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Magnetoelectric bilayer and multilayer structures of magnetostrictive and piezoelectric oxides

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Materials capable of field conversion, from magnetic to electric or vice versa, are of fundamental and technological importance. We report a giant magnetoelectric (ME) effect that results from stress-mediated electromagnetic coupling in bilayers and multilayers of nickel ferrite and lead zirconate titanate. Samples with layer thickness 10–200 μm were synthesized by doctor-blade techniques. The magnetoelectric voltage coefficient $\alpha_{\mathbf{E}}$ ranges from 460 mV/cm Oe in bilayers to 1500 mV/cm Oe for multilayers. The transverse effect is an order of magnitude stronger than longitudinal $\alpha_{\mathbf{E}}$. The ME coefficient is maximum at room temperature and a general increase in $\alpha_{\mathbf{E}}$ is observed with increasing frequency. Data on the dependence of $\alpha_{\mathbf{E}}$ on volume fraction of the two phases and bias magnetic field are in excellent agreement with a theoretical model for a perfectly bonded bilayer.

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I. INTRODUCTION

Conversion of electric to magnetic fields plays an important role in many devices. One way in principle to accomplish this is a composite of magnetostrictive and piezoelectric materials. In such composites, the field conversion is a two step process: magnetostriction induced mechanical deformation resulting in induced electric fields. Until now, interest in such transducers has been lacking because of conversion efficiencies that are an order of magnitude below theoretical predictions. Here we report on a novel class of materials that achieve the maximum efficiency.

The magnetoelectric (ME) effect is defined as the dielectric polarization of a material in an applied magnetic field or an induced magnetization in an external electric field.[1] In materials that are magnetoelectric (ME), the induced polarization **P** is related to the magnetic field **H** by the expression, $\mathbf{P}=\alpha\mathbf{H}$, where α is the second rank ME-susceptibility tensor. A parameter of importance is the ME voltage coefficient $\alpha_E=\delta E/\delta H$ with $\alpha=\varepsilon_0\varepsilon_r\alpha_E$, where ε_r is the relative permittivity. The effect, first observed in antiferromagnetic Cr_2O_3, is generally weak in single phase compounds.[2–6] A strong ME effect, however, could be realized in a ‘‘product-property’’ composite consisting of magnetostrictive (MS) and piezoelectric (PE) phases in which the mechanical deformation due to magnetostriction results in a dielectric polarization due to piezoelectric effects.[7] Van den Boomgaard synthesized bulk composites of cobalt ferrite or nickel ferrite with $BaTiO_3$ that yielded ME voltage coefficient α_E that was a factor 40–60 smaller than calculated values.[8,9] Possible causes for such low α_E include microcracks due to thermal expansion mismatch between the two phases, leakage current through low resistivity ferrites, porosity, and any impurity or undesired phases.

A multilayer structure is expected to be far superior to bulk composites since the PE layer can easily be poled electrically to enhance the piezoelectricity and the ME effect. In addition, MS layers enclosed in metal electrodes lead to series electrical connectivity for PE layers and further enhancement of piezoelectricity.[10,11] Harshe and co-workers proposed a theoretical model for a magnetostrictive-piezoelectric bilayer structure. The estimated $\alpha_{\mathbf{E}}$ for cobalt ferrite (CFO)–lead zirconate titanate (PZT), or –barium titanate, bilayer was in the range 0.2–5 V/cm Oe, depending on field orientations, boundary conditions, and material parameters.[11] They also prepared multilayers by sintering tape-cast ribbons.[10] Samples of CFO-$BaTiO_3$ structures did not show ME effects. The largest $\alpha_{\mathbf{E}}=75$ mV/cm Oe, a factor of 3–30 smaller than theoretical values, was measured for CFO-PZT. The low $\alpha_{\mathbf{E}}$ or the absence of ME effect is most likely due to unfavorable interface conditions and the following problems due to the use of platinum electrodes at the interface. (i) The electrode makes it a three-phase multilayer structure and leads to poor mechanical coupling between the two oxide layers, (ii) platinum with thermal expansion coefficient much higher than that of oxides will result in microcracks at the interface during sample processing, (iii) measurement conditions for ME effects might correspond to the inelastic region of stress-strain characteristics for Pt leading to a reduction in ME coefficients. In summary the use of appropriate MS and PE phases and the elimination of foreign electrodes are critically important for obtaining large ME effects in the multilayer (ML) structures.

