Journal of Alloys and Compounds 509 (2011) 5163–5166

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

# Large magnetoelectric effect and resonance frequency controllable characteristics in Ni–lead zirconium titanate–Ni cylindrical layered composites

K. Bi, W. Wu, Q.L. Gu, H.N. Cui, Y.G. Wang*

*College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, People's Republic of China*

ARTICLE INFO

*Article history:*
Received 14 July 2010
Received in revised form
29 September 2010
Accepted 5 February 2011
Available online 3 March 2011

*PACS:*
77.65.Ly
75.50.Cc
72.80.Tm
72.55.+s

*Keywords:*
Magnetoelectric
Resonance frequency
Cylindrical layered composites
Electroless deposition

ABSTRACT

Magnetoelectric (ME) Ni–PZT–Ni cylindrical layered composites have been prepared by electroless deposition. The ME effect was measured by applying both constant and alternating magnetic fields parallel and perpendicular to the cylinder axis direction. The ME voltage coefficient increases with cylinder diameter. Both experimental and calculated data indicate that the resonance frequency of Ni–PZT–Ni cylindrical layered composites decreases with increasing cylinder diameter. We can apply this characteristic of resonance frequency to design a kind of ME composites with the controllable resonance ME coupling.

## 1. Introduction

Magnetoelectric (ME) materials have stimulated the interest of researchers worldwide with promise of coupling between ferromagnetic and ferroelectric orders [1,2]. Such materials can display an electric polarization induced by an applied magnetic field or conversely a magnetization induced by an applied electric field [3]. Because the ME effect of single phase materials is weak and mostly appears at low temperature, ME composites have drawn more attention due to their much higher ME voltage coefficient at room temperature [4–9]. In ME composites, elastic deformation is made by an external magnetic field applied to the magnetostrictive phase by means of magnetostriction and then the strain is transmitted to the piezoelectric phase, resulting in an induced charge output from the piezoelectric effect [10]. Among them, it has been found that ME layered composites possess strong ME coupling due to their giant product effect of the magnetostrictive and piezoelectric effects.

In the past several years, researchers found that the magnetic field frequency affected significantly the ME coupling in the layered composites. When the layered composites operates in the resonance frequencies, its ME effect could be enhanced largely, generally yielding a ME voltage output of nearly two orders of magnitude over that in nonresonance frequencies [11–13]. It has been proved that the large ME voltage coefficients at the resonance frequencies make those ME layered composites suitable for applications in sensors, actuators and transducers [14,15]. Therefore, how to control the resonance frequencies of ME layered composites is an important research topic in order to meet the practical application demands.

The structure of Ni–lead zirconium titanate cylindrical composites, which was first systematically studied by Pan et al. [16], is obtained by electrodeposition. The ME voltage coefficient at resonance frequencies increases linearly with applied magnetic field, up to 30 $\mathrm{V\,cm^{-1}\,Oe^{-1}}$ at $H_{DC} = 8$ kOe. However, prior to the electrodeposition, the surfaces of the piezoelectric layer must be metallized with nonmagnetostrictive layers which reduce the ME coupling [17]. Electroless deposition is a convenient method to obtain functional films with good interfacial bonding on various substrates, even nonmetallic materials [18]. It can be used to fabricate ME layered composites with complex shapes and good mechanical coupling at interfaces with neither electrodes nor bonding layers. We have recently obtained Ni–Pb(Zr,Ti)$O_3$–Ni trilayers with desirable ME properties by electroless deposition [19,20]. In this work, we

---

* Corresponding author.
*E-mail address:* yingang.wang@nuaa.edu.cn (Y.G. Wang).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.02.025

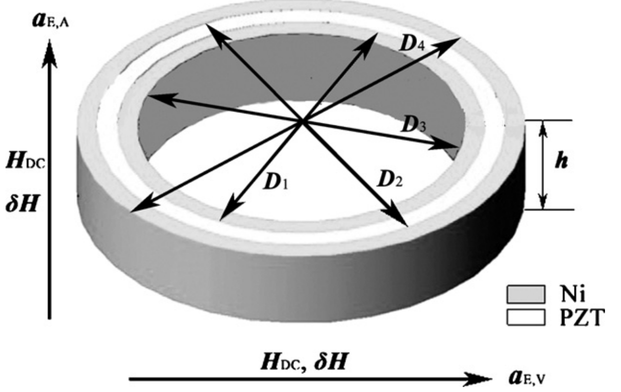

**Fig. 1.** The geometry arrangement of the Ni–PZT–Ni cylindrical layered composites.

studied ME effect and how to control the resonance frequency of Ni–lead zirconium titanate–Ni cylindrical layered composites derived by electroless deposition.

