Journal of Alloys and Compounds 489 (2010) 289–292

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Lattice, magnetic and electronic transport behaviors of Ge-doped Mn_3XC (X = Al, Zn, Ga)

Yongchun Wen, Cong Wang*, Ying Sun, Guanxin Liu, Man Nie, Lihua Chu

Center for Condensed Matter and Materials Physics, School of Science, Beijing University of Aeronautics and Astronautics, Beijing 100083, People's Republic of China

ARTICLE INFO

Article history:
Received 4 June 2009
Received in revised form
16 September 2009
Accepted 16 September 2009
Available online 23 September 2009

Keywords:
Antiperovskite
Magnetic phase transition
Ge
Electronic transport

ABSTRACT

The lattice, magnetic, and electronic transport properties of $Mn_3X_{1-y}Ge_yC$ (X = Al, Zn, and Ga; $y = 0, 0.5$) were investigated. Ge-doping does not change the antiperovskite structure, and only decreases the lattice constant in different degree. For all $Mn_3X_{1-y}Ge_yC$, Ge-doping makes the magnetic transition temperature decrease. The total behavior of $Mn_3Al_xGe_{1-x}C$ in temperature dependence of resistivity is metallic. For $Mn_3Ga_xGe_{1-x}C$, since the carrier densities in the ferromagnetic phase and antiferromagnetic one are different, with decreasing the temperature, the resistivity appears an abrupt increase.

1. Introduction

Antiperovskite structural compounds $M_3XC(N)$ (M = Mn and Ni, X = main group element), in which the M atoms are located at the face centered positions, the X atoms at the cubic corners, and the C atom at the body centered position, are well known for a couple of years [1]. Recently, researchers found that the kind of compounds show a wide variety of interesting physical phenomena such as superconductivity [2,3], negative thermal expansion [4–8], large magnetocaloric effect [9,10], giant magnetoresistance [11], a nearly zero temperature coefficient of resistivity [12] and magnetostriction [13]. These properties are closely correlated with their structure and magnetic phase transition. In addition, some of the antiperovskite compounds showed abnormal electronic and magnetic transport behaviors and lattice variation with changing temperature [14,15]. So, it is necessary to study the structure, electronic and magnetic transport of the cubic antiperovskite compounds. Doping in the X site can obviously alter the structure, electronic and magnetic transport in M_3XC, which probably leads to the discovery of a promising material. Takenaka and Takagi reported that the discontinuous lattice contraction near the magnetic transition temperature region was modified into continuous contraction by introducing the element Ge into X position in $Mn_3X_{1-x}Ge_xN$ [4]. In our previous experiments, although, Mn_3CuN did not show magnetovolume effect (MVE), $Mn_3Cu_{1-x}Ge_xN$ (X = 0.15, 0.3, 0.4, 0.5 and 0.55) indicated a big MVE [5]. Meanwhile, the variation in the magnetism or transport by Ge-doping is more complicated than the variation in the crystal structure. The mechanism of these intriguing properties was primarily investigated lately [16]. Mn_3XC (X = Al, Zn, and Ga) presents complicated magnetic structure, and shows many interesting physical properties. In order to study the role of doping Ge in Mn_3XC, the crystal structure, magnetic and electronic transport properties of Ge-doped Mn_3XC were investigated.

2. Experimental details

Polycrystalline samples $Mn_3X_{1-y}Ge_yC$ (X = Al, Zn, Ga) were prepared using manganese, aluminum, zinc, germanium, graphite powders and gallium ingots of 3N purity as the starting powder materials. They were mixed in the stoichiometric proportion and pressed into pellets. The pellets were wrapped by tantalum foil, and then placed in an evacuated quartz tube whose vacuum was about 10^{-4} Pa. The sealed tube was heated to 600 °C for 24 h in a box furnace. The samples were sintered in a box furnace at 800 °C for 5 days, then cooled down to room temperature. The procedure was repeated until a pure single phase was got.

X-ray diffraction patterns at room temperature were collected in a Rigaku D/MAX 2200PC diffractometer using Cu Kα radiation. Software named Powder X [17] was used for indexing and calculating lattice constant. For the measurement of coefficient of thermal expansion (CTE), variable temperature X-ray diffraction from 150 to 325 K was used to measure the variation of lattice constants on an X'Pert PRO MPD diffractometer. The magnetic properties were investigated by a superconducting quantum-interference device (SQUID, Quantum Design) magnetometer. The temperature dependences of the electrical resistivity were measured by a physical property measurement system (PPMS). Increasing rate of temperature is 5 K/min. The error bar value of lattice constant is less than 0.0002 Å.

