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Large room-temperature rotating magnetocaloric effect in $NdCo_4Al$ polycrystalline alloy

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ABSTRACT

The magnetic refrigeration based on rotating magnetocaloric effect (MCE) is promising to build a simplified magnetic cooling system. Until now, most magnetic refrigerants for rotating MCE are single crystal and work at low temperature, which hinder the development of this refrigeration technology. In present paper, we report a large room-temperature rotating MCE in a magnetic-field-aligned $NdCo_4Al$ polycrystalline alloy. A large rotating magnetic entropy change of 1.3 J kg^{-1} K^{-1} under 10 kOe and a broad operating temperature window of 52 K are achieved. The origin of large rotating MCE in $NdCo_4Al$ polycrystalline alloy and its advantages for rotating magnetic refrigeration are discussed.

1. Introduction

The magnetocaloric effect (MCE) refers to the temperature change in a magnetic material caused by an external magnetic field change in the adiabatic process. The magnetic refrigeration based on MCE is an attractive cooling technology for its environmental safety and high efficiency, which could potentially replace the common vapor compression cycle technology in use nowadays. For conventional working method of magnetic refrigeration, the magnetocaloric materials need to be moved in and out of the magnetic field zone, which requires a large working space. Recently, an alternative magnetic refrigeration concept, rotating MCE, has been proposed, which is promising to solve this problem [1–6]. The schematic of the implementation of rotating MCE is shown in Fig. 1(a). Magnetic refrigeration can be realized by rotating refrigerants in a constant magnetic field zone instead of moving them in and out of the magnetic field zone, which offers the possibility to build a simplified and compact magnetic cooling system. According to the working principle of rotating MCE, the refrigerant should show different values of MCE with the variation of magnetic field direction, i.e. anisotropic MCE. Up to now, large rotating MCE has been observed in some single crystals, such as $HoMn_2O_5$ [3], $TmMnO_3$ [4], and $ErFeO_3$ [5], due to strong magnetocrystalline anisotropy (MCA) of rare earth ions. However, the operating temperature of most of them are far below room temperature [3–5,7], which hinders their applications for the household appliances. Recently, a giant rotating MCE has been reported in $NdCo_5$ single crystal, which peak temperature of rotating MCE is close to the room temperature [2]. However, from the practical application point of view, the working temperature of this magnetic refrigerant needs to be further increased. Besides, the high cost and complexity of preparation for single crystal is another hurdle that should be overcome to fulfill $NdCo_5$ for rotating magnetic refrigeration.

$NdCo_5$ is a ferromagnetic intermetallic compound which crystallizes in a hexagonal $CaCu_5$-type structure with $P6/mmm$ space group. In this alloy, MCA of Co sublattice favors the c axis (first-order anisotropic constant $K_{1Co}>0$), while the Nd sublattice tends to have a planar (ab plane) MCA ($K_{1Nd}<0$). Due to the existence of these two types of MCA and the competition between them, $NdCo_5$ would undergo two second-order spin-reorientation (SR) transitions at T_{SR1}=250 K and T_{SR2}=290 K, respectively [8–14]. It is reported that partial substitution of Al for Co in $NdCo_5$ would remarkably increase the SR temperature, which is attributed to the modification of magnetic anisotropy by Al-doping [15–18]. In addition, the magnetic-field-aligned technology is proved to be an effect approach to achieve textured polycrystalline compounds, which can show large MCA as well [15,16,19]. Based on this method, we prepare an orientated $NdCo_4Al$ polycrystalline alloy and investigate its rotating MCE. The experimental results indicate that this magnetic-field-aligned alloy has a large low-field rotating MCE at room temperature.

2. Experimental

Polycrystalline sample of $NdCo_4Al$ was prepared by arc melting the stoichiometric amount of the high purity elements. For a better

