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Strong enhancement of the direct magnetoelectric effect in strained ferroelectric-ferromagnetic thin-film heterostructures

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The direct magnetoelectric (ME) effect resulting from polarization changes induced in a ferroelectric film by the application of a magnetic field to a ferromagnetic substrate is described using the nonlinear thermodynamic theory. We show that the ME voltage coefficient of heterostructures involving the Terfenol-D substrate and $\mathrm{Pb(Zr_{1-x}Ti_x)O_3}$ (PZT) films may reach a giant value of 50 $\mathrm{V\,cm^{-1}\,Oe^{-1}}$. This remarkable feature is due to a favorable combination of considerable strain sensitivity of polarization and low electric permittivity in compressively strained PZT films. The theory also predicts a further dramatic increase in ME coefficients at the strain-induced transitions between different ferroelectric phases.

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I. INTRODUCTION

The direct magnetoelectric (ME) effect is potentially useful for the magnetic field sensing, magnetic recording read heads, current measurement probes for high-power electric transmission systems, and for energy harvesting.[1–3] Since the ME response of single-phase magnetoelectric materials is too small for device applications,[4] intensive experimental and theoretical studies were focused on multiferroic composites combining ferroelectric and ferromagnetic materials.[5] It was found, in particular, that laminate composites involving piezoelectric $\mathrm{Pb(Zr_{1-x}Ti_x)O_3}$ (PZT) and magnetostrictive Terfenol-D layers display very high ME voltage coefficients exceeding 1 $\mathrm{V\,cm^{-1}\,Oe^{-1}}$.[1] The replacement of a ceramic PZT layer in such composite by the ⟨001⟩-oriented $\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}PbTiO_3}$ (PMN-PT) single crystal increases the ME coefficient up to 10 $\mathrm{V\,cm^{-1}\,Oe^{-1}}$.[1] Interestingly, considerable ME effect was found recently even in industrially produced multilayer capacitors consisting of alternating layers based on $\mathrm{BaTiO_3}$ and Ni.[3] In addition to bulk ME composites, thin-film multiferroic heterostructures were investigated, such as PZT-Pd-$\mathrm{Co_xPd_{1-x}}$ multilayers[6] and $\mathrm{BaTiO_3\text{-}CoFe_2O_4}$ columnar nanostructures[7] fabricated on passive substrates and PZT films grown on the ferromagnetic $\mathrm{La_{1.2}Sr_{1.8}Mn_2O_7}$ crystal.[8]

The theoretical studies of ME effects in multiferroic composites and heterostructures were predominantly based on *linear* constitutive equations.[5,9–12] The linear theory predicted, in particular, that the ME voltage coefficient of PZT/Terfenol-D multilayers with ideal interfacial coupling may be as large as 5 $\mathrm{V\,cm^{-1}\,Oe^{-1}}$.[9] The influence of imperfect interfacial bonding on the ME responses of multiferroic laminates was later modeled phenomenologically.[10] Using a linear theory, Nan *et al.*[11] also evaluated the direct ME effect in the thin-film ferroelectric-ferromagnetic heterostructures fabricated on thick passive substrates. These authors did not study, however, the expected dependence of the magnetic-field-induced polarization on the lattice strains created in the ferroelectric phase by a dissimilar substrate. Moreover, the mechanical boundary conditions employed in their calculations correspond to the three-dimensional clamping of heterostructure (all components of the strain tensor are fixed), whereas the substrate actually produces the two-dimensional clamping only (three strains and three stresses remain constant).[13] Accordingly, a finite ME response was incorrectly predicted for a ferromagnetic-ferroelectric bilayer clamped by a thick substrate.

