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Coupling interaction in 1-3-type multiferroic composite thin films

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Using the time-dependent Ginzburg-Landau equation, the coupling interaction of the ferroelectric (FE) and ferromagnetic (FM) phases in epitaxial 1-3-type multiferroic thin films was investigated considering the effect of elastic stress arising from the FE/FM and film/substrate interfaces. The result of the authors shows that the maximum polarization and magnetization appear with the FM fractions of 70% and 30%, respectively. The significant changes of the FE and FM properties are caused by the special structure in which the induced misfit strain greatly affects the anisotropy of the crystals and the properties of the materials.
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There has been considerable interest in developing multiferroic materials for their potential applications, such as multiple-state memories, spintronics, and sensors.[1] Single materials, such as Bi-based compounds[2,3] and rare earth manganites,[4] have been extensively studied, and the magnetoelectric (ME) effects usually exit in low temperatures. Composites[5,6] of ferroelectric (FE) and ferromagnetic (FM) substances together have been made which exhibit a large ME response at room temperature. Understanding of this phenomenon is still a challenge, especially in single phase multiferroic materials. As widely believed, the coupling effect in the composite thin films is induced by the elastic interaction, and the effect of strain is regarded to be significant or even dominant.[7]

The effects of strain on the FE or FM properties of traditional materials have been extensively studied.[8,9] For an epitaxial multiferroic thin film of 1-3 type, the stress can arise from the lattice misfit of the adjacent phases both in the vertical and transverse directions. Multiferroic composite structures with optimum strain/stress states should be found to attain strong ME coupling. Theoretical approaches[10] based on the experimental data have been used to describe the FE and FM coupling and predicted general trends. However, more details of the complex external/internal stress interactions have not been investigated.

In this work, we study the evolution of the spontaneous polarization and magnetization fields in 1-3-type multiferroic thin films in the framework of the time-dependent Ginzburg-Landau (TDGL) equations. The elastic energy of the system is established as function of the volume fractions of the FM part.

We consider a 1-3-type multiferroic thin film with the FM part embedded in the FE material matrix grown on a rigid substrate. A diagram of our model is shown in Fig. 1. We assume that the magnetic component is perpendicular to the interface of the film/substrate, the same direction as the FE polarization in tetragonal $\mathrm{BaTiO_3}$ below the critical phase transition temperatures.[11] Since the properties of the material are the same along the x and y axes, the order parameters can be simplified to the functions of x and z. The total free energy of the system with the order parameters P for the FE phase and M for the FM phase can be written as[11]

$$F = F_l^E + F_l^M + F_{\mathrm{elas}} + F_{\mathrm{surf}}, \tag{1}$$

where F_l^E and F_l^M are the Landau-type bulk free energies of the FE and FM phases, respectively, F_{elas} is the elastic energy of the total body, and F_{surf} is the surface energy describing the relaxation of the surface lattices and the relaxation or restriction of the interfacial lattice. F_l^E, F_l^M, and F_{surf} can be expressed as

$$F_l^E = (1-f)\int_v \left[\frac{A^E}{2}(T - T_{C0}^E)P^2 + \frac{B^E}{4}P^4 + \frac{C^E}{6}P^6 + \frac{D_{44}^E}{2}\left(\frac{\partial P}{\partial x}\right)^2 + \frac{D_{11}^E}{2}\left(\frac{\partial P}{\partial z}\right)^2 \right] dv, \tag{2}$$

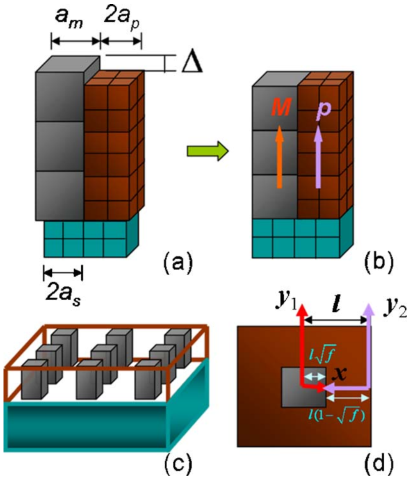

FIG. 1. Schematic of the calculation model. (a) Schematic illustration of the freestanding states of each part. (b) The state after transmutation with lattices well matched. (c) Heterostructure of the 1-3-type with the FM phase (in gray) embedded in the FE phase (in crimson) on a rigid substrate (in blue). (d) The cross section of one element in which l is half of the element length.