This paper details two primary accomplishments. (i) Observation of a record high ME coefficient $\alpha_{\mathbf{E}}$, 460–1500 mV/cm Oe, in nickel ferrite (NFO)–PZT bilayers and multilayers. (ii) Theoretical analysis that accounts very well for the volume and applied static magnetic-field dependence of $\alpha_{\mathbf{E}}$. Samples of NFO-PZT were synthesized by doctor-blade techniques. Magnetoelectric characterization involved measurements of transverse and longitudinal $\alpha_{\mathbf{E}}$ as a function of bias magnetic field, frequency, temperature and volume fraction for the PE and MS-phases. We observe a transverse effect that is at least an order of magnitude larger than the longitudinal effect. The ME coefficient is maximum at room temperature. With increasing frequency, α_E is found to increase. An exponential increase in α_E occurs for increasing volume of the magnetostrictive phase in the multilayer.

The measured α_E-values in NFO-PZT are the largest ever measured for any system. For comparison, the best α_E value for a single phase material is 20 mV/cm Oe for Cr_2O_3,[2,3] and is 75 mV/cm Oe for multilayers of $CoFe_2O_4$(CFO)-PZT.[10] The main reasons, as discussed later, for our accomplishments are (i) the choice of nickel ferrite that has a high pseudo-piezomagnetic effect and (ii) the existence of an ideal NFO-PZT interface as evident from the remarkable agreement between theory and data. In view of the fact that CFO-PZT composites have comparable material parameters, the interface plays an important role in the dynamics of ferromagnetic domain motion and the consequent stress mediated electromagnetic coupling. Anticipated impacts of this report are (i) studies directed at an understanding of the physics of the NFO-PZT interface, and (ii) interest in the composites for useful technologies. The materials are potential candidates for magnetoelectric memory devices, electrically controlled magnetic devices, magnetically controlled piezoelectric devices, and smart sensors.[12] In the following sections, we provide details on the synthesis and magnetoelectric characterization of NFO-PZT bilayers and multilayers. Theoretical estimates based on a model that assumes perfect interface bonding have been obtained for comparison with data.

II. SAMPLE PREPARATION

Both bilayers and multilayers of NFO-PZT were synthesized from thick films prepared by tape casting. The process involves (i) preparation of submicron-size powder of NFO and PZT, (ii) thick-film tapes by doctor-blade techniques, and (iii) lamination and sintering of bilayers and multilayers. Nickel ferrite powder obtained by standard ceramic techniques and commercial PZT (Ref. 13) were used. For tape casting,[14] powders of NFO or PZT were mixed with a solvent (ethyl alcohol) and a dispersant (Blown Menhaden fish oil) and ball milled for 24 h, followed by a second ball milling with a plasticizer (butyl benzyl phthalate) and a binder (polyvinyl butyral) for 24 h. The slurries thus obtained were cast into tapes on silicon-coated mylar sheets using a tape caster consisting of a pair of stationary micrometer-controlled blades and a moveable casting bed. It was possible to obtain $10\times 20\,\mathrm{cm}^2$ tapes with the thickness in the range 10–200 μm. The tapes were arranged to obtain the desired structure, laminated under high pressure (3000–5000 psi) and high temperature (400 K), and heated at 1000 K for binder evaporation. The final sintering was carried out at 1400–1500 K.

Bilayers were made with 200-μm-thick films of NFO and PZT. Multilayers contained alternate layers of NFO and PZT, totaling $n+1$ layers of NFO and n layers of PZT ($n=5-29$), with a layer thickness of 10–20 μm. Structural studies were done with x-ray diffraction on multilayers, crushed power samples, and samples with exposed interface by etching away the top layer. There was no evidence for any impurity phases. Magnetic parameters such as the saturation magnetization, anisotropy, and g value were in agreement with values expected for nickel ferrite.[15] Thus the high-temperature processing did not result in any impurity phases or degradation of the quality of the magnetic phase.