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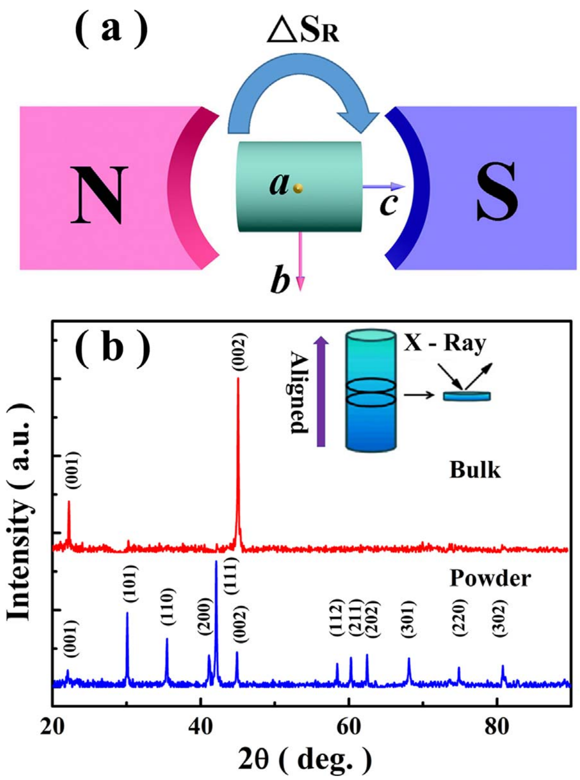

Fig. 1. (Color online) (a) A schematic for the implementation of the rotating MCE by rotating.refrigerants in a constant magnetic field, (b) X-ray diffraction patterns of a field-oriented sample and a free powder of $NdCo_4Al$ at room temperature.

homogeneity the sample was annealed at 1173 K for a week in an evacuated quartz tube. Magnetic-field-aligned $NdCo_4Al$ alloy was prepared at 350 K by solidifying the mixture of epoxy resin and the powder specimen (≦40 μm) in a magnetic field of 5 kOe. At 350 K, the easy magnetization axis of $NdCo_4Al$ alloy was *c* axis [15–19] and the magnetic moments would arrange along that direction. The hexagonal $CaCu_5$-type structure (*P*6/*mmm* space group) for polycrystalline $NdCo_4Al$ Alloy was confirmed by X-ray powder diffraction (XRD) analysis at room temperature with Cu Kα radiation. Magnetic measurements were carried out using a vibrating sample magnetometer (7407, Lakeshore) under a magnetic field up to 10 kOe. Specific heat of $NdCo_4Al$ polycrystalline alloy was investigated from 220 K to 360 K in physical property measurement system (6000, Quantum Design).

3. Results and discussion

To characterize the preferred orientation of magnetic-field-aligned alloy, a transverse section of the sample with the direction perpendicular to the magnetic field is cut for XRD measurement. For comparison, the XRD pattern for the polycrystalline powder is also presented. As shown in Fig. 1(b), the powder sample displays a random crystallographic orientation and all the peaks can be indexed as the hexagonal $CaCu_5$-type structure. In the case of magnetic-field-aligned alloy, many diffraction peaks are remarkably suppressed and only two greatly enhanced (001) and (002) peaks can be observed, indicating that the sample is orientated along *c* axis by a magnetic-field-aligned technology.

Temperature dependence of magnetization (*M*–*T* curve) for the magnetic-field-aligned $NdCo_4Al$ alloy is measured from 220 K to 360 K with a magnetic field of 2 kOe parallel and perpendicular to *c* axis, respectively. In the low temperature, the MCA of Nd sublattice is larger than that of Co sublattice, and consequently, the total magnetic moment lies in the *ab* plane. When the axial MCA of Co sublattice is dominant, the *c* axis becomes the easy magnetization direction. Due to

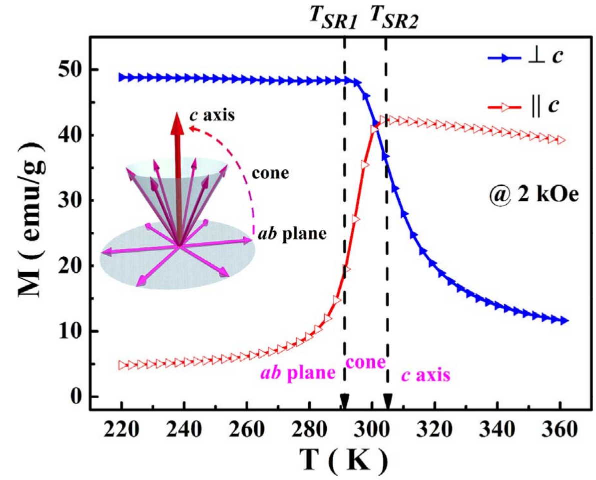

Fig. 2. (Color online) Temperature dependence of magnetization of the magnetic-field-aligned $NdCo_4Al$ alloy with H||and⊥c axis, respectively.

