

## Coupling interaction in multiferroic BaTiO<sub>3</sub>-CoFe<sub>2</sub>O<sub>4</sub> nanostructures

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2005 J. Phys. D: Appl. Phys. 38 2321

(<http://iopscience.iop.org/0022-3727/38/14/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 117.32.153.144

This content was downloaded on 07/07/2017 at 10:17

Please note that [terms and conditions apply](#).

You may also be interested in:

[Theory of the magnetoelectric effect in multiferroic epitaxial Pb\(Zr<sub>0.3</sub>, Ti<sub>0.7</sub>\)O<sub>3</sub>/La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub> heterostructures](#)

ChongGui Zhong and Qing Jiang

[Design of magnetoelectric multiferroic heterostructures by topology optimization](#)

Kyung Ho Sun and Yoon Young Kim

[Theory of magnetoelectric coupling in 2?2-type magnetostrictive/piezoelectric composite film with texture](#)

Chao-Qian Liu, Wei-Dong Fei and Wei-Li Li

[Phenomenological theory of 1–3 type multiferroic composite thin film](#)

XiaoYan Lu, Biao Wang, Yue Zheng et al.

[Thermodynamic theory of strain-mediated direct magnetoelectric effect in multiferroicfilm–substrate hybrids](#)

V G Kukhar, N A Pertsev and A L Kholkin

[Strain-modulated magnetocapacitance of vertical ferroelectric?ferromagnetic nanocomposite heteroepitaxial films](#)

Huaping Wu, Bin Xu, Aiping Liu et al.

[Potentials and challenges of integration for complex metal oxides in CMOS devices and beyond](#)

Y Kim, C Pham and J P Chang

[The single-phase multiferroic oxides: from bulk to thin film](#)

W Prellier, M P Singh and P Murugavel

# Coupling interaction in multiferroic BaTiO<sub>3</sub>–CoFe<sub>2</sub>O<sub>4</sub> nanostructures

Gang Liu<sup>1</sup>, Ce-Wen Nan<sup>1,3</sup>, Z K Xu<sup>2</sup> and Haydn Chen<sup>2</sup>

<sup>1</sup> State Key Laboratory of New Ceramics and Fine Processing and Department of Materials Science and Engineering, Tsinghua University Beijing 100084, People's Republic of China

<sup>2</sup> Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, People's Republic of China

E-mail: [cwnan@mail.tsinghua.edu.cn](mailto:cwnan@mail.tsinghua.edu.cn)

Received 19 January 2005, in final form 18 May 2005

Published 1 July 2005

Online at [stacks.iop.org/JPhysD/38/2321](http://stacks.iop.org/JPhysD/38/2321)

## Abstract

Recent experimental results (Zheng *et al* 2004 *Science* **303** 661) have shown that a 1-3-type BaTiO<sub>3</sub>–CoFe<sub>2</sub>O<sub>4</sub> composite film exhibited a strong coupling between the ferroelectric and ferromagnetic order parameters. The coupling interaction in the nanostructured multiferroic film could be different from that in a bulk composite because there exists a giant residual stress/strain in the film. In this paper, by considering the influence of the three-dimensional residual strain in the film, the magnetically induced polarization of the nanostructured BaTiO<sub>3</sub>–CoFe<sub>2</sub>O<sub>4</sub> multiferroic films has been studied using the Landau–Ginsberg–Devonshire thermodynamic theory. The calculation results show that the 1-3-type nanostructured composite film could produce a ferroelectric–ferromagnetic coupling larger than that of its bulk counterpart which is in broad agreement with the experimental results. The 2-2-type nanostructured composite films were found to produce much less coupling interaction in comparison with the 1-3-type film. The dependence of multiferroic coupling on composition and temperature was analysed on the basis of the calculated results.

## 1. Introduction

Multiferroic materials have attracted great interest owing to their multi-functionality [1–3], which provides significant potential for application as next-generation multi-functional devices. In these multiferroic materials, the coupling interaction between the multiferroic orders could produce some new effects, such as the magnetoelectric [1–3] and/or the magnetodielectric effect [4]. The magnetoelectric response is the appearance of an electric polarization on applying a magnetic field and/or the appearance of magnetization on applying an electric field. This magnetically induced ferroelectric polarization has been observed in TbMnO<sub>3</sub> at a low temperature of ~20 K and a high magnetic field of ~9 T [5]. More importantly, the multiferroic composites formed by the combination of the ferromagnetic and the ferroelectric substances, such as combinations of piezoelectric ceramics (e.g. BaTiO<sub>3</sub>, lead–zirconate–titanate PZT) and ferrite or rare-earth-iron alloys

(e.g. Terfenol-D), have been recently found to exhibit a large magnetoelectric response at room temperature [6–8]. The magnetoelectric behaviour in these multiferroic composites is dependent on their microstructure and the coupling interaction across the ferromagnetic–ferroelectric interface [9].