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$$F_l^M = f\int_v \left[\frac{A^M}{2}(T-T_{C0}^M)M^2 + \frac{B^M}{4}M^4 + \frac{D_{44}^M}{2}\left(\frac{\partial M}{\partial x}\right)^2 + \frac{D_{11}^M}{2}\left(\frac{\partial M}{\partial z}\right)^2\right]dv, \tag{3}$$

$$F_{\text{surf}} = (1-f)\int_s \frac{P^2}{2\delta^{p_z}}ds + f\int_s \frac{M^2}{2\delta^{m_z}}ds + \int_{s_i}\left(\frac{P^2}{2\delta^{p_x}} + \frac{M^2}{2\delta^{m_x}}\right)ds, \tag{4}$$

where A^E, B^E, C^E, D_{44}^E, D_{11}^E and T_{C0}^E are the Landau-type bulk free energy expansion coefficients and Curie temperature, respectively, of the FE phase. A^M, B^M, D_{44}^M, D_{11}^M and T_{C0}^M are the Landau-type bulk free energy expansion coefficients and Curie temperature, respectively, of the FM phase. f is the volume fraction of the FM phase. v and s are the volume and the surface area of the element, respectively. s_i is the interface area of the two phases. δ_{p_x}, δ_{p_z} and δ_{m_x}, δ_{m_z} are the extrapolation lengths along the x and z axes for the FE and FM phases, respectively.

The spontaneous strains (eigenstrains)[12] induced by the ferroelectric or ferromagnetic transition are $\varepsilon_{ij}^E = Q_{ijkl}^E P_k P_l$ and $\varepsilon_{ii}^M = \frac{3}{2}\lambda_{100}\left(m_i^2 - \frac{1}{3}\right)$, $\varepsilon_{ij}^M = \frac{3}{2}\lambda_{111}m_i m_j (i \neq j, m = M/M_s)$,[13] where Q is the electrostrictive coefficient tensor, and $\lambda_{100}, \lambda_{111}$ are magnetostrictive coefficients. M_s is the saturation magnetization of the bulk FM material. For a plane problem, a diagonal matrix with all elements of $\frac{3}{2}\lambda_{100}$ is denoted as λ.

In our system, the elastic energy is

$$F_{\text{elas}} = F_{\text{elas}}^E + F_{\text{elas}}^M, \quad F_{\text{elas}}^E = (1-f)\int_v f_{\text{elas}}^E dv,$$

$$F_{\text{elas}}^M = f\int_v f_{\text{elas}}^M dv, \tag{5}$$

where $f_{\text{elas}}^E = \frac{1}{2}C_{ijkl}^E e_{kl}^p e_{ij}^p = \frac{1}{2}C_{ijkl}^E(\varepsilon_{kl}^p - \varepsilon_{kl}^E)(\varepsilon_{ij}^p - \varepsilon_{ij}^E)$ and $f_{\text{elas}}^M = \frac{1}{2}C_{ijkl}^M e_{kl}^m e_{ij}^m = \frac{1}{2}C_{ijkl}^M(\varepsilon_{kl}^m - \varepsilon_{kl}^M)(\varepsilon_{ij}^m - \varepsilon_{ij}^M)$ are the elastic energy densities in the FE and FM parts, respectively. C_{ijkl}^E and C_{ijkl}^M are the elastic moduli, e_{kl}^p and e_{kl}^m are the elastic strains of the FE and FM phases, respectively. ε_{kl}^p and ε_{kl}^m are the corresponding total strains. ε_{kl}^E and ε_{kl}^M denote the FE and FM spontaneous strains. Considering a rigid substrate, and assuming that the substrate matches well with the film, the average strain induced by the substrate as a function of volume fraction can be written as $\varepsilon_{11}^p = \varepsilon_{22}^p = \varepsilon_{11}^m = \varepsilon_{22}^m = \varepsilon_{11}^0 = (\sqrt{f}/\tilde{a}_m + (1-\sqrt{f})/a_p)a_s^{\text{eff}} - 1$, where a_p and $a_m = 2\tilde{a}_m$ are the lattice parameters of the FE and FM materials, respectively. Because of the differences of the lattice parameters, dislocations usually form during deposition and will affect the properties of the thin film.[14] An effective substrate parameter is introduced to describe this.[15]

$$a_s^{\text{eff}} = \frac{a_s}{\rho a_s + 1}, \quad \rho = \frac{\tilde{\varepsilon}_{11}^0}{a_0}\left(1 - \frac{h_\rho}{h}\right), \tag{6}$$

where a_s is the lattice parameter of the substrate, ρ is the equilibrium linear dislocation density at the deposition temperature, $\tilde{\varepsilon}_{11}^0 = 1 - (1/a_s)(\tilde{a}_m a_p/[\sqrt{f}a_p + (1-\sqrt{f})\tilde{a}_m])$ is the average misfit strain at the growth temperature, $a_0 = \sqrt{f}\tilde{a}_m + (1-\sqrt{f})a_p$ is the average in-plane lattice parameter of the film, and $h_\rho = \sqrt{f}h_\rho^m + (1-\sqrt{f})h_\rho^p$ is the average critical thickness for dislocation generation, below which dislocation is not feasible.