Recently, Liu *et al.*[14,15] attempted to calculate the magnetically induced polarization in $\mathrm{BaTiO_3\text{-}CoFe_2O_4}$ heterostructures with the aid of the Landau-Ginzburg-Devonshire thermodynamic theory of ferroelectrics. However, they used incorrect approach based on the minimization of the Gibbs free energy G, which does not describe the effect of *internal* mechanical stresses on the physical properties of such heterostructures. Indeed, the elastic energy contribution to G is negative, which is valid only for material systems subjected to *external* stresses. The correct theoretical approach to the description of internally strained heterostructures, therefore, should be based on the minimization of the modified thermodynamic potential $\tilde{G}$ or the Helmholtz free energy F, where the elastic energy contribution is positive.[13,16]

In this paper, the direct ME effect in hybrid ferroelectric-ferromagnetic heterostructures is described using a *nonlinear* thermodynamic theory. We focus on material systems with the 2-2 connectivity, which combine a thin ferroelectric film with a thick ferromagnetic substrate in order to maximize this effect. The influence of lattice strains on the polarization and electric permittivity of a ferroelectric film is explicitly taken into account in the calculations. It is shown that the strain state of ferroelectric film has a strong impact on the ME response of the studied multiferroic heterostructure.

II. THERMODYNAMIC CALCULATIONS

Consider a single-crystalline ferroelectric film sandwiched between two continuous electrodes. The film is assumed to be epitaxially grown on a bottom electrode ensur-

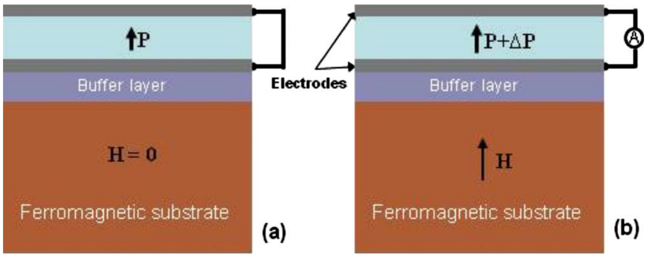

FIG. 1. (Color online) Schematic representation of a hybrid material system involving a thin ferroelectric film deposited on a thick ferromagnetic substrate. The film is sandwiched between two continuous electrodes enabling the measurements of magnetoelectric coefficients. The film average polarization (a) equals **P** in the initial state and (b) changes to **P**+Δ**P** under a magnetic field **H** applied to the substrate.

ing the (001) crystallographic orientation of the film lattice, as it happens in many ferroelectric heterostructures. The electrode-ferroelectric-electrode trilayer should be fabricated on a thick ferromagnetic substrate, which may require the deposition of an additional buffer layer (Fig. 1). The initial strain state of an epitaxial film is defined by the lattice matching to the bottom electrode, which may be strained itself due to the mechanical interaction with the substrate. Restricting our analysis to the films of perovskite ferroelectrics grown on the (001)-oriented cubic or tetragonal bottom electrodes, we can introduce the relations $u_{11}=u_{22}=u_m$ and $u_{12}=0$ for the in-plane strains imposed on the prototypic cubic state of a ferroelectric material. The misfit strain u_m is given by the formula $u_m=(b^*-a_0)/a_0$, where b^* is the effective in-plane lattice parameter of the bottom electrode and a_0 is the lattice constant of a stress-free prototypic phase.[13]

When an external magnetic field **H** is applied to the heterostructure, macroscopic deformations $u^s_{ij}(\mathbf{H})$ appear in a ferromagnetic substrate due to the magnetostriction. In the material systems with perfect mechanical coupling at the interfaces, the substrate deformations change the in-plane film strains as $u_{11}=u_m+u^s_{11}(\mathbf{H})$, $u_{22}=u_m+u^s_{22}(\mathbf{H})$, and $u_{12}=u^s_{12}(\mathbf{H})$. Then the ME polarization coefficients α_{ij} can be calculated from the relation

$$\alpha_{ij}=\frac{\partial\langle P_i\rangle}{\partial u_{11}}\frac{\partial u^s_{11}}{\partial H_j}+\frac{\partial\langle P_i\rangle}{\partial u_{22}}\frac{\partial u^s_{22}}{\partial H_j}+\frac{\partial\langle P_i\rangle}{\partial u_{12}}\frac{\partial u^s_{12}}{\partial H_j}, \qquad (1)$$