## 2. Experimental details

The hollow Pb(Zr,Ti)$O_3$ (PZT) cylinders were cut with the dimensions of $D_1 \times D_2 \times h$ mm$^3$, where the inner diameter $D_1$ = 21 mm, 23 mm and 25 mm, the corresponding outer diameter $D_2$ = 22 mm, 24 mm and 26 mm, and the height $h$ = 5 mm. The pretreatment process applied prior to the electroless deposition consisted of the following steps: roughening, sensitization, activation and reduction. The PZT cylinders were dipped into a nickel sulfate bath for the deposition of Ni layers. The bath composition and operation parameters of electroless deposition are described in details elsewhere [19]. The pH of the bath was adjusted using sodium hydroxide and measured with an electronic pH meter (Orion model 720A). The thickness of Ni layers was controlled by the electroless deposition time. In this experiment, the resulting total thickness of the two Ni layers was approximately 82 μm and identical for all the composites. After the electroless deposition, Ni–PZT–Ni cylindrical layered composites were poled in an electrical field of 30 kV cm$^{-1}$ along the radial direction. The geometry arrangement of the Ni–PZT–Ni cylindrical layered composites is shown illustratively in Fig. 1.

The ME effect of Ni–PZT–Ni cylindrical layered composites was measured by applying both constant ($H_{DC}$) and alternating ($\delta H$) magnetic fields parallel (axial mode) and perpendicular (vertical mode) to the cylinder axis direction. The induced voltage signal $\delta V$ across the sample was amplified and measured by an oscilloscope. The dc bias magnetic field $H_{DC}$ could be changed in the range of 0–8 kOe, and the superimposed ac magnetic field $\delta H$ was generated by Helmholtz coils. The ME voltage coefficient was calculated based on $\alpha_E = \delta V/(t_{PZT}\delta H)$, where $t_{PZT}$ is the thickness of PZT layer. In this experiment, $\delta H$ = 1.2 Oe as the amplitude of the ac current through the coil is equal to 1 A.

## 3. Results and discussion

Fig. 2(a) shows representative data on bias magnetic field $H_{DC}$ dependence of magnetoelectric voltage coefficient ($\alpha_{E,A}$). The magnetic fields are applied in axis direction. The measurements were carried out at $f$ = 1 kHz on a Ni–PZT–Ni cylindrical layered composites with the dimension of Ø23 mm × Ø24 mm × 5 mm. Data are shown for increasing $H_{DC}$. On increasing $H_{DC}$ from zero, it is seen that $\alpha_{E,A}$ depends strongly on $H_{DC}$. One observes a sharp increase in $\alpha_{E,A}$ to a maximum at $H_{DC}$ = 270 Oe. With further increase in $H_{DC}$, $\alpha_{E,A}$ decreases rapidly to a near-zero value because the magnetostriction of Ni is saturated. We also performed measurements on the ac magnetic field frequency $f$ dependence of the ME coupling with the bias magnetic field $H_{DC}$ = 270 and 7000 Oe. $\alpha_{E,A}$ was measured as $f$ was varied from 1 to 150 kHz. Typical $\alpha_{E,A}$ versus $f$ profile is shown in Fig. 2(b). Upon increasing $f$, we observe a sharp peak in $\alpha_{E,A}$ at resonance frequency of $f_r$ = 45.4 kHz. The measured quality factor for the resonance was Q ≈ 85. The maximum of $\alpha_{E,A}$ with $H_{DC}$ = 270 Oe is much smaller than that with $H_{DC}$ = 7000 Oe. The inset shows $\alpha_{E,A}$ dependence on $H_{DC}$ at the resonance frequency of $f_r$ = 45.4 kHz. On increasing $H_{DC}$ from zero, the $\alpha_{E,A}$ increases linearly until a maximum value is reached at a certain $H_{DC}$, and then decreases subsequently as the $H_{DC}$ increases further. With further increase in $H_{DC}$, $\alpha_{E,A}$ increases linearly even though $H_{DC}$ > 8000 Oe.