More recently, nanostructured BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> multiferroic composites have been deposited in a film-on-substrate geometry [10]. The coupling interaction between BaTiO<sub>3</sub> and CoFe<sub>2</sub>O<sub>4</sub> in the multiferroic nanostructures is still found to be due to elastic interaction as in the bulk composites. However, the mechanical constraint arising from the film-on-substrate and the good bonding between the ferromagnetic and the ferroelectric phases in the nanostructured films could significantly affect the coupling interactions, thus resulting in a magnetoelectric effect and/or magnetically induced polarization at room temperature. Therefore, the theoretical and experimental study of these multiferroic nanostructures has been of significant interest.

For the bulk ferroelectric/ferromagnetic multiferroic systems, several theoretical methods or approaches have been

<sup>3</sup> Author to whom any correspondence should be addressed.

suggested to describe the coupling magnetic–mechanical–electric interactions, including the Green’s function technique [7, 9, 11], the finite element method [12] and the simple averaging method [13]. Recently, a theoretical description of such multiferroic nanostructured films has been proposed by using the Green’s function technique to estimate the magneto-electric effect or the magnetically induced polarization, which takes account of the influence of spontaneous polarization and the constraint effect by the substrate and present a new set of constitutive equations for the multiferroic nanostructured films [14]. In this paper, a phenomenological model based on the Landau–Ginsberg–Devonshire (LGD) thermodynamic theory is used to investigate multiferroic BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> nanostructure films. The calculated results by the present thermodynamic method are in good agreement with those using the Green’s function technique [14] and the available experimental results from Zheng *et al* [10].

## 2. Theoretical framework

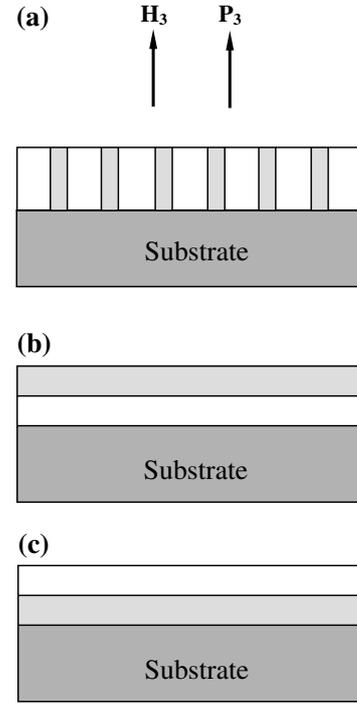
According to the LGD thermodynamic theory, which has been extensively and successfully used to understand the ferroelectric behaviours of perovskite films [15–17], the Gibbs free energy of the ferroelectric BaTiO<sub>3</sub> could be written as follows:

$$\begin{aligned} \Delta G = & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) \\ & + \alpha_{12}(P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) \\ & + \alpha_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_1^2 + P_3^2) + P_3^4(P_1^2 + P_2^2)] \\ & + \alpha_{123}P_1^2 P_2^2 P_3^2 - \frac{1}{2}s_{11}(X_1^2 + X_2^2 + X_3^2) \\ & - s_{12}(X_1 X_2 + X_2 X_3 + X_3 X_1) - \frac{1}{2}s_{44}(X_4^2 + X_5^2 + X_6^2) \\ & - Q_{11}(X_1 P_1^2 + X_2 P_2^2 + X_3 P_3^2) \\ & - Q_{12}[X_1(P_2^2 + P_3^2) + X_2(P_1^2 + P_3^2) + X_3(P_1^2 + P_2^2)] \\ & - Q_{44}(P_2 P_3 X_4 + P_1 P_3 X_5 + P_1 P_2 X_6), \end{aligned} \quad (1)$$

where  $\Delta G$  is Gibbs free energy function for unit area of BaTiO<sub>3</sub>,  $\alpha_i$ ,  $\alpha_{ij}$  and  $\alpha_{ijk}$  the dielectric stiffness and higher-order stiffness coefficients at constant stress;  $X_{ij}$  the stress in the BaTiO<sub>3</sub>;  $s_{ij}$  the elastic compliance coefficient and  $Q_{ij}$  the electrostrictive constant in polarization notation. The first partial derivatives of the energy with respect to the components of  $P$  and  $X$  give the conjugate parameters of the electric field  $E$  and the negative of the strain  $-\varepsilon$ , respectively,

$$\frac{\partial \Delta G}{\partial P_i} = E_i, \quad \frac{\partial \Delta G}{\partial X_{ij}} = -\varepsilon_{ij}^p. \quad (2)$$