where $\langle P_i\rangle$ are the mean values of the polarization components P_i ($i=1, 2, 3$) in the ferroelectric film. In the symmetric case ($u^s_{11}=u^s_{22}$ and $u^s_{12}=0$), which will be analyzed below, Eq. (1) reduces to

$$\alpha_{i3}=\frac{\partial\langle P_i\rangle}{\partial u_m}\frac{\partial u^s_{11}}{\partial H_3}, \qquad (2)$$

where the derivatives $\partial\langle P_i\rangle/\partial u_m$ correspond to the dependence of mean polarization components on the isotropic biaxial strain $u_m=u_{11}=u_{22}$.

Equation (2) describes the typical experimental situation,[5] where the magnetic field **H** is applied along the x_3 axis orthogonal to the interface. To ensure the equality $u^s_{11}=u^s_{22}$ and the absence of field-induced shear deformation u^s_{12}, this axis should represent a symmetry axis of the substrate at least of the fourth order. This condition is satisfied, in particular, for polycrystalline Terfenol-D, a highly magnetostrictive alloy $Tb_{1-x}Dy_xFe_2$, which represents a suitable substrate material strongly enhancing the direct ME effect. (On the macroscopic level, Terfenol-D polycrystal is isotropic in the plane perpendicular to the field direction.) The field-induced deformations u^s_{ii} of Terfenol-D vary nonlinearly with the magnetic field intensity with the maximum longitudinal deformation u^s_{33} being on the order of 0.1%.[17] For Terfenol-D rods not subjected to external mechanical stresses, the dependence of u^s_{33} on the field intensity H_3 may be approximated by the function

$$u^s_{33}=\lambda_s\left[\coth\left(\frac{3\chi_m H_3}{M_s}\right)-\frac{M_s}{3\chi_m H_3}\right]^2, \qquad (3)$$

where λ_s is the saturation magnetostriction deformation, χ_m is the initial magnetic susceptibility, and M_s is the magnetization.[18] Importantly, Eq. (3) captures both the quadratic field dependence at $H_3\to 0$ and the saturation regime in high magnetic fields. Since the transverse deformations can be evaluated from the condition $u^s_{11}=u^s_{22}=-0.5u^s_{33}$,[19] the derivative $\partial u^s_{11}/\partial H_3$ involved in Eq. (2) can be readily calculated as a function of the bias magnetic field. Although this derivative tends to zero at $H_3\to 0$ and at very high fields, its magnitude strongly increases in the range of intermediate bias fields with the maximum value of about 1.8×10^{-8} m/A reached at $H_3\approx 100$ Oe.[17]

Let us proceed now to the calculation of the derivatives $\partial\langle P_i\rangle/\partial u_m$ defining the first factor in Eq. (2). These derivatives depend on the strain sensitivities $S_i=\partial P_i/\partial u_m$ of polarization components and on the domain structure existing in an epitaxial ferroelectric film. In order to maximize the discussed ME effect, the film should be poled prior to the measurements by an electric field sufficient to remove antiparallel 180° domains. Owing to the screening effect of metallic electrodes, thus formed homogeneous polarization state will remain stable after switching off the poling field.[20] Therefore, we shall assume that the film acquires a single-domain state so that $\partial\langle P_i\rangle/\partial u_m$ becomes equal to the strain sensitivity S_i.[21] The latter can be calculated using the nonlinear thermodynamic theory of epitaxial ferroelectric films through the dependences of polarization components on the misfit strain u_m.[22] For the tetragonal c phase ($P_1=P_2=0$ and $P_3\neq 0$) formed in compressively strained films ($u_m<0$), the out-of-plane polarization P_3 can be calculated analytically. In the P^6 approximation valid for $PbTiO_3$ and PZT films, the calculation gives the following relation:

$$P_3^2=-\frac{a^*_{33}}{3a_{111}}+\sqrt{\frac{a^{*2}_{33}-3a_1a_{111}}{9a^2_{111}}+\frac{2Q_{12}}{3a_{111}(s_{11}+s_{12})}u_m}, \qquad (4)$$

where $a^*_{33}=a_{11}+Q^2_{12}/(s_{11}+s_{12})$, a_1, a_{11}, and a_{111} are the dielectric stiffness and higher-order stiffness coefficients at constant stress, Q_{12} is the electrostrictive constant, and s_{ln} are the film elastic compliances at constant polarization. It should be noted that Eq. (4) does not take into account the suppression of P_3 by the depolarizing field since it should be negligible in the discussed relatively thick films sandwiched between continuous electrodes, which are short-circuited before the ME measurements. The influence of depolarizing field on the ME polarization coefficient $\alpha_{33} = \partial P_3 / \partial H_3$ can be neglected as well because α_{33} is evaluated by measuring an electric current flowing in the external circuit (see Fig. 1).

Using Eq. (4), we obtain the strain sensitivity $S_3 = \partial P_3 / \partial u_m$ of polarization in the c phase as

$$S_3 = \frac{Q_{12}}{2(s_{11}+s_{12})(a_{33}^* + 3a_{111}P_3^2)P_3}. \tag{5}$$

It can be seen that S_3 depends on the film polarization $P_3(u_m)$ and, therefore, is not a constant quantity. Substituting into Eqs. (4) and (5) the involved material parameters known for PZT solid solutions,[23,24] we can quantify the strain sensitivity of polarization in PZT films. The calculation shows that at a representative large compressive strain of $u_m = -16 \times 10^{-3}$ the sensitivity of $P_3 > 0$ at room temperature amounts to $S_3 \approx -6.4$ C/m^2 in PZT 20/80 films and to $S_3 \approx -9.6$ C/m^2 in PZT 40/60 ones. When the misfit strain approaches a critical value u_m^* above which the c phase becomes less stable than the r phase,[24] the magnitude of strain sensitivity increases by almost two times (see Fig. 2) with $S_3 \approx -11.4$ C/m^2 in the PZT 20/80 film ($u_m^* \cong +2.43 \times 10^{-3}$) and $S_3 \approx -16.8$ C/m^2 in the PZT 40/60 one ($u_m^* \cong -2.95 \times 10^{-3}$).

Multiplying the strain sensitivity S_3 by the field-dependent piezomagnetic response $\partial u_{11}^s / \partial H_3$ of the substrate, one can calculate the ME polarization coefficient α_{33} of PZT/Terfenol-D heterostructures as a function of the bias magnetic field H_3. At a representative piezomagnetic coefficient $\partial u_{11}^s / \partial H_3 = -5 \times 10^{-9}$ m/A corresponding to a moderate bias ~400 Oe,[17] it appears to be in the range $\alpha_{33} \approx (3\text{–}6) \times 10^{-8}$ s/m at the Zr content $x = 20\%$ and $\alpha_{33} \approx (5\text{–}8) \times 10^{-8}$ s/m at $x = 40\%$. These values are close to the maximum ME response $\alpha_{33} \approx 6.5 \times 10^{-8}$ s/m measured in PZT/Terfenol-D bulk laminate composites.[1]