* Corresponding author. Tel.: +86 10 82338346; fax: +86 10 82338346.
E-mail address: congwang@buaa.edu.cn (C. Wang).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.09.075

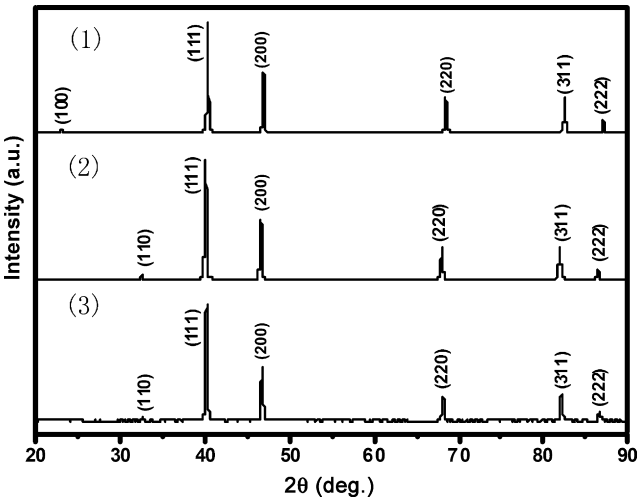

Fig. 1. X-ray diffraction patterns of $Mn_3Al_{0.5}Ge_{0.5}C$ (a), $Mn_3Zn_{0.5}Ge_{0.5}C$ (b) and $Mn_3Ga_{0.5}Ge_{0.5}C$ (c).

3. Results and discussion

As a represent, the indexed XRD patterns for the $Mn_3Al_{0.5}Ge_{0.5}C$, $Mn_3Zn_{0.5}Ge_{0.5}C$ and $Mn_3Ga_{0.5}Ge_{0.5}C$ samples are given in Fig. 1. The index table of the XRD patterns, observed and calculated for $Mn_3Al_{0.5}Ge_{0.5}C$ compound, is showed in Table 1. The observed data $\theta_{obs.}$ and $d_{obs.}$ are in good agreement with the calculated ones $\theta_{cal.}$ and $d_{cal.}$, respectively. According to these results, the samples are in pure antiperovskite cubic structure, and they have the same space group $Pm\bar{3}m$ (No. 221). The calculated lattice constants are shown in Table 2. Ge-doping does not change the structure, and only decreases the lattice constants for Mn_3AlC, Mn_3ZnC, and Mn_3GaC, which is due to smaller atom radius of Ge than that of Al, Zn, and Ga, respectively. Since Mn–C bond is very stable [1] and the C atom is very small, the Mn atoms reside at ⟨0.5, 0.5, 0⟩, the C atoms at [0.5,0.5,0.5], and the other atoms at [0,0,0].

Fig. 2 presents the temperature dependence of the susceptibility of $Mn_3Al_{1-x}Ge_xC$, $Mn_3Zn_{1-x}Ge_xC$, and $Mn_3Ga_{1-x}Ge_xC$ compounds. The Curie temperature T_C is determined by the crossing point of two tangent lines of the susceptibility curve. T_T is the transition temperature from ferromagnetic to antiferromagnetic. Every T_C is shown in Table 3. All these experiments show that Ge-doping decreases the magnetic order transition temperature. Ge-doping causes a lattice distortion where the overall structure remains cubic