Ignoring the distortion in the plane, we find $\varepsilon_{12}^p = \varepsilon_{21}^p = \varepsilon_{12}^m = \varepsilon_{21}^m = 0$. The other strains,$\varepsilon_{i3}^p$ and ε_{i3}^m, are derived from the mechanical equilibrium equations for the whole sample body under the surface-free condition and the displacement consistent condition, from which $\varepsilon_{33}^p = (-1/C_{11E})(2C_{12}^0\varepsilon_{11}^0 - q_{11}^E P^2 - f_m)$ and $\varepsilon_{33}^m = (-1/C_{11M})(2C_{12}^0\varepsilon_{11}^0 - q_{11}^M M^2/M_s^2 - f_p)$ are found for the FE and FM phases, respectively.[11] Substituting the above results into Eq. (5), the elastic energy density functions can be derived.

As shown in Fig. 1, two local coordinates are used for the FE and FM phases. The temporal evolution of the polarization and magnetization fields can be described by the TDGL equations[16]

$$\frac{\partial P(x,z,t)}{\partial t} = -L^E\frac{\delta F}{\delta P(x,z,t)} = -L^E(1-f)\left[A^E(T-T_{C0}^E)P + B^E P^3 + C^E P^5 - D_{44}^E\frac{\partial^2 P}{\partial x^2} - D_{11}^E\frac{\partial^2 P}{\partial z^2} + \delta f_{\text{elas}}^E/\delta P\right], \tag{7}$$

$$\frac{\partial M(x,z,t)}{\partial t} = -L^M\frac{\delta F}{\delta M(x,z,t)} = -L^M f\left[A^M(T-T_{C0}^M)M + B^M M^3 - D_{44}^M\frac{\partial^2 M}{\partial x^2} - D_{11}^M\frac{\partial^2 M}{\partial z^2} + \delta f_{\text{elas}}^M/\delta M\right], \tag{8}$$

where L^E and L^M are kinetic coefficients related to the domain wall mobilities. $A^M = 1/(2\chi T_{C0}^M)$ and $B^M = 1/(2\chi)$.

The variation of the expression of elastic energy [Eq. (5)] with respect to the polarization and magnetization order parameters can be derived as

$$\delta f_{\text{elas}}^E/\delta P = -2P[(q_{c11} - 2q_{c33}C_{120}/C_{11E})\varepsilon_{11}^0 - (q_{cq} - q_{c33}/C_{11E})P^2 - f_m q_{c33}/C_{11E}], \tag{9}$$

$$\delta f_{\text{elas}}^M/\delta M = -2m/M_s^2\lambda_{11}[(C_{12}^M - C_{11}^M C_{120}/C_{11M})2\varepsilon_{11}^0 - C_{11}^M(\lambda_{11} - q_{11}^M/C_{11M})(m^2 - 1/3) - f_p C_{11}^M/C_{11M}], \tag{10}$$

where $q_{c11} = 2Q_{12}(C_{11}^E + C_{12}^E) + 2Q_{11}C_{12}^E$, $q_{c33} = 2Q_{12}C_{12}^E + Q_{11}C_{11}^E$, and $q_{cq} = Q_{12}[2Q_{12}(C_{11}^E + C_{12}^E) + 2Q_{11}C_{12}^E)] + Q_{11}(2Q_{12}C_{12}^E + Q_{11}C_{11}^E)$. The surface items yield the boundary conditions

$$\frac{\partial P}{\partial z} = \mp\frac{P}{\delta_{pz}} \quad \text{for } z = \pm\frac{h}{2}, \quad \frac{\partial P}{\partial x} = -\frac{P}{\delta_{px}} \quad \text{for } x = l_p,$$

$$\frac{\partial P}{\partial n} = 0 \quad \text{for } x = 0, \quad \frac{\partial M}{\partial z} = \mp\frac{M}{\delta_{mz}} \quad \text{for } z = \pm\frac{h}{2},$$

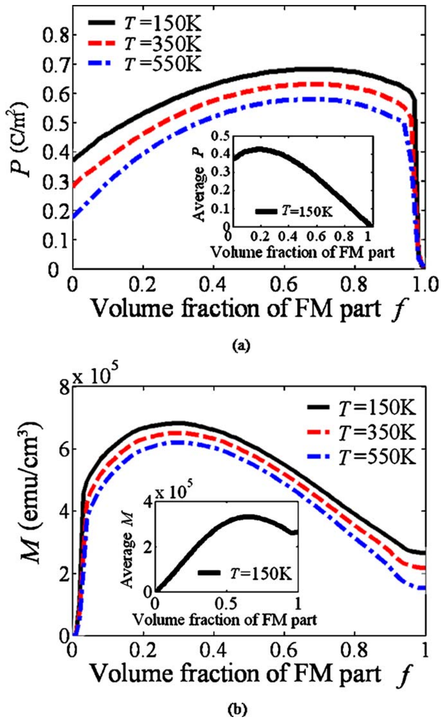

FIG. 2. Average (a) spontaneous polarization and (b) magnetization of each part vs the volume fraction of FM phase under different temperatures. The insets are the average values of the total sample under the temperature $T=150$ K.