the strong competition between these two MCAs, the conical arrangement of magnetic moment which is between the *ab* plane and the *c* axis is produced. As a result, the arrangement of magnetic moment would undergo plane-cone and cone-axis SR transitions, which occur around T_{SR1} and T_{SR2}, respectively. As shown in Fig. 2, upon partial substitution of Al for Co, T_{SR1} and T_{SR2} of $NdCo_4Al$ alloy are 293 K and 305 K, which are larger than these of $NdCo_5$ single crystal, respectively [2]. It is worth noting that the magnetization mainly increases or decreases with the increase of temperature, for the magnetic field parallel and perpendicular to *c* axis, respectively. The different *M*–*T* behavior for $NdCo_4Al$ alloy is attributed to the change of MCA with the variation of temperature and meaningful for achieving enhanced rotating MCE, which will be discussed later.

Fig. 3(a) and (b) present magnetic field dependence of magnetization for $NdCo_4Al$ alloy at 270 K and 360 K, respectively. At 270 K, the magnetization tends to be saturated at 5 kOe with the magnetic field perpendicular to *c* axis and the saturation magnetization is 62 emu/g. However, for the magnetic field parallel to *c* axis, the magnetization curve does not show a tendency of saturation even at 10 kOe, revealing the characteristic of hard magnetization axis. On the contrary, at 360 K, the magnetization tends to be saturated at 2 kOe with the magnetic field parallel to *c* axis and the saturation magnetization is 57 emu/g, suggesting that the easy magnetization axis has changed from *ab* plane to *c* axis above T_{SR2}. As a result, a hard magnetization behavior is observed when the magnetic field is perpendicular to *c* axis, which is shown in Fig. 3(b). Angle dependence of magnetization curves are measured by rotating the magnetic-field-aligned $NdCo_4Al$ alloy from parallel to perpendicular to *c* axis under a magnetic field of 2 kOe. Here, θ is defined as the angle between the magnetic-field-aligned direction (*c* axis) and the applied magnetic field direction. As shown in the insets of Fig. 3(a) and (b), the magnetization decreases or increases gradually by rotating the sample from 0° to 90°, respectively, suggesting that the rotating MCE can be detected in this magnetic-field-aligned polycrystalline alloy.

A series of selected isothermal curves for $NdCo_4Al$ alloy are measured from 220 K to 360 K with the magnetic field parallel and perpendicular to *c* axis, which are shown in Fig. 3(c) and (d), respectively. In the case of parallel direction, the magnetization first increases monotonously with increasing temperature until 300 K since the easy magnetization direction gradually changes from *ab* plane to *c* axis. However, when the temperature is higher than T_{SR2}, *c* axis becomes the easy magnetization axis, and then the magnetization decreases with increasing temperature [15], which leads to some crossovers in isothermal magnetization curves. As the magnetic field is perpendicular to *c* axis, the magnetization decreases monotonously