The ME voltage coefficient $\alpha_{E33} = \partial E_3 / \partial H_3$, which defines the magnetically induced output voltage under open-circuit conditions, can be calculated from α_{33} via the relation $\alpha_{E33} = \alpha_{33}/(\varepsilon_0 \varepsilon_{33})$, where ε_{33} is the relative out-of-plane permittivity of the ferroelectric film and ε_0 is the permittivity of the vacuum. For epitaxial PZT films, the dielectric response was calculated as a function of the misfit strain in our earlier paper.[24] At $u_m = -16 \times 10^{-3}$, the permittivity ε_{33} is about 60 in the PZT 20/80 film and about 80 in the PZT40/60 one, which gives $\alpha_{E33} \approx 50$ V cm^{-1} Oe^{-1} for both compositions. Since the film dielectric response increases significantly as u_m tends to u_m^*, the ME voltage coefficient decreases down to about 40 V cm^{-1} Oe^{-1} near u_m^* (see Fig. 3). Nevertheless, the magnitude of α_{E33} remains much larger than the maximum static ME coefficient displayed by the PZT/Terfenol-D bulk laminate composite ($\alpha_{E33} < 5$ V cm^{-1} Oe^{-1}) and even by the PMN-PT/Terfenol-D one ($\alpha_{E33} \approx 10$ V cm^{-1} Oe^{-1}).[1] This remarkable feature is explained by the fact that the out-of-plane permittivity of epitaxial PZT films stabilized in the tetragonal c phase ($\varepsilon_{33} < 200$) is much lower than the permittivities of PZT ceramic ($\varepsilon_{33} \approx 1250$) and PMN-PT single crystal ($\varepsilon_{33} \approx 4300$) employed in the experimental investigations. It should be noted that the ME voltage coefficient of PZT/Terfenol-D multilayers predicted by the linear theory is about 5 V cm^{-1} Oe^{-1} only.[9]

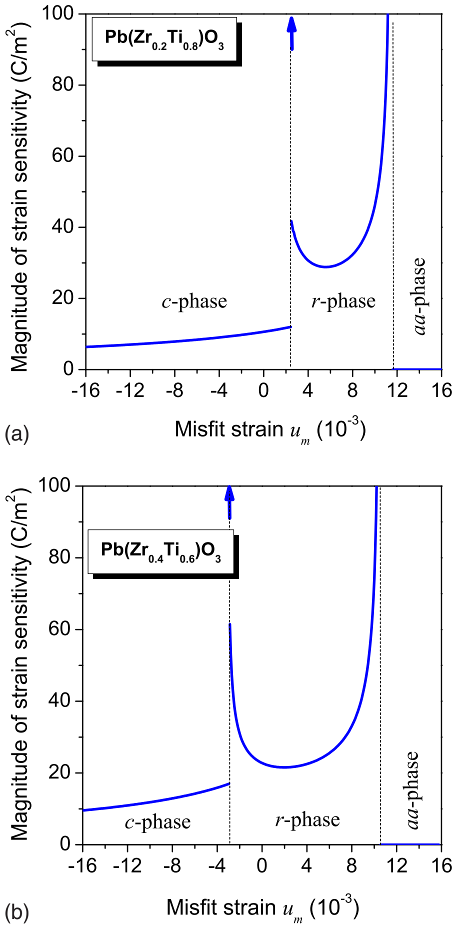

FIG. 2. (Color online) Magnitude of the strain sensitivity S_3 of the out-of-plane polarization P_3 at room temperature calculated for single-domain epitaxial PZT (a) 20/80 and (b) 40/60 films subjected to the isotropic biaxial in-plane strain u_m. The arrow indicates drastic increase in the sensitivity at strain changes inducing the $r \rightarrow c$ phase transition. The vertical dashed lines show the critical misfit strains u_m^* and u_m^{**}.

When the ferroelectric film in a hybrid heterostructure stabilizes in the monoclinic r phase ($u_m^* < u_m < u_m^{**}$), all three polarization components P_i become different from zero so that the direct ME effect acquires additional features. Using the dependences $P_i(u_m)$ reported for PZT films,[24] we calculated their strain sensitivities S_i as functions of the misfit strain. Figure 2 shows variations in the sensitivity S_3 of the out-of-plane polarization in PZT 20/80 and 40/60 films.[25] It can be seen that the magnitude of S_3 varies nonmonotonically within the stability range of the r phase, being larger than in the c phase and rising steeply near the critical strains u_m^* and u_m^{**} limiting this range. Accordingly, the ME polarization coefficient α_{33} should also increase dramatically near the strain-induced phase transitions in the ferroelectric film. In contrast, the ME voltage coefficient α_{E33} is large only near the $r \rightarrow c$ phase transition (see Fig. 3) because enormous increase in the permittivity ε_{33} at the second-order $r \rightarrow aa$ phase transition[24] makes the output voltage negligible.