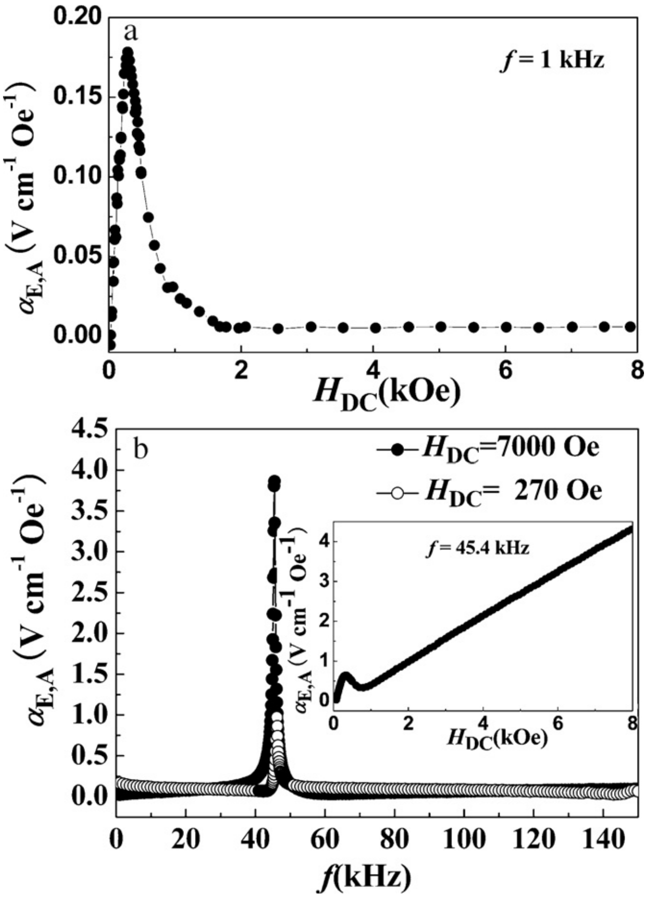

**Fig. 2.** (a) Bias magnetic field $H_{DC}$ dependence of magnetoelectric voltage coefficient ($\alpha_{E,A}$) at $f$ = 1 kHz and (b) ac magnetic field frequency $f$ dependence of $\alpha_{E,A}$ with different $H_{DC}$ for Ni–PZT–Ni cylindrical layered composites with the dimension of Ø23 mm × Ø24 mm × 5 mm when the magnetic fields are applied in axis direction. The inset shows $\alpha_{E,A}$ dependence on $H_{DC}$ at the resonance frequency of $f_r$ = 45.4 kHz.

Magnetostriction of Ni layers does not play any role in the high field region as it is already saturated. The $\alpha_{E,A}$ increases linearly with $H_{DC}$ from 1.5 kOe to 8 kOe because of the piezoinductive effect of Ni–PZT–Ni cylindrical layered composites, which results from combination of the electromagnetic induction in the Ni cylindrical layers and the piezoelectric effect in the PZT cylinder [21,22]. Compared with the plate Ni–PZT–Ni composites only used for low magnetic field sensor, the Ni–PZT–Ni cylindrical layered composites can also be used for applications in high magnetic field sensor because of the linear relationship between $\alpha_{E,A}$ and $H_{DC}$ above 1.5 kOe.

Fig. 3(a) shows representative data on bias magnetic field $H_{DC}$ dependence of magnetoelectric voltage coefficient ($\alpha_{E,V}$). The magnetic fields are applied perpendicular to the cylinder axis. It can be seen that the behavior of $\alpha_{E,V}$ with $H_{DC}$ is similar to that of $\alpha_{E,A}$ with $H_{DC}$. The maximum of $\alpha_{E,V}$ is higher than that of $\alpha_{E,A}$ due to the influence of shape demagnetization on the magnetostriction of the magnetostrictive phase [23]. Fig. 3(b) shows ac magnetic field frequency $f$ dependence of $\alpha_{E,V}$ with different $H_{DC}$. The resonance frequency shown in Fig. 3(b) is the same as that shown in Fig. 2(b). But the maximum of $\alpha_{E,V}$ with $H_{DC}$ = 270 Oe is much higher than that with $H_{DC}$ = 7000 Oe. The inset shows $\alpha_{E,V}$ dependence on $H_{DC}$ at the resonance frequency of $f_r$ = 45.4 kHz. It can be seen that the behavior of $\alpha_{E,V}$ dependence on $H_{DC}$ at the resonance frequency is