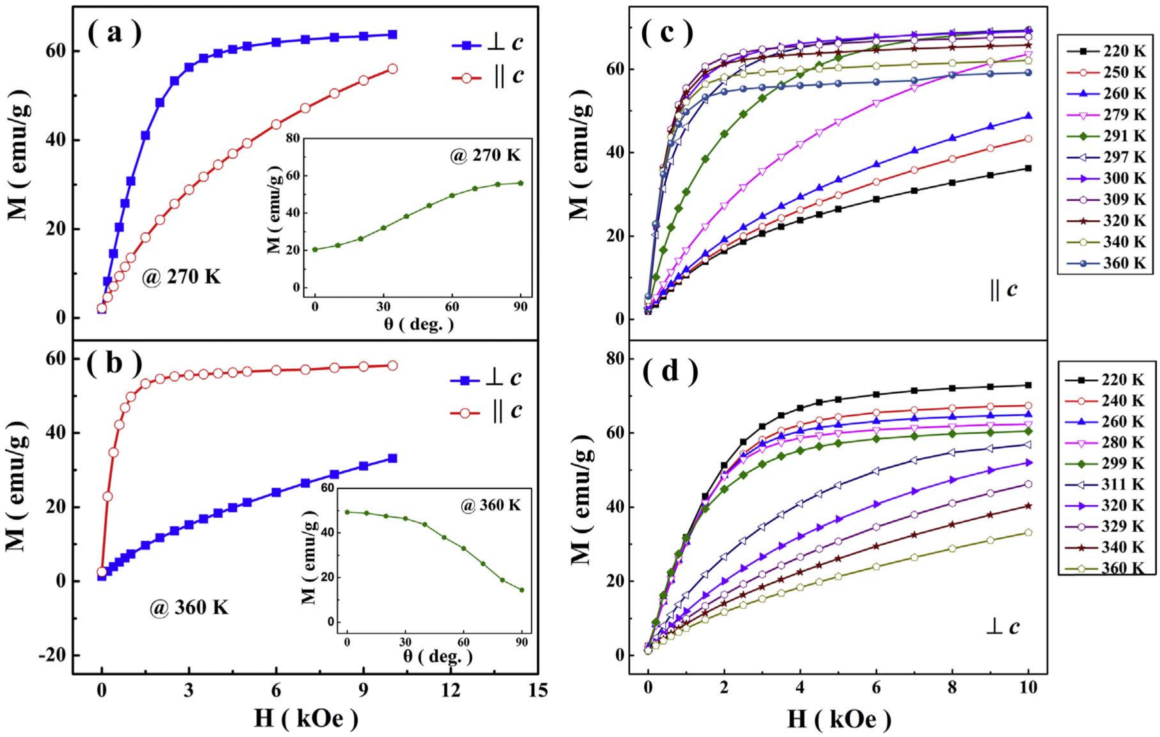

Fig. 3. (Color online) Isothermal magnetization curves of $NdCo_4Al$ alloy for H||c and H⊥c (a) at 270 K (b) at 360 K, respectively. The insets show angle dependence of magnetization measured by rotating the alloy from 0° to 90° under 2 kOe at 270 K and 360 K, respectively. Isothermal magnetization curves of $NdCo_4Al$ alloy for (c) H||c and (d) H⊥c.

with increasing temperature, which is shown in Fig. 3(d). Noted that the saturation magnetization of $NdCo_4Al$ is less than that of $NdCo_5$[2], which is attributed to the substitution of non-magnetic Al atoms [15–19].

The value of rotating MCE ($\Delta S_R(\theta)$) can be obtained by using the following equation [20]:

$$\Delta S_R(\theta)=\Delta S_M(\theta)-\Delta S_M(90°)=\mu_0\int_0^H\left(\frac{\partial M(\theta)}{\partial T}\right)_H dH-\int_0^H\left(\frac{\partial M(90°)}{\partial T}\right)_H dH \tag{1}$$

Here $\Delta S_M(\theta)$ is defined as the magnetic entropy change at that angle. According to Eq. (1), we can find that the enhanced rotating MCE can be achieved in materials which $\Delta S_M(90°)$ and $\Delta S_M(\theta)$ are opposite in sign. For example, one is positive MCE and the other is negative one. Thus in these materials, the absolute value of $\Delta S_R(\theta)$ is larger than that of $\Delta S_M(\theta)$ along any direction. Actually, most of rotating magnetocaloric materials [3–7,21] do not match this condition except the SR materials [2] which their easy magnetization axis varies with the temperature.

Fig. 4 shows temperature dependence of ΔS_M of $NdCo_4Al$ polycrystalline alloy with magnetic field parallel and perpendicular to *c* axis, respectively. Here ΔS_M is calculated from magnetization data in Fig. 3(a) and (b) by using the Maxwell relation [20]. Since $NdCo_4Al$ undergoes a second-order SR transition [17], its magnetic hysteresis effect can be ignored in this calculation and ΔS_M can be evaluated accurately [22,23]. It can be clearly seen that $NdCo_4Al$ presents a large anisotropic MCE: an inverse MCE is observed with magnetic field parallel to *c* axis while it changes to a conventional MCE with magnetic field perpendicular to *c* axis. Such a sign change of ΔS_M is due to the SR transition, which can be inferred from the *M-T* curves in Fig. 2. With a magnetic field change of 10 kOe, the peak values of ΔS_M reach up to 1.1 J kg^{-1} K^{-1} at 290 K and −1.1 J kg^{-1} K^{-1} at 305 K, for the magnetic field parallel and perpendicular to *c* axis, respectively. The solid curve in Fig. 4 represents the result of rotating MCE with the $NdCo_4Al$ alloy rotating from 90° to 0°. It is obvious that the maximum value of ΔS_M increases to 1.3 J kg^{-1} K^{-1}, which is larger than that of