The magnetostriction λ is an important parameter for theoretical estimates of $\alpha_\mathbf{E}$ for the composite. In the ferromagnetic phase, the magnetostriction due an ac field $\delta\mathbf{H}$ in the presence of a bias field **H** leads to pseudopiezomagnetic effects that in turn give rise to the necessary coupling to the piezoelectric phase in the composite. In order to maximize the ME coefficient, **H** must correspond to the maximum in the slope of λ vs **H** characteristics. The standard strain-gauge method (Micro-Measurement Group Strain Indicator—Model 3800 and series WK strain gauges) and an electromagnet with a maximum field of 5 kOe were used for the measurement of λ. Figure 1 shows the static field **H** dependence of parallel (λ_{11}) and perpendicular (λ_{13}) magnetostriction, corresponding to **H** parallel or perpendicular to the sample plane. [We assume a three-dimensional coordinate system (1,2,3) with the sample in the (1,2) plane]. The room-temperature data are for a multilayer with $n=14$ and a layer thickness of 14 μm. The parallel magnetostriction λ_{11} is negative (the figure shows the magnitude) and is a factor of 3–10 larger than λ_{13}. One observes saturation of λ for **H** values above 1200 Oe. We did not observe any dependence of λ either on the number of layers or on the layer thickness.

Samples were then polished, electrical contacts were made with silver paint, and poled. The poling procedure involved heating the sample to 420 K and the application of an electric field **E** of 20 kV/cm. As the sample was cooled to 300 K, **E** was increased progressively to 50 kV/cm over a duration of 30 min. The dielectric constant for the composite was in agreement with the expected values for PZT (Ref. 16). The piezoelectric coefficient, another important parameter for the piezoelectric phase and the composite, measured with a (Pennebaker—Model 8000) d_{33} tester was in the range 70–170 pm/V.

III. MAGNETOELECTRIC EFFECTS

The parameter of importance for the multilayers is the magnetoelectric voltage coefficient $\alpha_\mathbf{E}$. Magnetoelectric

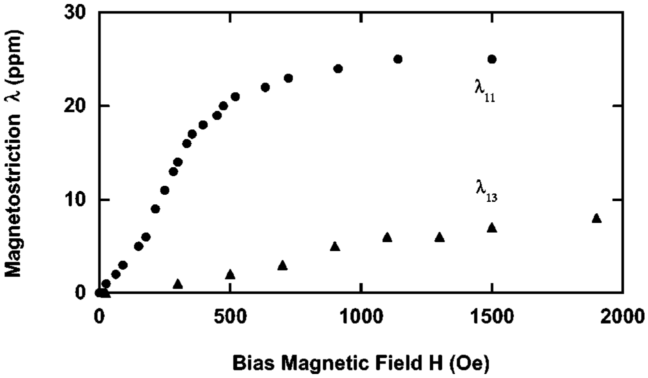

FIG. 1. The bias magnetic field **H** dependence of the magnetostriction for a multilayer composite of nickel ferrite (NFO) and lead zirconate titanate (PZT). The sample contained $n+1$ layers of NFO and n layers of PZT, with $n=14$ and a layer thickness of 14 μm. The data at room temperature are for **H** parallel (λ_{11}) and perpendicular (λ_{13}) to the plane of the multilayer composite, and are used for theoretical estimates of magnetoelectric-voltage coefficient. λ_{11} is negative, but the figure shows the magnitude.