$$\frac{\partial M}{\partial x} = -\frac{M}{\delta_{px}} \quad \text{for } x = l_m, \quad \frac{\partial M}{\partial n} = 0 \quad \text{for } x = 0, \tag{11}$$

where $l_p=(1-\sqrt{f})l$ and $l_m=\sqrt{f}l$. l is the length of the sample as shown in Fig. 1, and h is the thickness of the film.

Using the finite difference method, the coupling equations are solved neglecting the depolarization. The approximate material constants used for the $\text{BaTiO}_3-\text{CoFe}_2\text{O}_4$ system from Refs. 10 and 17 are given in Ref. 18. Because of the limited experimental data, D_{11}^M and D_{44}^M are given with considerable values. The value of the extrapolation lengths are usually about 5–45 nm for BaTiO_3; here, 45 nm is used for the two phases, which may add some discrepancy compared with the actual values for the system. The thickness of the film and the total length of the sample l are taken as 200 and 100 nm, respectively.

The average polarization and magnetization in each separated phase versus the volume fraction of the FM part for selected temperatures are shown in Fig. 2. The insets are the average values in the whole sample. Both temperature and volume fraction influence the behaviors of the FE and FM materials. A maximum spontaneous polarization appears when $f=70\%$ and the average value of P in the total sample reaches the maximum at $f=20\%$ [Fig. 2(a)]. The increase of the polarization with the volume fraction of FM part is due to the larger lattice mismatch with a bigger volume fraction of CoFe_2O_4, whose lattice parameter deviates more from that of the substrate. The average magnetizations in the FM part and in the whole sample reach maximal when $f=30\%$ and $f=70\%$, respectively [Fig. 2(b)]. A sharp decrease of the polarization and increase of magnetization are displayed when f is more than 0.9 and less than 0.1, respectively. This is largely due to the size effect and below a critical size, the materials keep parastates.

In fact, there are two cases for the stress effect on the two phases. One is that the compressive stress from the lattice mismatch of the substrate and thin film is large enough to make both lattices elongate along the c axis. It will assist the FE phase transition but hamper the FM phase transition because of a negative value of magnetostrictive coefficient. For the other case, the substrate depresses the FM phase and extends the FE phase in the vertical direction. Such an effect assists both phase transitions. Factors such as the temperature, the substrate, the parameters of each phase, and the directions of the ease polarization and magnetization will affect the stress field.

In summary, a coupled FE and FM model for the 1-3-type epitaxial thin films was studied based on a real-space finite difference solution of the two system TDGL equations. The spontaneous polarization and magnetization are two times more than the corresponding bulk value in such a high anisotropy system induced by the misfit stress from the FE/FM and film/substrate interfaces. The eigenstrains induced by the polarization greatly affect the anisotropy of the FM crystal, but those induced by the magnetization have less effect on the FE phase because of the small magnetostrictive value.

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[18] List of the parameters (units are in SI) $C_{11}^E=C_{22}^E=C_{33}^E=1.66\times10^{11}$, $C_{12}^E=C_{13}^E=C_{23}^E=0.77\times10^{11}$, $Q_{11}=Q_{22}=Q_{33}=0.11$, $Q_{12}=Q_{13}=Q_{23}=-0.043$, $A^E=3.3\times10^5$, $B^E=3.6\times10^6\times(T-448.15)$, $C^E=6.6\times10^9$, $D_{11}^E=2.7\times10^{-9}$, $D_{44}^E=0.45\times10^{-9}$, and $T_{C0}^E=383.15$; $a_p=3.99$, $a_m=8.38$, $a_s=3.905$, $C_{11}^M=C_{22}^M=C_{33}^M=2.86\times10^{11}$, $C_{12}^M=C_{13}^M=C_{23}^M=1.73\times10^{11}$, $\lambda_{100}=-470\times10^{-6}$, $M_s=300\times10^3$, $\chi=1.5\times10^4$, and $T_{C0}^M=793$. $D_{11}^M=7.2\times10^{-17}$, $D_{44}^M=3.6\times10^{-17}$, and $\delta_{\text{px}}=\delta_{\text{pz}}=\delta_{\text{mx}}=\delta_{\text{mz}}=45$ nm.