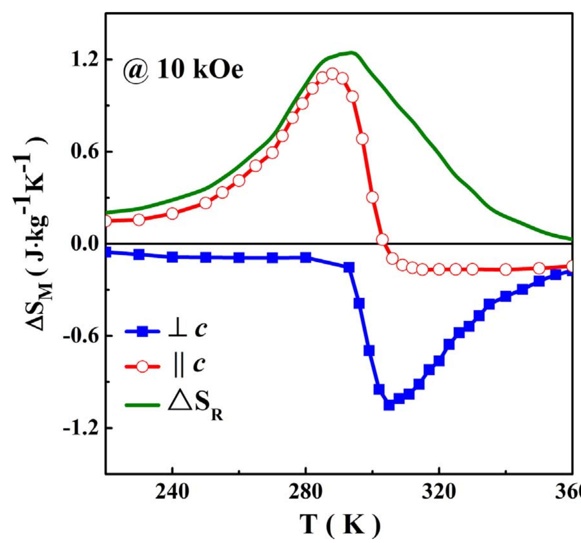

Fig. 4. (Color online) Temperature dependence of magnetic entropy changes of $NdCo_4Al$ alloy for H||c, H⊥c and rotating MCE under 10 kOe.

most rotating magnetocaloric materials reported so far, such as $HoMn_2O_5$ (0.9 J kg^{-1} K^{-1} at 10 kOe) and $TbMnO_3$ (0.7 J kg^{-1} K^{-1} at 10 kOe) [3,21]. Moreover, the peak temperature for rotating MCE in $NdCo_4Al$ alloy is 295 K, which is higher than that of $NdCo_5$ single crystal [2]. To our best knowledge, this is the first time to report a large room-temperature rotating MCE in a polycrystalline alloy.

The refrigerant capacity (RC) is another criterion for evaluating the MCE. It can be estimated based on the $\Delta S_M - T$ curves using the approach [20]:

$$RC=\int_{T_2}^{T_1}|\Delta S_M|dT \tag{2}$$

where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of ΔS_M peak, respectively. With the magnetic field parallel and perpendicular to c axis, the values of RC under 10 kOe are 28 J kg^{-1} and 26 J kg^{-1}, respectively. It is worth pointing out that, by rotating the sample from 90° to 0°, the operating temperature region (T_2–T_1) is largely broadened to 55 K (from 265 K to 320 K). As a result, the RC of MCE is greatly enhanced and reaches up to 52 J kg^{-1}, which are significantly larger than those of $ErFeO_3$ single crystal (20 J kg^{-1} at 10 kOe) and $HoMn_2O_5$ single crystal (15 J kg^{-1} at 10 kOe) [3,5]. It isreported that, RC of most of anisotropic magnetocaloric materials decreases when they act as rotating MCE refrigerant. For example, RC of DyNiSi decreases from 434 J kg^{-1} to 328 J kg^{-1} under 50 kOe [6]. This resultis due to the fact that its ΔS_M (90°) and ΔS_M (0°) are same in sign and ΔS_R is then reduced according to Eq. (1). Since theoperating temperature regions of rotating MCE are almost unchanged, RC of DyNiSi is consequently decreased. However, in the case of $NdCo_4Al$ alloy, not only ΔS_R is increased but also the operating temperature region increases from 28 K to 55 K, which results in a large rotating MCE at room temperature.

As mentioned above, magnetic anisotropy plays a key role in obtaining large rotating MCE. Thus the study of rotating MCE are mainly focused on single crystals because polycrystalline materials have random crystallographic orientation and weak magnetic anisotropy. In our work, a large rotating MCE is observed in a textured $NdCo_4Al$ polycrystalline alloy, which is prepared by a magnetic-field-aligned technology. Compared to the preparation of single crystal, this technology is easy and low cost, which makes it possible for studying rotating MCE in more polycrystalline materials.