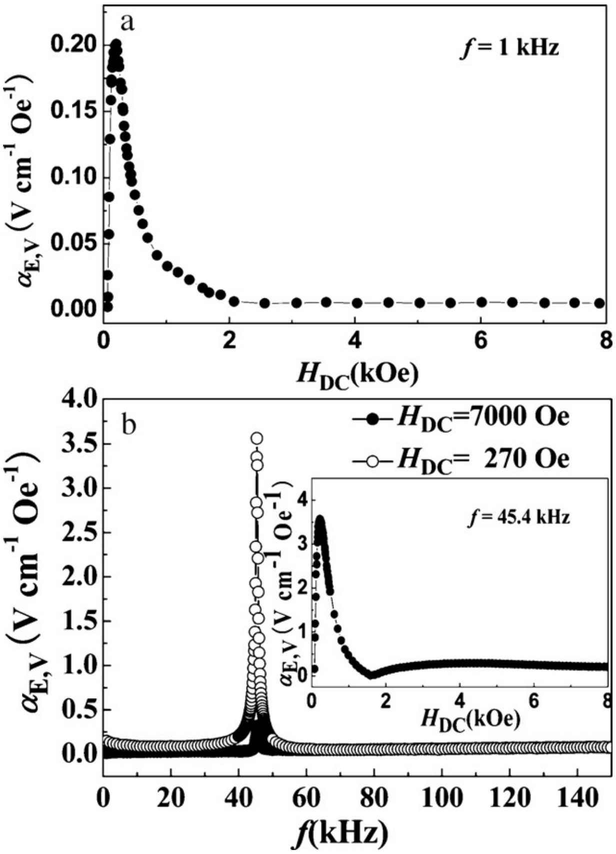

**Fig. 3.** (a) Bias magnetic field $H_{DC}$ dependence of magnetoelectric voltage coefficient ($\alpha_{E,V}$) at $f$ = 1 kHz and (b) ac magnetic field frequency $f$ dependence of $\alpha_{E,V}$ with different $H_{DC}$ for Ni–PZT–Ni cylindrical layered composites with the dimension of Ø23 mm × Ø24 mm × 5 mm when the magnetic fields are applied perpendicular to the cylinder axis. The inset shows $\alpha_{E,V}$ dependence on $H_{DC}$ at the resonance frequency of $f_r$ = 45.4 kHz.