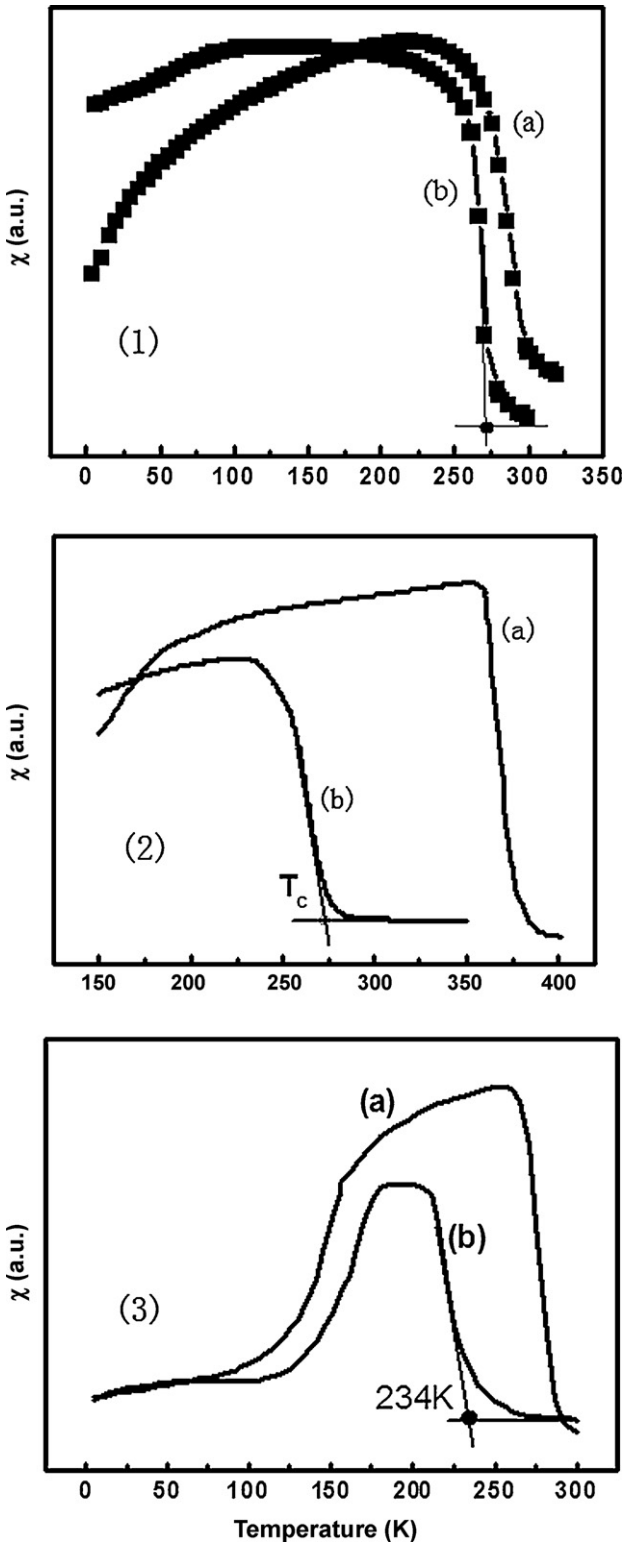

Fig. 2. Temperature dependence of the magnetic susceptibility for (1) $Mn_3Al_{1-x}Ge_xC$, (2) $Mn_3Zn_{1-x}Ge_xC$ and (3) $Mn_3Ga_{1-x}Ge_xC$. The (a) and (b) represent $X = 0$ and 0.5, respectively.

Table 1
The index table of the XRD pattern of $Mn_3Al_{0.5}Ge_{0.5}C$ compound.

hkl	$\theta_{obs.}$ (°)	$d_{obs.}$ (Å)	$\theta_{obs.}$ (°)	$d_{obs.}$ (Å)	DIFF. (θ)
100	11.48457	3.87020	11.47175	3.87309	0.00869
111	20.15130	2.23643	20.14997	2.23613	−0.00280
200	23.43808	1.93693	23.43882	1.93655	−0.00487
220	34.23795	1.36925	34.23103	1.36934	0.00279
311	41.27787	1.16773	41.27138	1.16778	0.00236
222	43.54557	1.11819	43.54762	1.11807	−0.00617

SQRT((SUM(TH_{O-C})^2)/(JREF − NPAR)) × 1000 = 0.06949; R-factor: 0.00016.

Table 2
The lattice constant of $Mn_3X_{1-y}Ge_yC$ compound (X = Al, Zn, and Ga; $y = 0$, 0.5).

Compounds	$x = 0$	$x = 0.5$
$Mn_3Al_{1-x}Ge_xC$	3.8763 Å	3.8731 Å
$Mn_3Zn_{1-x}Ge_xC$	3.9164 Å	3.8965 Å
$Mn_3Ga_{1-x}Ge_xC$	3.8932 Å	3.8792 Å

All of the lattice constants' errors are less than 0.0002 Å.

antiperovskite, which is analogous to the local lattice distortion in the giant negative thermal expansion material $Mn_3Cu_{1-x}Ge_xN$ [18]. For $Mn_3X_{1-y}Ge_yC$, the local distortion results in the local disorder in magnetic structure. Ge is nonmagnetic atom. For the reasons given above, the local magnetic disorder due to Ge-doping in $Mn_3X_{1-y}Ge_yC$ reduces the coupling intensity of magnetic

Table 3
The Curie temperature of $Mn_3X_{1-y}Ge_yC$ compound (X = Al, Zn, and Ga; $y = 0, 0.5$).