We consider three types of nanostructured BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> multiferroic films, i.e. (1) 1-3-type film with CoFe<sub>2</sub>O<sub>4</sub> nanopillars (shaded) embedded in the BaTiO<sub>3</sub> matrix (figure 1(a)), (2) BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> 2-2-type (P/M) with the BaTiO<sub>3</sub> layer (white) deposited first on the substrate of SrRuO<sub>3</sub> and then the CoFe<sub>2</sub>O<sub>4</sub> layer (shaded) deposited on the BaTiO<sub>3</sub> layer (figure 1(b)) and (3) CoFe<sub>2</sub>O<sub>4</sub>/BaTiO<sub>3</sub> 2-2-type (M/P) with the CoFe<sub>2</sub>O<sub>4</sub> layer (shaded) deposited first on the substrate and then the BaTiO<sub>3</sub> layer (white) on the CoFe<sub>2</sub>O<sub>4</sub> layer (figure 1(c)). The mechanical boundary conditions for BaTiO<sub>3</sub> in the M/P 2-2-type films are essentially the same as those proposed by Pertsev *et al* [15], i.e.  $\partial \Delta G / \partial X_1 = \partial \Delta G / \partial X_2 = -\varepsilon_{11}^p$ ,  $\partial \Delta G / \partial X_6 = 0$ ,  $X_3 =$



**Figure 1.** Schematic illustration of the nanostructured multiferroic BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> in (a) 1-3-type films with CoFe<sub>2</sub>O<sub>4</sub> nanopillars (shaded) embedded in the BaTiO<sub>3</sub> matrix (white), (b) P/M 2-2-type film with the BaTiO<sub>3</sub> layer deposited first on the substrate SrRuO<sub>3</sub> and then the CoFe<sub>2</sub>O<sub>4</sub> layer (shaded) on the piezoelectric layer and (c) M/P 2-2-type film with the CoFe<sub>2</sub>O<sub>4</sub> layer (shaded) deposited first on the substrate and then the BaTiO<sub>3</sub> layer on the CoFe<sub>2</sub>O<sub>4</sub> layer. The applied magnetic field and the polarization are along the epitaxial direction.

$X_4 = X_5 = 0$  and  $\varepsilon_{11}^p = \varepsilon_{11}^{ms} + \varepsilon_{s11}^p$ , where  $\varepsilon_{s11}^p$  is the in-plane residual constraint strain in piezoelectric BaTiO<sub>3</sub> layer that results from a lattice mismatch with the substrate and the magnetostrictive layer and  $\varepsilon_{11}^{ms}$  is the magnetically induced strain in the external magnetic field that should be passed from the CoFe<sub>2</sub>O<sub>4</sub> layer to the BaTiO<sub>3</sub> layer. In comparison, in the 1-3-type films, there also exists a strain along the 3-direction or the epitaxial direction besides the in-plane strains. Correspondingly, the mechanical boundary conditions for the BaTiO<sub>3</sub> phase in the 1-3-type composite film are  $\partial \Delta G / \partial X_1 = \partial \Delta G / \partial X_2 = -\varepsilon_{11}^p$ ,  $\partial \Delta G / \partial X_3 = -\varepsilon_{33}^p$ ,  $\partial \Delta G / \partial X_4 = \partial \Delta G / \partial X_5 = \partial \Delta G / \partial X_6 = 0$ ,  $(1-f)\varepsilon_{11}^p + f\varepsilon_{11}^m = 0$  ( $f$  is the volume fraction of the magnetostrictive phase),  $\varepsilon_{33}^p = \varepsilon_{33}^m$  and  $\varepsilon_{ij}^m = \varepsilon_{sij}^m + \varepsilon_{ij}^m$ , where the superscript p and m refer to the piezoelectric BaTiO<sub>3</sub> phase and magnetostrictive CoFe<sub>2</sub>O<sub>4</sub> phase, respectively. As for the P/M 2-2-type films, the CoFe<sub>2</sub>O<sub>4</sub> layer is clamped by the substrate directly and thus on applying the magnetic field the magnetostrictive behaviour in the CoFe<sub>2</sub>O<sub>4</sub> layer is restricted almost completely.