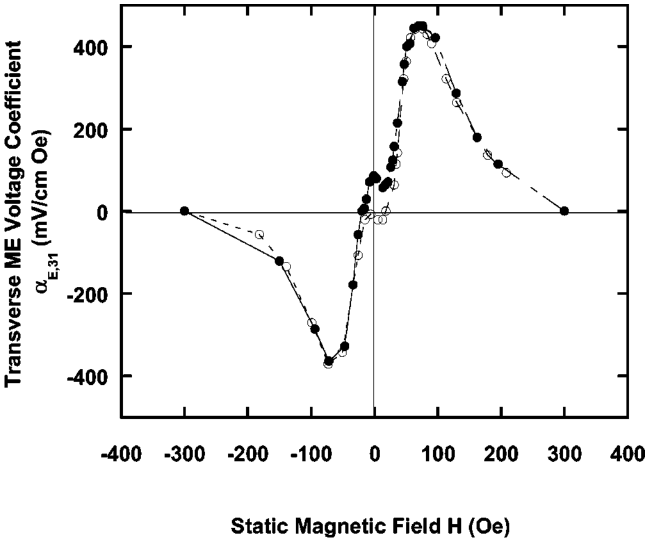

FIG. 2. Transverse magnetoelectric (ME) voltage coefficient $\alpha_{\mathbf{E},31} = \delta \mathbf{E}_3 / \delta \mathbf{H}_1$ at room temperature as a function of static magnetic field **H** for a two-layer structure consisting of 200-μm films of NFO and PZT. The field **H** and a 1-kHz ac magnetic field $\delta \mathbf{H}_1$ are applied parallel to each other and parallel to the sample plane and the induced electric field $\delta \mathbf{E}_3$ is measured perpendicular to the sample plane. The open (filled) circles are the data points for increasing (decreasing) **H**. The lines are guides to the eye.

measurements are usually performed under two distinctly different conditions: (i) the induced magnetization is measured for an applied electric effect or (ii) the induced polarization is obtained for an applied magnetic field. We measured the electric field produced by an alternating magnetic field applied to the composite. A set up in which the sample was subjected to a bias field **H** (with the use of an electromagnet) and an ac field $\delta \mathbf{H}$ (1 Oe at 10 Hz–1 kHz) produced by a pair of Helmholtz coils was used. The sample was shielded from stray electric fields. We implemented lock-in detection for accurate determination of $\alpha_{\mathbf{E}}$ for two different field orientations: (i) transverse $\alpha_{\mathbf{E}}$ or $\alpha_{\mathbf{E},31}$ for **H** and $\delta \mathbf{H}$ parallel to each other and to sample plane, and $\delta \mathbf{E}$ measured perpendicular to the sample plane and (ii) longitudinal $\alpha_{\mathbf{E},33}$ for all the three fields parallel to each other and perpendicular to the sample plane. A liquid-helium glass dewar and a nonmetallic sample insert were used for studies on temperature dependence of ME effects.

Figure 2 shows the static magnetic-field dependence of the transverse ME coefficient $\alpha_{\mathbf{E},31}$ for a two-layer composite of NFO-PZT, each layer with a thickness of 200 μm. The data at room temperature are for a frequency of 1 kHz and *for unit thickness of the piezoelectric phase*. As **H** is increased from zero, $\alpha_{\mathbf{E},31}$ increases, reaches a maximum value of 460 mV/cm Oe at 70 Oe, and then drops rapidly to zero above 300 Oe. There is no evidence for hysteresis in Fig. 2 except at fields close to zero. We observed a phase difference of 180° between the induced voltages for $+\mathbf{H}$ and $-\mathbf{H}$. As discussed later, the magnitude and the field dependence in Fig. 2 are related to the slope of λ vs H characteristics in Fig. 1 and can be understood in terms of pseudo-piezomagnetic effects in nickel ferrite.