Compounds	$x = 0$	$x = 0.5$
$Mn_3Al_{1-x}Ge_xC$	315 K	275 K
$Mn_3Zn_{1-x}Ge_xC$	380 K	273 K
$Mn_3Ga_{1-x}Ge_xC$	288 K	238 K

The errors are less than 1 K.

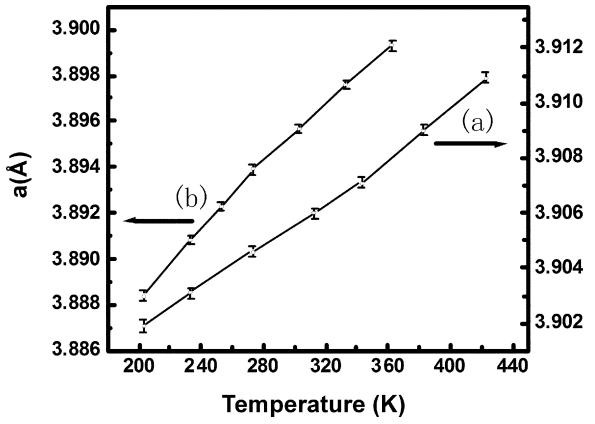

Fig. 3. Temperature dependence of the lattice constant for (a) Mn_3ZnC and (b) $Mn_3Zn_{0.5}Ge_{0.5}C$.

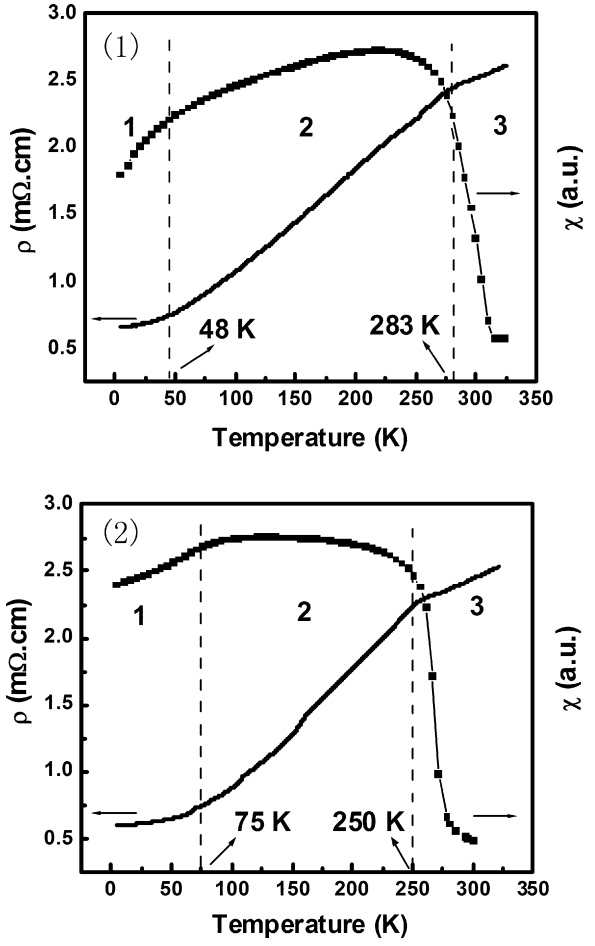

Fig. 4. Temperature dependence of the magnetic susceptibility and the electrical resistivity for (1) Mn_3AlC and (2) $Mn_3Al_{0.5}Ge_{0.5}C$.

moments, which means that T_C decreases. Moreover, we performed the temperature dependence of the lattice constant of $Mn_3Zn_{1-y}Ge_yC$. As seen in Fig. 3, with increasing the temperature, the linear coefficient of thermal expansion (LCTE) displays an inflexion at 350 K in Mn_3ZnC and at 250 K in $Mn_3Zn_{0.5}Ge_{0.5}C$, respectively. The reason of LCTE changing should be that there exists a small magnetovolume effect near T_C. Mn_3GaC exhibits complicated magnetic phase transitions, and the ground state of Mn_3GaC is antiferromagnetic at ambient pressure. Ge-doping increases T_T, and narrows the region of the intermediate state where both the AFM and FM components are present.