Based on the above mechanical boundary conditions, the polarization of the epitaxially grown  $c$ -phased BaTiO<sub>3</sub> ( $P_1 = P_2 = 0$ ,  $P_3 \neq 0$ ) or the nanostructured multiferroic films could be calculated from the following stationary electric equilibrium condition:

$$\frac{\partial \Delta G}{\partial P_3} = E_3 = 0. \quad (3)$$

**Table 1.** Properties of BaTiO<sub>3</sub> used in the present calculations [15].

Parameters	Expression or values
$\alpha_1$ (V m C <sup>-1</sup> )	$3.3(T - 110) \times 10^{5a}$
$\alpha_{11}$ (V m <sup>5</sup> C <sup>-3</sup> )	$3.6(T - 175) \times 10^6$
$\alpha_{111}$ (V m <sup>9</sup> C <sup>-5</sup> )	$6.6 \times 10^9$
$\alpha_{12}$ (V m <sup>5</sup> C <sup>-3</sup> )	$4.9 \times 10^8$
$\alpha_{112}$ (V m <sup>9</sup> C <sup>-5</sup> )	$2.9 \times 10^9$
$Q_{11}$ (m <sup>4</sup> C <sup>-2</sup> )	0.11
$Q_{12}$ (m <sup>4</sup> C <sup>-2</sup> )	-0.043
$S_{11}$ (10 <sup>12</sup> m <sup>2</sup> N <sup>-1</sup> )	8.1
$S_{12}$ (10 <sup>12</sup> m <sup>2</sup> N <sup>-1</sup> )	-3.5

<sup>a</sup> The temperature is in °C.

Taking the 1-3-type multiferroic film as an example, equation (3) together with the above mentioned boundary conditions yields the following:

$$P_3^2 = \frac{-A_1 \pm \sqrt{A_1^2 - 12\alpha_{111}A_2A_3}}{6\alpha_{111}A_2}, \quad (4)$$

$$A_1 = 2\alpha_{11}A_2 + 2Q_{11}A_4 + 4Q_{12}A_5 - A_8,$$

$$A_2 = (s_{11} + 2s_{12})(s_{11} - s_{12}),$$

$$A_3 = \alpha_1A_2 - Q_{11}A_6 - 2Q_{12}A_7 + A_9,$$

$$A_4 = Q_{11}(s_{11} + s_{12}) - 2Q_{12}s_{12},$$

$$A_5 = Q_{12}s_{11} - Q_{11}s_{12},$$

$$A_6 = \varepsilon_{33}^p(s_{11} + s_{12}) - 2\varepsilon_{11}^p s_{12},$$

$$A_7 = \varepsilon_{11}^p s_{11} - \varepsilon_{33}^p s_{12},$$

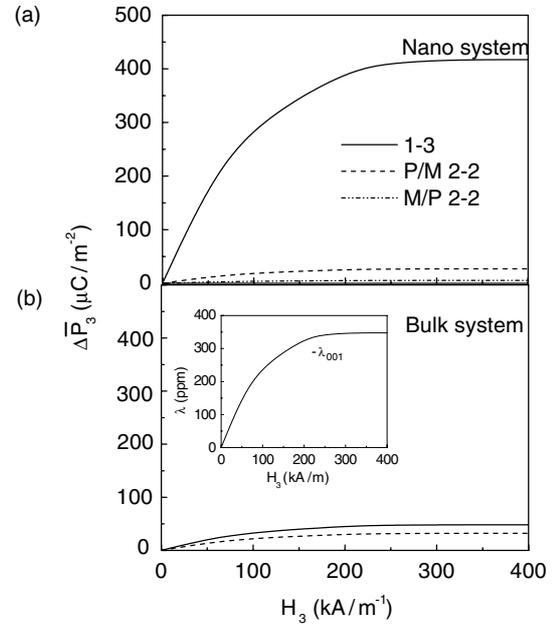
$$A_8 = \frac{[s_{11}(2A_5^2 + A_4^2) + 2s_{12}(A_5^2 + 2A_4A_5)]}{A_2},$$

$$A_9 = \frac{[s_{11}(2A_5A_7 + A_4A_6) + 2s_{12}(A_5A_7 + A_4A_7 + A_5A_6)]}{A_2}.$$

When no external magnetic field is applied,  $\varepsilon_{ij}^p$  is composed only of the residual strain, and the polarization corresponding to  $H_3 = 0$  can be regarded as the spontaneous polarization  $P_3^s$ . After applying the external magnetic field,  $\varepsilon_{ij}^p$  is composed of not only the residual strain but also the magnetically induced strain passed from the magnetostrictive CoFe<sub>2</sub>O<sub>4</sub> phase. As a result, a magnetically induced polarization,  $\Delta P_3$ , is produced, i.e.  $\Delta P_3 = P_3(H_3) - P_3(H_3 = 0)$ . The magnetically induced polarization indicates a coupling between the ferroelectric order and the ferromagnetic order and it is easily understood that this multiferroic coupling is dependent on the applied magnetic field. Besides, the dielectric constants are temperature dependent (see equation (1) and table 1) and the relationship between  $\varepsilon_{11}^p$  and  $\varepsilon_{11}^m$  for the 1-3-type film is dependent on the composition,  $f$ . Therefore, the magnetically induced polarization should then be dependent on the temperature and the composition as well which will be discussed in the next section.