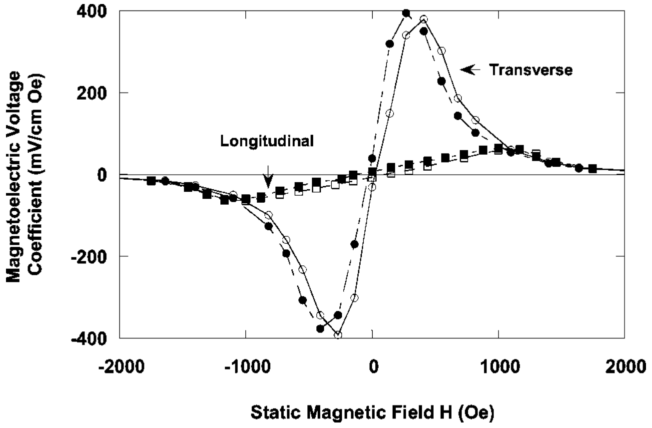

FIG. 3. Static-field dependence of room-temperature transverse and longitudinal ME voltage coefficients, $\alpha_{\mathbf{E},31}$ and $\alpha_{\mathbf{E},33}$, respectively, for a multilayer composite with $n=14$. The thickness of each layer is 14 μm. For longitudinal ME effects the fields **H**, $\delta \mathbf{H}$ (1 kHz), and $\delta \mathbf{E}$ are parallel to each other and perpendicular to the sample plane. The open (filled) circles are the data points for increasing (decreasing) **H**. The lines are guides to the eye.

Similar field dependence of both the transverse and longitudinal ME voltage coefficients, $\alpha_{E,31}$ and $\alpha_{E,33}$, respectively, are shown in Fig. 3 for a multilayer composite. The data at room temperature for a 1 kHz ac field are for a sample consisting of alternate layers of NFO (15) and PZT (14), each layer with a thickness of 14 μm so that the effective thickness of PZT is the same as for the bilayer. Comparison of data in Figs. 2 and 3 indicates the following. In multilayers, (i) ME effects are observed over a wider field range, (ii) the field for maximum $\alpha_{E,31}$ is shifted to higher fields, and (iii) the peak value of $\alpha_{E,31}$ is 15% smaller than for the bilayer. One observes in Fig. 3 a noticeable hysteresis in the field dependence of $\alpha_{E,31}$ and $\alpha_{E,33}$. The variation of $\alpha_{E,33}$ with H is linear up to 1000 Oe, and the longitudinal ME effect is almost an order of magnitude weaker than the transverse effect.

The variation of the multilayer $\alpha_{E,31}$ with frequency and temperature are shown in Fig. 4. Upon increasing the frequency from 20 Hz to 10 kHz, one observes an overall increase of 25% in the ME voltage coefficient, but a substantial fraction of the increase occurs over the 1–10 kHz range (except at 353 K). These variations are most likely due to frequency dependence of the dielectric constant for the constituent phases and the piezoelectric coefficient for PZT. Data on temperature dependence of $\alpha_{E,31}$ at 100 Hz are shown in Fig. 4. A peak in $\alpha_{E,31}$ is observed at room temperature and it decreases when T is either increased or decreased from room temperature. Detailed temperature dependence of material parameters for both phases is necessary for an understanding of these results.

According to a theoretical model to be discussed in the following section, α_E is expected to be dependent sensitively on the ratio of volumes of the magnetostrictive (m) and piezoelectric (p) phases, $f = v_m / v_p$. We obtained data on such dependence in multilayers of nickel ferrite (with a small substitution of Zn for Ni)-PZT. Studies were performed on multilayers with $n=10$ and a series of layer thicknesses to obtain