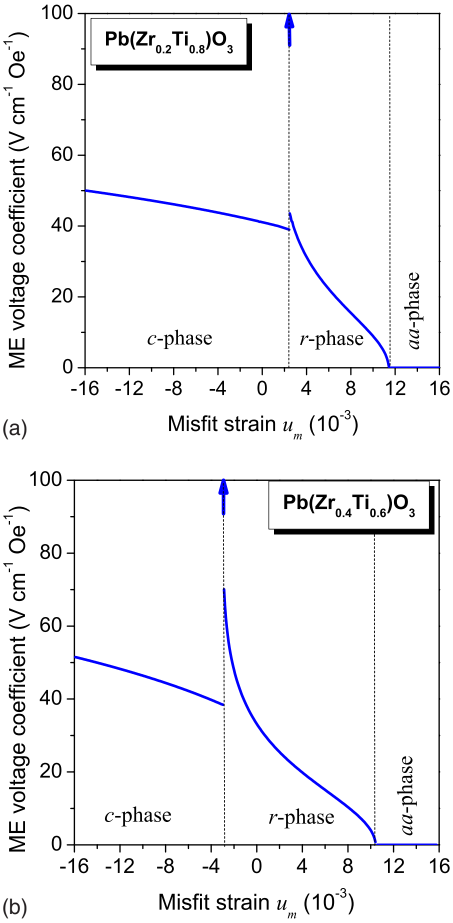

FIG. 3. (Color online) Magnetoelectric voltage coefficient α_{E33} at room temperature calculated for a hybrid heterostructure involving the Terfenol-D substrate and the single-domain epitaxial PZT (a) 20/80 or (b) 40/60 film subjected to the isotropic biaxial in-plane strain u_m. The piezomagnetic coefficient $\partial u_{11}^s / \partial H_3$ of Terfenol-D is taken to be equal to -5×10^{-9} m/A. The arrow indicates drastic increase in α_{E33} at strain changes inducing the $r \rightarrow c$ phase transition.

It should be emphasized that the ME responses described above correspond to weak driving magnetic fields δH_3 which do not change the phase state of a ferroelectric film during the ME measurement. If the applied magnetic field δH_3 is high enough to induce a phase transition in the film, the measured ME coefficient becomes strongly dependent on the magnitude of δH_3. In particular, when the $r \rightarrow c$ transformation takes place, the polarization change $\delta P_3(\delta H_3)$ increases drastically due to a jump of P_3 at this first-order phase transition. As a result, the magnitude of the strain sensitivity S_3 may exceed 100 C/m^2 in the PZT 20/80 and 40/60 films (Fig. 2) which leads to the ME polarization coefficient $\alpha_{33} > 5 \times 10^{-7}$ s/m and the ME voltage coefficient $\alpha_{E33} > 100$ V cm^{-1} Oe^{-1}, as indicated in Fig. 3.

III. CONCLUDING REMARKS

In this paper, we studied the direct magnetoelectric effect in hybrid ferroelectric-ferromagnetic heterostructures with the aid of the nonlinear thermodynamic theory of ferroelectric thin films. To that end, the strain sensitivity of polarization in PZT thin films was calculated as a function of the misfit strain in the epitaxial system. Taking into account the field-dependent piezomagnetic response of ferromagnetic substrate, we evaluated ME coefficients of PZT/Terfenol-D heterostructures. The ME voltage coefficient α_{E33}, which represents the figure of merit characterizing the performance of material system for magnetic field sensors, was found to be enormously high for hybrids involving compressively strained ferroelectric films.

This theoretical prediction is quite general since the enhancement of α_{E33} results predominantly from strongly reduced permittivity of such films, where the polar axis is orthogonal to the film surfaces. For a given ferroelectric-ferromagnetic couple, the ME response of a thin-film heterostructure should be much larger than that of a bulk composite, which usually has a high permittivity.[1] This superiority is expected for highly textured polycrystalline films as well and awaits its experimental confirmation.