### 3. Results and discussion

From [10], the out-of-plane residual strains in the 1-3-type nanostructured film with  $[001]_{\text{BaTiO}_3} \parallel [001]_{\text{CoFe}_2\text{O}_4}$  are given as  $\varepsilon_{33}^p = -\varepsilon_{33}^m = 0.8\%$  and the in-plane residual strains are determined as  $\varepsilon_{s11}^p = \varepsilon_{s11}^m = -1.2\%$  based on the lattice mismatch both between BaTiO<sub>3</sub> and the substrate and between



**Figure 2.** Dependence of the magnetically induced polarization,  $\Delta P_3$ , on the magnetic field,  $H_3$ , for (a) the nanostructured BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> films and (b) the bulk BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> composites ( $f = 0.35$ ) at room temperature. The inset in (b) is the magnetostrictive behaviour for CoFe<sub>2</sub>O<sub>4</sub>.

CoFe<sub>2</sub>O<sub>4</sub> and the substrate. However, in a P/M 2-2-type film only the lattice mismatch between BaTiO<sub>3</sub> and the substrate is simply considered, so that the in-plane residual strain is approximately  $\varepsilon_{s11}^p = \varepsilon_{s11}^m = -1.0\%$ .

For quantitative purposes, the ferroelectric properties, including the spontaneous polarization and the magnetically induced polarization in all the three types of nanostructured BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> multiferroic films are calculated using the values of parameters listed in table 1, the residual strains and the magnetostrictive behaviour for CoFe<sub>2</sub>O<sub>4</sub> as shown inset in figure 2(b) [18].

#### 3.1. Ferroelectric properties of the nanostructured films

According to the LGD phenomenological thermodynamic theory, the relative dielectric constant  $\kappa_{33}$  of the tetragonal BaTiO<sub>3</sub> phase is related to the inverse of the second derivation of  $\Delta G$  (equation (1)) with respect to the polarization component  $P_3$  and is given by the following:

$$\frac{\kappa_{33}}{\kappa_0} = \left( \frac{\partial^2 \Delta G}{\partial P_3^2} \right)^{-1} \quad (5)$$

with  $\kappa_0$  being the vacuum dielectric permittivity. Also, the piezoelectric strain coefficients  $d_{ij}$  are defined as follows [19]:

$$d_{31} = b_{31}\kappa_{33}, \quad d_{33} = b_{33}\kappa_{33}, \quad (6)$$

where  $b_{kj}$  are the piezoelectric polarization-related coefficients

$$b_{ij} = -\frac{\partial^2 \Delta G}{\partial P_i \partial X_j}. \quad (7)$$

Using equation (1) and (5)–(7), the spontaneous polarization and the dielectric and piezoelectric constants can be calculated

**Table 2.** Comparison between the calculated and the measured [10] parameters for the 1-3-type multiferroic films.

	Predicted values	Experimental values
$P_3^s$ ( $\mu\text{C cm}^{-2}$ )	17.5	16.7
$E_c$ ( $\text{MV m}^{-1}$ )	11.2	9.1
$\kappa_{33}/\kappa_0$	330	270
$d_{33}$ ( $\text{pm V}^{-1}$ )	12.5	$\sim 10$

as  $P_3^s = 12.6 \mu\text{C cm}^{-2}$ ,  $\kappa_{33}/\kappa_0 = 650$ ,  $d_{33} = 18.0 \text{ pm V}^{-1}$ , and  $d_{31} = -7.1 \text{ pm V}^{-1}$  for the nanostructured P/M 2-2-type films; and  $P_3^s = 17.5 \mu\text{C cm}^{-2}$ ,  $\kappa_{33}/\kappa_0 = 270$ ,  $d_{33} = 12.5 \text{ pm V}^{-1}$  and  $d_{31} = -5.0 \text{ pm V}^{-1}$  for the nanostructured 1-3-type film under no applied magnetic field (table 2). These calculations for the nanostructured 1-3-type film are in good agreement with the measured values of  $P_3^s \approx 16.7 \mu\text{C cm}^{-2}$ ,  $\kappa_{33}/\kappa_0 < 330$ ,  $d_{33} \sim 10 \text{ pm V}^{-1}$  [10].