Fig. 4 displays the temperature dependence of resistivity of $Mn_3Al_{1-y}Ge_yC$ ($y = 0, 0.5$). For the purpose of the comparison with

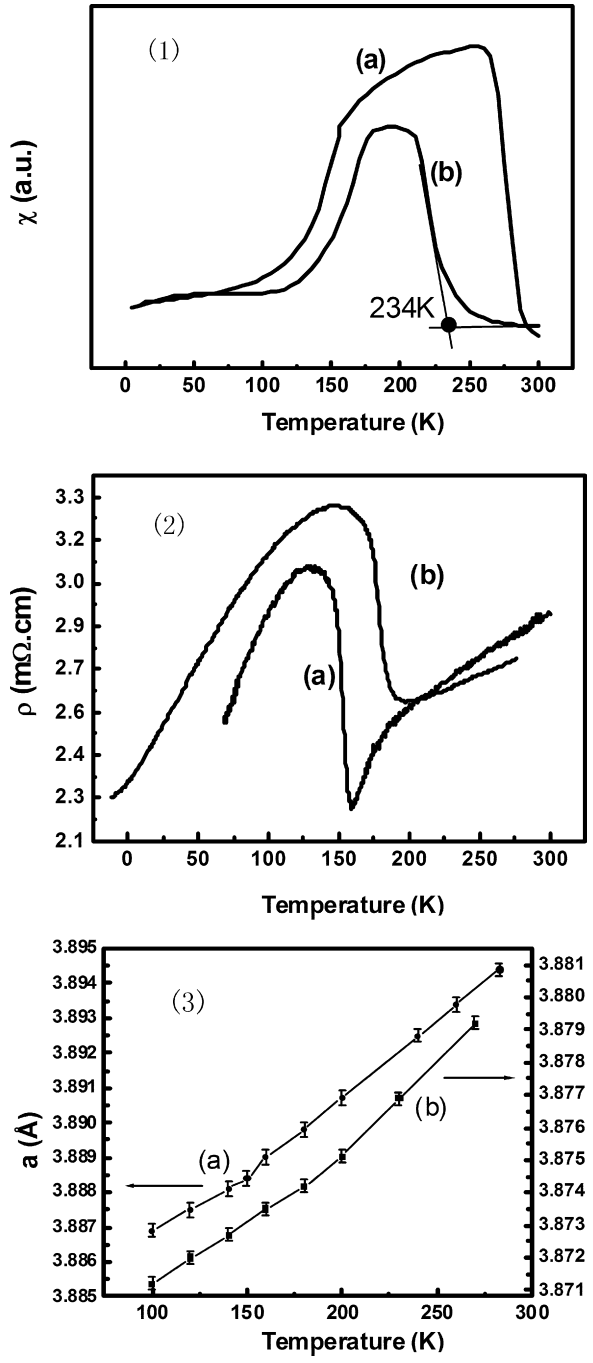

Fig. 5. Temperature dependence susceptibility (1), electrical resistivity (2) and lattice constant (3) for Mn_3GaC (a) and $Mn_3Ga_{0.5}Ge_{0.5}C$ (b).

magnetic phase transition, the temperature dependence of the susceptibility of $Mn_3Al_{1-x}Ge_xC$ is attached. The total behavior in temperature dependence of resistivity is metallic. Both resistivity curves can be divided into three stages, respectively. The transition temperatures are 48 and 283 K for Mn_3AlC, 75 and 250 K for $Mn_3Al_{0.5}Ge_{0.5}C$, respectively. In the gross, the 3rd stage is corresponding to paramagnetic (PM) state, the 2nd stage to ferromagnetic state, and 1st stage to antiferromagnetic state. Obviously, the $d\rho/dT$ of stage 2 is the biggest. For stages 2 and 3, the temperature dependence of the transport can be explained by the magnetic scattering mechanism. In magnetic materials, besides the lattice contribution to the transport, which decrease with decreasing temperature, an invariable spin-disorder contribution exists in the PM state. In FM (or FI) state, the orientation of the magnetic moments becomes ordered and the conduction electrons suffer smaller scattering probability than that in the PM state. As a result, the mean free path of electrons becomes longer and the resistivity rapidly decreases.

Fig. 5 shows the temperature dependence of resistivity of $Mn_3Ga_{1-y}Ge_yC$. Both Mn_3GaC and $Mn_3Ga_{0.5}Ge_{0.5}C$ have the similar ρ–T curve which is different from that of $Mn_3Al_{1-y}Ge_yC$. The resistivities first decrease with decreasing the temperature, then rise abruptly at a certain temperature (158 K for Mn_3GaC and 190 K for $Mn_3Ga_{0.5}Ge_{0.5}C$) to reach a maximum, and finally decrease with a further decrease in temperature. The temperature where the resistivity abruptly jumps is consistent with the transition temperature between the antiferromagnetic and intermediate (comprising FM and AFM) phases. K. Kamishima et al. reported that the charge carrier density of Mn_3GaC in the ferromagnetic (FM) phase was about five times larger than that in the antiferromagnetic (AFM) phase [11]. So, the resistivity abruptly increases when the intermediate state transform into AFM one. Obviously, the resistivity of $Mn_3Ga_{0.5}Ge_{0.5}C$ is similar to that of Mn_3GaC.