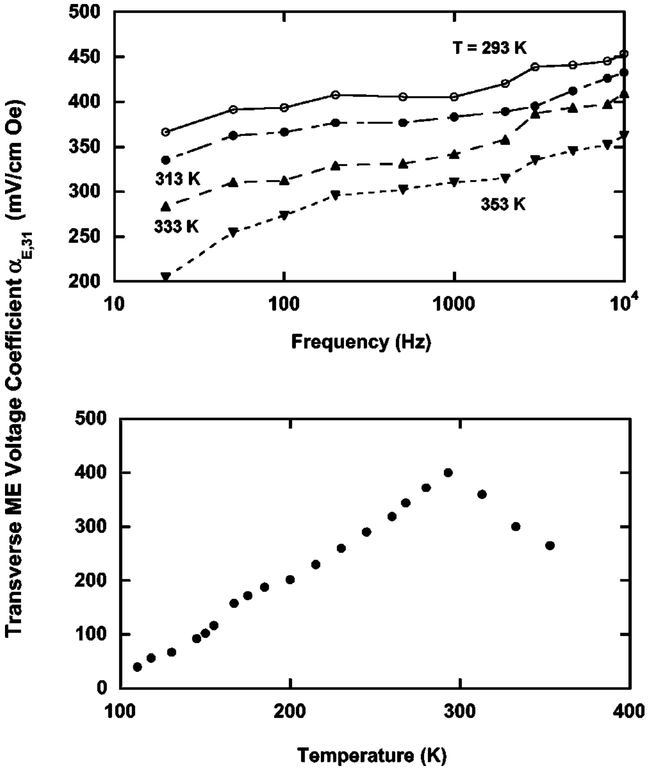

FIG. 4. Frequency and temperature dependence of the transverse coefficient $\alpha_{\mathbf{E},31}$ for the multilayer with $n=14$. The lines are guides to the eye. Values of $\alpha_{\mathbf{E},31}$ are for the bias field **H** corresponding to maximum value in the ME effect. The temperature dependence is for a frequency of 100 Hz.

samples with the necessary volume fractions. Figure 5 shows the **H** dependence of $\alpha_{\mathbf{E},31}$ on *f* values. One essentially observes features similar to the field dependence in Fig. 3. With increasing *f*, a rapid increase in $\alpha_{\mathbf{E},31}$ is evident in Fig. 5. Another observation of importance is the up-shift in the bias magnetic field corresponding to maximum $\alpha_{\mathbf{E},31}$ with increasing *f*. Figure 6 shows the variation of the peak value of $\alpha_{\mathbf{E},31}$ with *f*. One notices an exponential increase in $\alpha_{\mathbf{E},31}$ as the volume of the magnetostrictive component is increased and it levels at high volumes. The data indicate more than an order of magnitude increase in $\alpha_{\mathbf{E}}$ as *f* is increased from 0.2 to 5.5 and a maximum of 1500 mV/cm Oe is obtained for $f=2.2$.

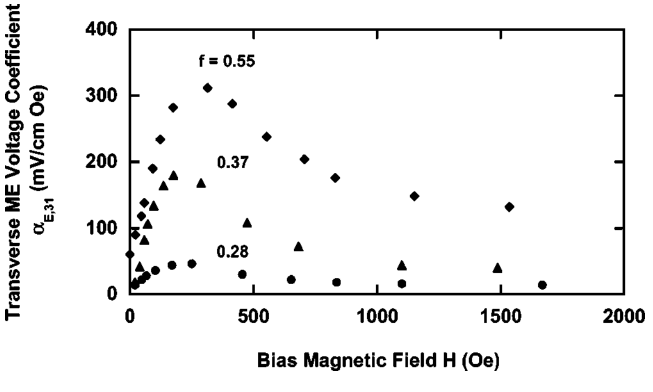

FIG. 5. Room temperature $\alpha_{\mathbf{E},31}$ at 100 Hz as a function of **H** for multilayers with $n=10$. The thickness of NFO and PZT layers was controlled to obtain a series of volume ratio of the magnetostrictive (v_m) to piezoelectric (v_p) phases, $f=v_m/v_p=0.22-5.5$. The data are for $f=0.28$, 0.37, and 0.55.

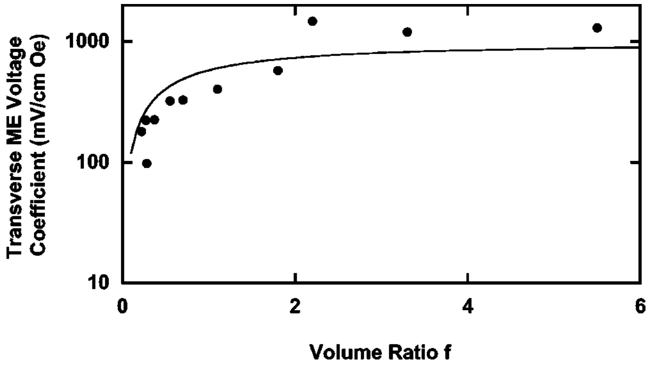

FIG. 6. Variation of the transverse coefficient $\alpha_{\mathbf{E},31}$ with $f=v_m/v_p$, for the multilayer. The solid line represents theoretical values for a two-layer structure. Values of $\alpha_{\mathbf{E},31}$ are for the bias field **H** corresponding to maximum value in the ME effect and for a frequency of 100 Hz.