In similarity with the converse ME effect in ferromagnetic-ferroelectric heterostructures,[26] the direct ME response may further increase dramatically at the strain-induced phase transitions in films with nanoscale thicknesses. This anomalous ME behavior is not limited to PZT films. Evidently, it may be also displayed by the heterostructures involving other multiaxial ferroelectrics, where strain-driven phase transitions can take place.

In our theoretical analysis, the magnetic field was taken to be orthogonal to the film-substrate interface. We also assumed that the substrate has a symmetry axis ensuring that magnetic-field-induced deformations u_{ij}^s are transversely isotropic, as in a properly oriented tetragonal crystal, for example. In this practically important situation, the application of magnetic field to the heterostructure does not induce the anisotropy of in-plane strains u_{11} and u_{22} and a shear strain u_{12} in the film. The general case of $u_{11} \neq u_{22}$ and $u_{12} \neq 0$ can be treated using the modified thermodynamic potential of a ferroelectric film introduced in Ref. 27. However, the second-order term $a_3^* P_3^2$ in this potential, which is related to the out-of-plane polarization P_3, is sensitive to the mean in-plane strain $(u_{11}+u_{22})/2$ only.[27] Therefore, the ME coefficients α_{3j} and α_{E3j} of heterostructures involving tetragonal ferroelectric films ($P_1 = P_2 = 0$ and $P_3 \neq 0$) will be still governed by the strain sensitivity $S_3(u_m)$ of polarization, which was calculated in this paper.

It should be also emphasized that the biaxial in-plane strain u_m in the ferroelectric film depends on several parameters of the heterostructure. The first source of strain is the lattice mismatch between the film and bottom electrode at the growth temperature T_g.[13] The resulting misfit strain, however, partially relaxes in thick films due to the generation of misfit dislocations at T_g. A difference in the thermal-expansion coefficients between the film and substrate represents the second source of strain, which makes u_m a temperature-dependent quantity.[28] Last, the application of a bias magnetic field **H** during the ME measurements slightly changes the film strains as well. The algebraic sum of these three contributions gives the total film strain u_m, which can be regarded as a fixed parameter determining the ME response at a given temperature and bias field. Accordingly, the ME coefficients should be described as functions of the total strain u_m as plotted in Figs. 2 and 3.

Finally, we note that in the discussed heterostructures involving perovskite ferroelectrics the misfit dislocations should not play significant detrimental role during the ME measurements performed at temperatures $T \sim 300$ K and below. Indeed, it is known that well below the growth temperature $T_g \sim 900$ K these dislocations become immobile in perovskite ferroelectrics because high Peierls barriers existing here suppress the dislocation glide in the crystal lattice. Therefore, the film strains caused by the magnetic-field-induced substrate deformations cannot relax via the nucleation and motion of misfit dislocations. These additional strains are fully transferred from the substrate to the film at any ferroelectric and electrode thicknesses much smaller than the substrate thickness.

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[1] J. Ryu, S. Priya, K. Uchino, and H.-E. Kim, J. Electroceram. **8**, 107 (2002).

[2] M. Vopsaroiu, J. Blackburn, A. Muniz-Piniella, and M. G. Cain, J. Appl. Phys. **103**, 07F506 (2008).

[3] C. Israel, N. D. Mathur, and J. F. Scott, Nature Mater. **7**, 93 (2008).

[4] M. Fiebig, J. Phys. D **38**, R123 (2005).

[5] C. W. Nan, M. I. Bichurin, S. Dong, D. Viehland, and G. Srinivasan, J. Appl. Phys. **103**, 031101 (2008).

[6] S.-K. Kim, J.-W. Lee, S.-C. Shin, H. W. Song, C. H. Lee, and K. No, J. Magn. Magn. Mater. **267**, 127 (2003).

[7] H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, and R. Ramesh, Science **303**, 661 (2004).