4. Conclusions

We have prepared pure cubic antiperovskite $Mn_3X_{1-y}Ge_yC$ (X = Al, Zn, Ga; y = 0, 0.5), and investigated the structure, magnetic, and transport properties. Ge-doping does not change the antiperovskite structure, and only decreases the lattice constant in different degree. Although the overall structure of $Mn_3X_{1-y}Ge_yC$ remains cubic antiperovskite, Ge-doping causes the local lattice distortion. The local structural distortion provokes the local magnetic disorder which reduces the coupling intensity of magnetic moments. So, Ge-doping makes T_C decrease. For $Mn_3Al_xGe_{1-x}C$, the total behavior in temperature dependence of resistivity is metallic. However, with decreasing the temperature, the resistivity of $Mn_3Ga_xGe_{1-x}C$ possesses an abrupt increase. The abrupt jump is consistent with the transition temperature between the antiferromagnetic and intermediate phases, which is because the carrier density of $Mn_3Ga_{1-x}Ge_xC$ in the ferromagnetic phase is more than that in the antiferromagnetic one.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (NSFC) (No. 50772008), and Foundation of the State Key Laboratory of Shanghai Institute of Ceramics (SKL200603SIC).

References

[1] D. Fruchart, E.F. Bertaut, J. Phys. Soc. Jpn. 44 (1978) 781.
[2] T. He, Q. Huang, A.P. Ramirez, Y. Wang, K.A. Reran, N. Rogado, M.A. Hayward, M.K. Haas, J.S. Slusky, K. Inumara, H.W. Zandbergen, N.P. Ong, R.J. Cava, Nature (London) 411 (2001) 54.
[3] S.Q. Wu, Z.F. Hou, Z.Z. Zhu, Physica B 403 (2008) 4232–4235.
[4] K. Takenakaa, H. Takagi, Appl. Phys. Lett. 87 (2005) 261902.
[5] Y. Sun, C. Wang, Y.C. Wen, K.G. Zhu, Appl. Phys. Lett. 91 (2007) 231913.
[6] S. Iikubo, K. Kodama, K. Takenaka, H. Takagi, S. Shamoto, Phys. Rev. B 77 (2008) 020409 (R).
[7] R. Huang, L. Li, F. Cai, X. Xu, L. Qian, Appl. Phys. Lett. 93 (2008) 081902.
[8] K. Takenaka, K. Asano, M. Misawa, H. Takagi, Appl. Phys. Lett. 92 (2008) 011927.
[9] M.H. Yu, L.H. Lewis, A.R. Moodenbaugh, J. Appl. Phys. 93 (2003) 10128.
[10] T. Tohei, H. Wadaa, T. Kanomatab, J. Magn. Magn. Mater. 272–276 (2004) e585.
[11] K. Kamishima, T. Goto, H. Nakagawa, N. Miura, M. Ohashi, N. Mori, Phys. Rev. B 63 (2000) 024426.
[12] E.O. Chi, S. Kim, N.H. Hur, Solid State Commun. 120 (2001) 307.
[13] K. Asano, K. Koyama, K. Takenaka1, Appl. Phys. Lett. 92 (2008) 161909.
[14] W.S. Kim, E.O. Chi, J.C. Kim, N.H. Hur, Solid State Commun. 119 (2001) 507.
[15] W.J. Feng, D. Li, W.J. Ren, Y.B. Li, W.F. Li, J. Li, Y.Q. Zhang, Z.D. Zhang, J. Alloys Compd. 437 (2007) 27–33.
[16] S. Iikubo, K. Kodama, K. Takenaka, H. Takagi, M. Takigawa, S. Shamoto, Phys. Rev. Lett. 101 (2008) 205901.
[17] C. Dong, J. Appl. Crystallogr. 32 (1999) 838.
[18] S. Likubo, K. Kodama, K. Takenaka, H. Takagi, M. Takigawa, S. Shamoto, Phys. Rev. Lett. 101 (2008) 205901.