In addition, when an external electric field  $\hat{E}_3$  is applied, the total Gibbs free energy  $G$  is given as follows:

$$G = \Delta G - \hat{E}_3 P_3. \quad (8)$$

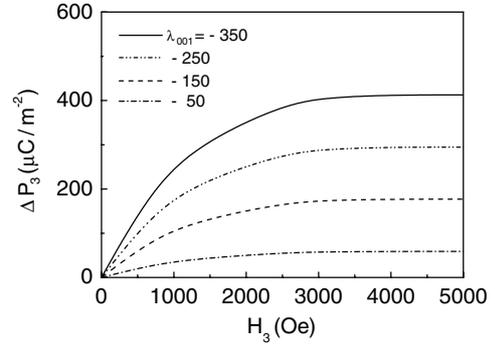
The stability condition of the dielectric stiffness  $\chi_{33} = \partial^2 G / \partial P_3^2 > 0$  for the ferroelectric phase makes it possible to calculate the minimum polarization which can exist in an antiparallel electric field [20]. From the condition of  $\chi_{33} = 0$ , the critical polarization  $P_3^{\text{cri}}$  could be obtained in a similar form to equation (8), and as a result the coercive field  $\hat{E}_c$  is given from  $\partial G / \partial P_3 = 0$  as follows:

$$\hat{E}_c = \left. \frac{\partial \Delta G}{\partial P_3} \right|_{P_3 = P_3^{\text{cri}}}. \quad (9)$$

For comparative purposes, the  $\hat{E}_c$  value is calculated as  $\sim 11.2 \text{ MV m}^{-1}$  for  $\text{BaTiO}_3$  in the nanostructured 1-3-type  $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$  composite film, also in agreement with the measured value of  $\sim 9.1 \text{ MV m}^{-1}$  [10].

### 3.2. Magnetically induced polarization in the multiferroic films

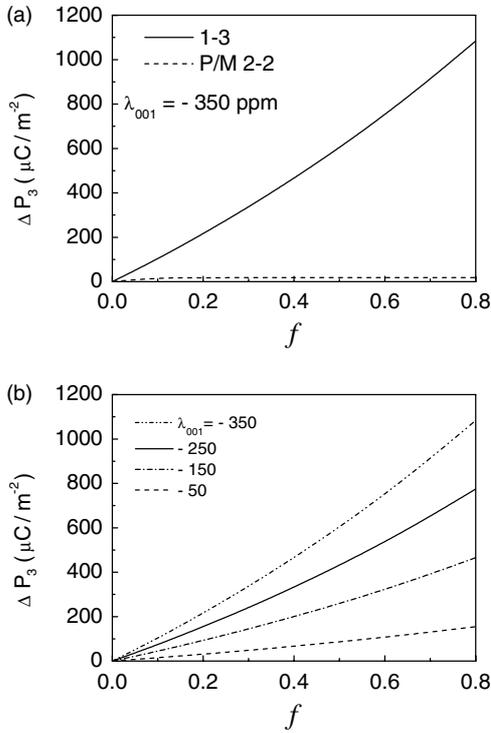
With the application of an external magnetic field, the polarizations of the multiferroic films will vary correspondingly. Figure 2(a) shows the calculated  $\Delta P_3$  in these three types of multiferroic films with  $f = 0.35$  at room temperature.  $\Delta P_3$  of the 1-3-type and P/M 2-2-type films increases nonlinearly with the magnetic field owing to the nonlinear dependence of the magnetostriction of  $\text{CoFe}_2\text{O}_4$  on the applied magnetic field, while  $\Delta P_3$  of the M/P 2-2-type film is almost equal to zero regardless of the application of the magnetic field. The reason for the latter result is that the  $\text{CoFe}_2\text{O}_4$  layer in the M/P 2-2-type film is fully constrained by the substrate so that the magnetostrictive capability is destroyed almost completely. It is particularly interesting to note that a large magnetically induced polarization is obtained in the 1-3-type films at room temperature. When the applied magnetic field increases from zero to 5000 Oe (0.5 T), the magnetically induced polarization in the 1-3-type film increases up to  $420 \mu\text{C m}^{-2}$ , on an equal level with

**Figure 3.** Dependence of the magnetically induced polarization,  $\Delta P_3$ , on the magnetic field,  $H_3$ , at various saturation magnetostrictions for 1-3-type nanostructured  $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$  composite films ( $f = 0.35$ ) at room temperature.