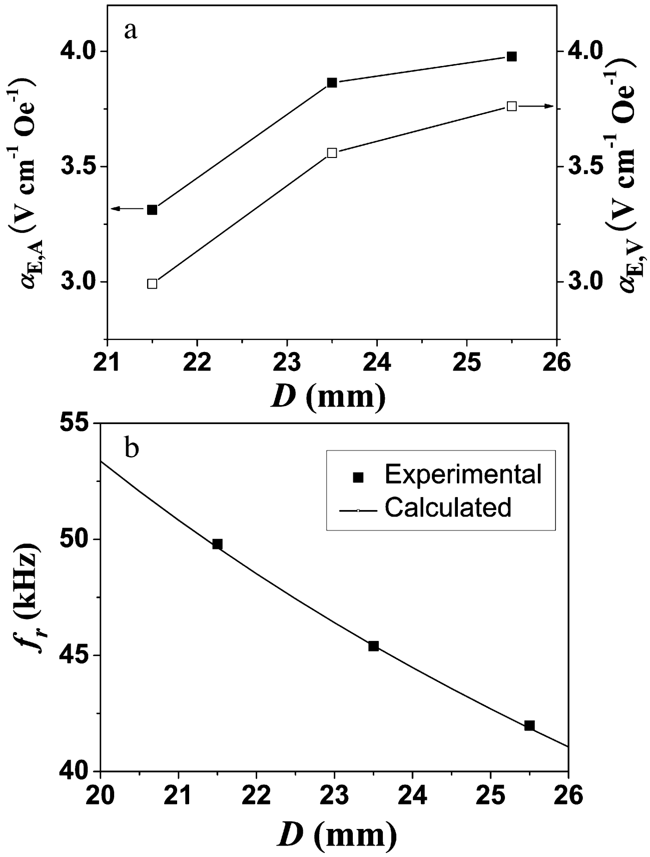

**Fig. 4.** (a) Cylinder diameter $D$ dependence of the maximum of $\alpha_{E,A}$ at $H_{DC}$ = 7000 Oe and $\alpha_{E,V}$ at $H_{DC}$ = 270 Oe for Ni–PZT–Ni cylindrical layered composites, (b) the dependence of the resonance frequency $f_r$ on cylinder diameter $D$ for Ni–PZT–Ni cylindrical layered composites. The solid squares are from experiments and the curve is calculated by Eq. (1).

much different from that of $\alpha_{E,A}$. On increasing $H_{DC}$ from zero, the $\alpha_{E,V}$ increases linearly until a maximum value is reached at a certain $H_{DC}$. With further increase in $H_{DC}$, $\alpha_{E,V}$ decreases rapidly to a certain value.

When $H_{DC}$ < 1.5 kOe, the magnetostriction of Ni is not saturated, the ME effect was generated in Ni–PZT–Ni cylindrical layered composites with magnetic fields parallel or perpendicular to the cylinder axis direction. When $H_{DC}$ > 1.5 kOe, as the magnetostriction is already saturated it does not play any role and there is no electromagnetic induction generated in the Ni cylindrical layers due to the magnetic fields applied perpendicular to the cylinder axis. Hence, the $\alpha_{E,V}$ presents a near-zero value, which is different from $\alpha_{E,A}$.

Fig. 4(a) shows cylinder diameter $D$ dependence of the maximum of $\alpha_{E,A}$ at $H_{DC}$ = 7000 Oe and $\alpha_{E,V}$ at $H_{DC}$ = 270 Oe for Ni–PZT–Ni cylindrical layered composites. One can see that both the maximum of $\alpha_{E,A}$ at $H_{DC}$ = 7000 Oe and the maximum of $\alpha_{E,V}$ at $H_{DC}$ = 270 Oe increase as cylinder diameter increases. The dependence of the resonance frequency $f_r$ on cylinder diameter $D$ is shown in Fig. 4(b). One observes that the resonance frequency of Ni–PZT–Ni cylindrical layered composites decreases with increasing cylinder diameter.

For the cylindrical layered composites consisting of mechanically coupled magnetostrictive and piezoelectric layers, the resonance frequency of ME composites is associated with the electromechanical resonance (EMR) of the piezoelectric layers [11]. The resonance frequency of radial vibration mode for Ni–PZT–Ni cylindrical layered composites is given by:

$$f_r = \frac{1}{\pi D}\sqrt{\frac{1}{\bar{\rho}\bar{s}_{11}}} \qquad (1)$$

where $f_r$ is the resonance frequency, $D$ is the average diameter, $\bar{\rho}$ is the average density, the equivalent elastic compliance $\overline{s_{11}}$ is given by:

$$\bar{s}_{11} = \frac{s_{11}^{N} s_{11}^{P}}{\upsilon_N s_{11}^{P} + \upsilon_P s_{11}^{N}} \qquad (2)$$

where $\upsilon_N$ and $\upsilon_P$ are the volume fractions of Ni and PZT layers, respectively, $s_{11}^{N}$ and $s_{11}^{P}$ are the respective elastic compliances of the layers.

The following parameters for Ni–PZT–Ni cylindrical layered composites can be used:

$$\bar{\rho} = 7.8 \times 10^3\,\mathrm{kg/m^3};\; s_{11}^{N} = 4.65 \times 10^{-12}\,\mathrm{m^2/N};\; s_{11}^{P} = 15 \times 10^{-12}\,\mathrm{m^2/N}$$

The calculated resonance frequencies for Ni–PZT–Ni cylindrical layered composites with different diameters are also shown in Fig. 4. It can be seen that the calculated resonance frequency decreases with increasing cylinder diameter, which agrees well with the experimental ones. From the above data one infers that the resonance frequency can be controlled by changing the cylinder diameter.