[8] M. A. Zurbuchen, T. Wu, S. Saha, J. Mitchell, and S. K. Streiffer, Appl. Phys. Lett. **87**, 232908 (2005).

[9] C. W. Nan, M. Li, and J. H. Huang, Phys. Rev. B **63**, 144415 (2001); C. W. Nan, G. Liu, and Y. Lin, Appl. Phys. Lett. **83**, 4366 (2003).

[10] M. I. Bichurin, V. M. Petrov, and G. Srinivasan, J. Appl. Phys. **92**, 7681 (2002); Phys. Rev. B **68**, 054402 (2003).

[11] C. W. Nan, G. Liu, Y. Lin, and H. Chen, Phys. Rev. Lett. **94**, 197203 (2005).

[12] V. M. Petrov, G. Srinivasan, M. I. Bichurin, and A. Gupta, Phys. Rev. B **75**, 224407 (2007).

[13] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).

[14] G. Liu, C. W. Nan, Z. K. Xu, and H. Chen, J. Phys. D **38**, 2321 (2005).

[15] G. Liu, C. W. Nan, and J. Sun, Acta Mater. **54**, 917 (2006).

[16] N. A. Pertsev, A. K. Tagantsev, and N. Setter, Phys. Rev. B **61**, R825 (2000).

[17] H. T. Savage, R. Abbundi, A. E. Clark, and O. D. McMasters, J. Appl. Phys. **50**, 1674 (1979); M. B. Moffett, A. E. Clark, M. Wun-Fogle, J. Linberg, J. P. Teter, and E. A. McLaughlin, J. Acoust. Soc. Am. **89**, 1448 (1991).

[18] This formula follows from the relation $u^s_{33} = \lambda_s \langle M_3 \rangle^2 / M_s^2$ combined with the field dependence of the mean magnetization $\langle M_3 \rangle$ described by the Langevin function $f(x) = \coth(x) - 1/x$; see X. J. Zheng and X. E. Liu, J. Appl. Phys. **97**, 053901 (2005), and references therein.

[19] This relation provides the volume conservation in strained Terfenol-D. It holds for the macroscopic deformations resulting from magnetization reorientations in a model polycrystal, where the crystallites have a cubic lattice with the same spatial orientation and a randomly oriented magnetization with fixed magnitude.

[20] N. A. Pertsev and H. Kohlstedt, Phys. Rev. Lett. **98**, 257603 (2007).

[21] We suppose that the single-domain state can be created in an epitaxial ferroelectric film even at small misfit strains near $u_m = 0$, where the formation of ferroelastic (non-180°) domains becomes energetically favorable [V. G. Kukhar, N. A. Pertsev, H. Kohlstedt, and R. Waser, Phys. Rev. B **73**, 214103 (2006)]. The domain nucleation may be suppressed by rapid cooling of a thin film subjected to a strong electric field.

[22] N. A. Pertsev and B. Dkhil, Appl. Phys. Lett. **93**, 122903 (2008).

[23] M. J. Haun, E. Furman, S. J. Jang, and L. E. Cross, Ferroelectrics **99**, 13 (1989).

[24] N. A. Pertsev, V. G. Kukhar, H. Kohlstedt, and R. Waser, Phys. Rev. B **67**, 054107 (2003).

[25] The strain sensitivities S_1 and S_2 of the in-plane polarization components are not further discussed in this paper. These sensitivities differ from zero in the monoclinic r phase and the orthorhombic aa phase and give rise to nonzero transverse ME coefficients α_{13} and α_{23}.

[26] N. A. Pertsev, Phys. Rev. B **78**, 212102 (2008).

[27] A. G. Zembilgotov, N. A. Pertsev, U. Böttger, and R. Waser, Appl. Phys. Lett. **86**, 052903 (2005).

[28] N. A. Pertsev, A. G. Zembilgotov, S. Hoffmann, R. Waser, and A. K. Tagantsev, J. Appl. Phys. **85**, 1698 (1999).