shen B G, Sun J R, Hu F X, Zhang H W and Chen Z H 2009 *Adv. Mater.* **21** 4545

[4] Pecharsky V K and Gschneidner K A Jr 1997 *Phys. Rev. Lett.* **78** 4494

[5] Hu F X, Shen B G, Sun J R and Zhang X X 2000 *Chin. Phys.* **9** 550

[6] Hu F X, Shen B G, Sun J R, Chen Z H, Rao G H and Zhang X X 2001 *Appl. Phys. Lett.* **78** 3675

[7] Wada H and Tanabe Y 2001 *Appl. Phys. Lett.* **79** 3302

[8] Tegus O, Brück E, Buschow K H J and de Boer F R 2002 *Nature* (London) **415** 150

[9] Hu F X, Shen B G and Sun J R 2000 *Appl. Phys. Lett.* **76** 3460

[10] Hu F X, Shen B G, Sun J R and Wu G H 2001 *Phys. Rev.* B **64** 132412

[11] Pecharsky V K and Gschneidner K A Jr 1999 *J. Magn. Magn. Mater.* **200** 44

[12] Shen J, Wu J F and Sun J R 2009 *J. Appl. Phys.* **106** 083902

[13] Gaudin E, Weill F and Chevalier B 2006 *Z. Naturforsch* **61b** 825

[14] Chevalier B, Gaudin E and Weill F 2007 *J. Alloys Compd.* **442** 149

[15] Shen J, Li Y X, Dong Q Y, Wang F and Sun J R 2008 *Chin. Phys.* B **17** 2268

[16] Gaudin E, Tencé S, Weill F, Fernandez J R and Chevalier B 2008 *Chem. Mater.* **20** 2972

[17] Jammalamadaka S N, Mohapatra N, Das S D, Iyer K K and Sampathkumaran E V 2008 *J. Phys.*: *Condens. Matter* **20** 425204

[18] Singh N K, Suresh K G, Nirmala R, Nigam A K and Malik S K 2007 *J. Appl. Phys.* **101** 093904

[19] Arora P, Tiwari P, Sathe V G and Chattopadhyay M K 2009 *J. Magn. Magn. Mater.* **321** 3278

[20] Chen J, Shen B G, Dong Q Y, Hu F X and Sun J R 2009 *Appl. Phys. Lett.* **95** 132504

[21] Canepa F, Napoletano M and Cirafici S 2002 *Intermetallics* **10** 731

[22] Zhang T, Chen Y, Teng B, Tang Y, Fu H and Tu M 2007 *Mater. Lett.* **61** 440

[23] Liu X B, Zhang S Y and Shen B G 2004 *Chin. Phys.* **13** 397

[24] Gschneidner Jr K A, Pecharsky V K, Pecharsky A O and Zimm C B 1999 *Mater. Sci. Forum* **315** 69

[25] Hu F X, Shen B G, Sun J R, Wang G J and Cheng Z H 2002 *Appl. Phys. Lett.* **80** 826

[26] Hu F X, Shen B G, Sun J R and Cheng Z H 2001 *Phys. Rev.* B **64** 12409

[27] Balli M, Fruchart D and Gignoux D 2007 *J. Phys.*: *Condens. Matter* **19** 236230

[28] Balli M, Fruchart D and Gignoux D 2008 *Appl. Phys. Lett.* **90** 232505

[29] Provenzano V, Shapiro A J and Shull R D 2004 *Nature* (London) **429** 853

[30] Zhang T B, Chen Y G and Tang Y B 2007 *J. Phys.* D: *Appl. Phys.* **40** 5778

[31] Tegus O, Brück E, Zhang L, Dagula, Buschow K H J and de Boer F R 2002 *Physica* B **319** 174