that of  $\text{TbMnO}_3$  at a low temperature ( $\sim 20 \text{ K}$ ) and a high magnetic field ( $\sim 9 \text{ T}$ ) [5]. In contrast, the magnetically induced polarization in the P/M 2-2-type  $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$  film is quite low and much less than that in the 1-3-type. This could be attributed mainly to the tremendous clamping effect in the 2-2-type film, where the in-plane constraint effect greatly inhibits the magnetostriction of the  $\text{CoFe}_2\text{O}_4$  layer. In the actual experiment [10], the 2-2-type  $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$  film is indeed found to exhibit far weaker magnetoelectric coupling than the 1-3-type one. For comparison, the cases in bulk 1-3 and 2-2-type  $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$  composites are also calculated by assuming the absence of residual strain, as shown in figure 2(b). The mechanical boundary condition of  $(1-f)\varepsilon_{11}^p + f\varepsilon_{11}^m = 0$  for the 1-3-type nanostructured multiferroic films should be revised as  $\varepsilon_{11}^p = \varepsilon_{11}^m$  for the 1-3-type bulk systems because the in-plane constraint will be released completely in bulk case. As seen in figure 2(b), the 1-3-type bulk composites exhibit a lower magnetically induced polarization than the 1-3 nanostructured counterparts, and the 2-2-type bulk composites also exhibit lower magnetically induced polarization than the 1-3-type. The present calculations are quite agreeable with those recently calculated by using the Green's function technique [14].

As shown in figure 2, the magnetically induced polarization of the nanostructured composite films is closely dependent on the magnetostrictive behaviour of the ferromagnetic phase. For further illustration, we take a few different values for the saturation magnetostriction  $\lambda_{001}$  (figure 3). As seen in figure 3, the magnetically induced polarization depends strongly on the magnetostriction. With the decrease in the saturation magnetostriction of the magnetostrictive phase, the magnetically induced polarization decreases monotonously. The comparison of figure 3 with figure 2(b) indicates that the magnetostrictive phase with  $\lambda_{001} = -50 \text{ ppm}$  in the 1-3-type nanostructured multiferroic films could produce an almost equally magnetically induced polarization to that caused by the magnetostrictive phase with  $\lambda_{001} = -350 \text{ ppm}$  in bulk systems.

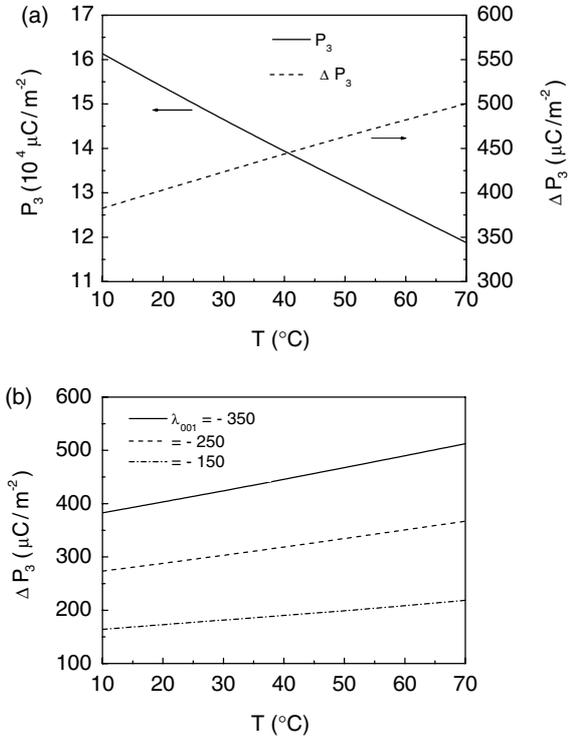
The entire discussion above is based on an assumption of  $f = 0.35$  [10]. For 1-3-type composite films, the volume fraction of the magnetostrictive phase will exert a significant influence on the magnetically induced polarization as shown in figure 4(a). On the contrary, the magnetically



**Figure 4.** (a) Dependence of the magnetically induced polarization,  $\Delta P_3$ , on the volume fraction,  $f$ , of CoFe<sub>2</sub>O<sub>4</sub> phase for both 1-3-type and 2-2-type nanostructured BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> composite films at room temperature; (b) dependence of the magnetically induced polarization,  $\Delta P_3$ , on  $f$  at various saturation magnetostrictions for 1-3-type nanostructured BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> composite films at room temperature.

induced polarization in 2-2-type composite films is insensitive to the constituent content, which proves again that the elastic coupling in 2-2-type composite films is very weak. For further illustration, figure 4(b) shows the variation of the magnetically induced polarization with  $f$  as a function of the saturation magnetostriction, from which the coupled influence from both  $f$  and the magnetostrictive behaviour on the magnetically induced polarization is quantitatively presented for 1-3-type composite films.

As mentioned above, the magnetically induced polarization is also dependent on the temperature,  $T$ . Although the spontaneous polarization of the BaTiO<sub>3</sub> phase increases with decreasing  $T$ , the magnetically induced polarization decreases at a lower temperature, as shown in figure 5(a). This contrary variation trend may be attributed to the larger spontaneous polarization at lower  $T$ , which makes further increases in polarization more difficult and so the magnetically induced polarization will decrease. However, the less the saturation magnetostriction, the less is the magnetically induced polarization sensitive to the temperature (figure 5(b)). In this sense, a lower  $f$  or a higher volume fraction of the BaTiO<sub>3</sub> should produce a magnetically induced polarization less sensitive to the test temperature. It is particularly interesting to note that at room temperature the calculated spontaneous polarization for the 1-3-type nanostructured BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> composite film with  $f = 0.35$  is about  $17.5 \mu\text{C cm}^{-2}$  (figure 5(a)), close to that measured by Zheng *et al* [10] of  $\sim 16.0 \mu\text{C cm}^{-2}$ .