4. Conclusions

In conclusion, a magnetic-field-aligned $NdCo_4Al$ polycrystalline alloy is prepared by magnetic-field-aligned technology. It undergoes two successive SR transitions at room temperature due to the variation of magnetization easy axis. With the magnetic field parallel and perpendicular to c axis, this alloy shows inverse and conventional MCE, respectively. Since ΔS_M(0°) and ΔS_M(90°) are opposite in sign, an enhanced rotating MCE is realized in this polycrystalline alloy. Moreover, the operating temperature region is greatly broadened to 55 K by rotating the sample from 90° to 0°, leading to a large value of RC of 52 J kg^{-1} under a low field of 10 kOe. The aforementioned advantages together with easy and low-cost preparing method make $NdCo_4Al$ polycrystalline alloy attractive for rotating magnetic refrigeration at room temperature.

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References

[1] M.D. Kuz'min, A.M. Tishin, J. Phys. D: Appl. Phys. 24 (1991) 2039.
[2] S.A. Nikitin, K.P. Skokov, Y.S. Koshkid'ko, Y.G. Pastushenkov, T.I. Ivanova, Phys. Rev. Lett. 105 (2010) 137205.
[3] M. Balli, S. Jandl, P. Fournier, M.M. Gospodinov, Appl. Phys. Lett. 104 (2014) 232402.
[4] J.L. Jin, X.Q. Zhang, H. Ge, Z.H. Cheng, Phys. Rev. B 85 (2012) 214426.
[5] R.X. Huang, S.X. Cao, W. Ren, S. Zhan, B.J. Kang, J.C. Zhang, Appl. Phys. Lett. 103 (2013) 162412.
[6] H. Zhang, Y.W. Li, E.K. Liu, Y.J. Ke, J.L. Jin, Y. Long, B.G. Shen, Sci. Rep. 5 (2015) 11929.
[7] G. Lorusso, O. Roubeau, M. Evangelisti, Angew. Chem. Int. Ed. Engl. 55 (2016) 3360.
[8] H. Bartholin, B.V. Laar, R. Lemaire, J. Schweizer, J. Phys. Chem. Solids 27 (1966) 1287.
[9] W. Frederick, M. Hoch, IEEE Trans. Magn. 11 (1975) 1434.
[10] M. Ohkoshi, H. Kobayshi, T. Katayama, M. Hirano, T. Tsushima, AIP Conf. Proc. 29 (1976) 616.
[11] A.S. Ermolenko, IEEE Trans. Magn. 12 (1976) 992.
[12] M. Ohkoshi, H. Kobayashi, T. Katayama, M. Hirano, T. Tsushima, IEEE Trans. Magn. 13 (1977) 1158.
[13] M.R. Ibarra, L. Morellon, P.A. Algarabel, O. Moze, Phys. Rev. B 44 (1991) 9368.
[14] P.A. Algarabel, A.D. Moral, M.R. Ibarra, J.B. Sousa, J.M. Moreira, J.F. Montenegro, J. Magn. Magn. Mater. 68 (1987) 177.
[15] H. Ido, K. Konno, T. Ito, S.F. Cheng, S.G. Sankar, W.E. Wallace, J. Appl. Phys. 69 (1991) 5551.
[16] H. Ido, W.E. Wallace, T. Suzuki, S.F. Cheng, V.K. Sinha, S.G. Sankar, J. Appl. Phys. 67 (1990) 4635.
[17] S.C. Ma, D.H. Wang, C.L. Zhang, H.C. Xuan, S.D. Li, Z.G. Huang, Y.W. Du, J. Alloy. Compd. 499 (2010) 7.
[18] K. Konno, H. Ido, S.F. Cheng, S.G. Sankar, W.E. Wallace, J. Appl. Phys. 73 (1993) 5929.
[19] H. Ido, K. Konno, S.F. Cheng, W.E. Wallace, S.G. Sankar, J. Appl. Phys. 67 (1990) 4638.
[20] K.A. GschneidnerJr, V.K. Pecharsky, A.O. Tsokol, Rep. Prog. Phys. 68 (2005) 1479.
[21] J.L. Jin, X.Q. Zhang, G.K. Li, Z.H. Cheng, L. Zheng, Y. Lu, Phys. Rev. B 83 (2011) 184431.
[22] M. Balli, D. Fruchart, D. Gignoux, R. Zach, Appl. Phys. Lett. 95 (2009) 072509.
[23] G.J. Liu, J.R. Sun, J. Shen, B. Gao, H.W. Zhang, F.X. Hu, B.G. Shen, Appl. Phys. Lett. 90 (2007) 032507.