## 4. Conclusion

Magnetoelectric Ni–PZT–Ni cylindrical layered composites have been successfully prepared by using electroless deposition. At the resonance frequency, $\alpha_{E,A}$ in the axial mode increases linearly even though $H_{DC} > 8000$ Oe. But the maximum of $\alpha_{E,V}$ in the vertical mode with $H_{DC} = 270$ Oe is much higher than that with $H_{DC} = 7000$ Oe. The maximum of $\alpha_{E,A}$ at $H_{DC} = 7000$ Oe and $\alpha_{E,V}$ at $H_{DC} = 270$ Oe increase as cylinder diameter increases. Both experimental and calculated data show that the resonance frequency of Ni–PZT–Ni cylindrical layered composites decreases with increasing cylinder diameter, which infers the resonance frequency can be controlled by changing the cylinder diameter.

## Acknowledgements

This work is supported by the Natural Science Foundation of Jiangsu Province of China (Grant No. BK2010505), the Funding of Jiangsu Innovation Program for Graduate Education (Grant No. CX10B_099Z) and the Scientific Research & Innovation Foundation of NUAA. Q.L.G. and H.N.C would like to acknowledge support from the National Innovative Experimental Program for College Students (No. 091028735).

## References

[1] M. Fiebig, J. Phys. D: Appl. Phys. 38 (2005) R123–R152.
[2] W. Eerenstein, N.D. Mathur, J.F. Scott, Nature 442 (2006) 759–765.
[3] L.D. Landau, E.M. Lifshitz, Electrodynamics of continuous media, Pergamon Press, Oxford, 1960, p. 417.
[4] V.J. Folen, G.T. Rado, E.W. Stalder, Phys. Rev. Lett. 6 (1961) 607–608.
[5] Y.M. Jia, H.S. Luo, X.Y. Zhao, F.F. Wang, Adv. Mater. 20 (2008) 4776–4779.
[6] J. Ma, Z. Shi, C.W. Nan, Adv. Mater. 19 (2007) 2571–2573.
[7] H.C. He, J. Wang, B.P. Zhou, C.W. Nan, Adv. Funct. Mater. 17 (2007) 1333–1338.
[8] M. Zeng, S.W. Or, H.L.W. Chan, J. Alloys Compd. 490 (2010) L5–L8.
[9] K. Bi, Y.G. Wang, D.A. Pan, W. Wu, Scripta Mater. 63 (2010) 589–592.
[10] C.W. Nan, Phys. Rev. B 50 (1994) 6082–6088.
[11] M.I. Bichurin, D.A. Filippov, V.M. Petrov, V.M. Laletsin, N. Paddubnaya, G. Srinivasan, Phys. Rev. B 68 (2003) 132408.
[12] S.X. Dong, J.R. Cheng, J.F. Li, D. Viehland, Appl. Phys. Lett. 83 (2003) 4812–4814.
[13] U. Laletsin, N. Padubnaya, G. Srinivasan, C.P. Devreugd, Appl. Phys. A: Mater. Sci. Process. 78 (2004) 33–36.
[14] S.X. Dong, J.F. Li, D. Viehland, J. Cheng, L.E. Cross, Appl. Phys. Lett. 85 (2004) 3534–3536.
[15] C.W. Nan, M.I. Bichurin, S.X. Dong, D. Viehland, G. Srinivasan, J. Appl. Phys. 103 (2008) 031101.
[16] D.A. Pan, Y. Bai, A.A. Volinsky, W.Y. Chu, L.J. Qiao, Appl. Phys. Lett. 92 (2008) 052904.
[17] C.W. Nan, G. Liu, Y.H. Lin, Appl. Phys. Lett. 83 (2003) 4366–4368.
[18] B.D. Barker, Surf. Technol. 12 (1981) 77–88.
[19] K. Bi, Y.G. Wang, Solid State Commun. 150 (2010) 248–250.
[20] K. Bi, Y.G. Wang, W. Wu, D.A. Pan, J. Phys. D: Appl. Phys. 43 (2010) 132002.
[21] Y.K. Fetisov, D.V. Chashin, G. Srinivasan, J. Appl. Phys. 106 (2009) 044103.
[22] Y.K. Fetisov, D.V. Chashin, Tech. Phys. Lett. 35 (2009) 710–712.
[23] G. Srinivasan, C. De Vreugd, V. Laletin, N. Paddubnaya, M. Bichurin, V. Petrov, D. Filippov, Phys. Rev. B 71 (2005) 184423.