**Figure 5.** (a) Dependence of both the spontaneous polarization,  $P_3$ , and the magnetically induced polarization,  $\Delta P_3$ , on temperature  $T$  for the 1-3-type BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> composite films ( $f = 0.35$ ) with  $\lambda_{001} = -350$  ppm; (b) dependence of the magnetically induced polarization,  $\Delta P_3$ , on temperature  $T$  at various saturation magnetostrictions for 1-3-type nanostructured BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> composite films ( $f = 0.35$ ).

## 4. Conclusions

The magnetically induced polarization in the nanostructured BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> multiferroic films has been calculated using the LGD thermodynamic theory. The calculation results show that the 1-3-type nanostructured BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> composite films exhibit a large magnetically induced polarization, but the 2-2-type films exhibit a much weaker magnetoelectric effect because of large in-plane constraint, which is in agreement with the experimental observations. The dependences of magnetically induced polarization on the composition and the temperature have also been revealed explicitly.

## Acknowledgments

This work was supported by the NSF of China (Grant Nos 50232030 and 50318002) and the State Key Project of Fundamental Research of China (Grant No 2002CB613303 & G2000067108).

## References

- [1] Fiebig M 2005 *J. Phys. D: Appl. Phys.* **38** R123
- [2] Nan C-W, Lin Y H and Huang J H 2002 *Ferroelectrics* **280** 153
- [3] Wang J *et al* 2003 *Science* **299** 1719
- [4] Lawes G, Ramirez A P, Varma C M and Subramanian M A 2003 *Phys. Rev. Lett.* **91** 257208
- [5] Kimura T, Goto T, Shintani H, Ishizaka K, Arima T and Tokura Y 2003 *Nature* **426** 55

- [6] van den Boomgaard J, Terrell D R, Born R A J and Giller H F J I 1974 *J. Mater. Sci.* **9** 1705  
Harshe G, Dougherty J P and Newnham R E 1993 *Int. J. Appl. Electromagn. Mater.* **4** 145
- [7] Nan C-W, Li M, Feng X Q and Yu S 2001 *Appl. Phys. Lett.* **78** 2527  
Nan C W, Li M and Huang J H 2001 *Phys. Rev. B* **63** 144415
- [8] Bichurin M I, Kornev I A, Petrov V M and Lisnevskaya I 1997 *Ferroelectrics* **204** 289  
Srinivasan G, Rasmussen E T, Levin B J and Hayes R 2002 *Phys. Rev. B* **65** 134402
- [9] Nan C-W, Liu G and Lin Y H 2003 *Appl. Phys. Lett.* **83** 4366  
Liu G, Nan C-W, Cai N and Lin Y H 2004 *J. Appl. Phys.* **95** 2660
- [10] Zheng H *et al* 2004 *Science* **303** 661
- [11] Nan C-W 1994 *Phys. Rev. B* **50** 6082
- [12] Liu G, Nan C-W, Cai N and Lin Y H 2004 *Int. J. Solid Struct.* **41** 4423
- [13] Harshe G 1991 *PhD Thesis* The Pennsylvania State University  
Bichurin M I, Petrov V M and Srinivasan G 2003 *Phys. Rev. B* **68** 054402
- [14] Nan C-W, Liu G, Lin Y H and Chen H 2005 *Phys. Rev. Lett.* **94** 197203
- [15] Pertsev N A, Zembilgotov A G and Tagantsev A K 1998 *Phys. Rev. Lett.* **80** 1988  
Pertsev N A, Tagantsev A K and Setter N 2000 *Phys. Rev. B* **61** R825
- [16] Li H, Roytburd A L, Alpay S P, Tran T D, Salamanca-Riba L and Ramesh R 2001 *Appl. Phys. Lett.* **78** 2354  
Ban Z G and Alpay S P 2003 *J. Appl. Phys.* **93** 504
- [17] Li Y L, Hu S Y, Liu Z K and Chen L Q 2001 *Appl. Phys. Lett.* **78** 3878
- [18] Engdahl G 2000 *Handbook of Giant Magnetostrictive Materials* (New York: Academic)
- [19] Devonshire A F 1951 *Phil. Mag.* **42** 1065
- [20] Pertsev N A *et al* 2003 *Appl. Phys. Lett.* **83** 3356