The most significant results in Figs. 2–6 are that (i) for equal volume of MS and PE phases, the maximum $\alpha_{\mathbf{E},31}$ ranges from 400 mV/cm Oe in multilayers to 460 mV/cm Oe in the bilayer and (ii) $\alpha_{\mathbf{E},31}$ increases with increasing volume of nickel ferrite and the largest measured value is 1500 mV/cm Oe for $v_m/v_p=2.2$. These values must be compared with 20 mV/cm Oe for Cr_2O_3, the best single-phase ME material.[2,3] It is more than an order of magnitude higher than reported values for ferrite-$BaTiO_3$ *bulk* composites,[8,9,17] and multilayers of CFO-PZT,[10,11] and a factor of 5 larger than that in laminated composites of Ni(Co, Cu)–Mn ferrite–PZT (Ref. 18).

IV. DISCUSSION

We first discuss a theoretical model for the bilayers and estimate the bias magnetic field and volume-fraction dependence of the magnetoelectric voltage coefficients for comparison with data. Following this, we discuss the possible cause of the giant ME effect in NFO-PZT structures. Harshe and co-workers provided a model for a two-layer structure in which no electric field is present in the MS layer, the top and bottom surfaces of the piezoelectric (PE) layers are equipotential surfaces, and the bias magnetic field **H** is uniform throughout the sample.[10] For the composite of interest, NFO-PZT, the assumptions are justified because of low electrical resistivity for NFO compared to PZT. The total strain at the interface is given by the expression

$$\mathbf{S}=s\mathbf{T}+d\mathbf{E}+q\mathbf{H}. \tag{1}$$

The three terms correspond to contributions from elastic (s compliance coefficient; **T**, stress tensor), piezoelectric (d, piezoelectric coefficient), and pseudopiezomagnetic effects (q, piezomagnetic coefficient). Although strain due to magnetostriction is λH^2, under appropriate bias field a linear pseudopiezomagnetic is expected resulting in a strain $q\mathbf{H}$. The ME coefficient α_E is estimated by the following procedure. (i) For an applied magnetic field δH, the total strain at the interface, which is the sum of elastic and magnetostrictive strains, is estimated. (ii) The strain-stress relationship is calculated for boundary conditions at the interface. (iii) The stress-electric field ($\delta\mathbf{E}$) relationship is estimated for appropriate boundary conditions. We are interested in a free body with a perfectly bonded interface. Denoting the magnetostrictive and the piezoelectric phases by m and p, respectively, one obtains for the transverse ME coefficient

$$\alpha_{\mathbf{E},31} = \delta\mathbf{E}_3/\delta\mathbf{H}_1 = \frac{-2d_{31}^p q_{11}^m v_m}{(s_{11}^m+s_{12}^m)\varepsilon_{33}^{T,p}v_p+(s_{11}^p+s_{12}^p)\varepsilon_{33}^{T,p}v_m-2(d_{31}^p)^2 v_m} \tag{2}$$

and the longitudinal coefficient

$$\alpha_{\mathbf{E},33} = \delta\mathbf{E}_3/\delta\mathbf{H}_3 = \frac{-2d_{31}^p q_{13}^m v_m}{(s_{11}^m+s_{12}^m)\varepsilon_{33}^{T,p}v_p+(s_{11}^p+s_{12}^p)\varepsilon_{33}^{T,p}v_m-2(d_{31}^p)^2 v_m}. \tag{3}$$

Here v denotes the volume and ε^T is the permittivity at constant stress. Since the ME voltage is induced in the PE phase, Eqs. (2) and (3) are expressions for per unit thickness of the PE phase. It is clear from Eqs. (2) and (3) that $\alpha_\mathbf{E}$ is directly proportional to the product of piezomagnetic and piezoelectric coefficients, and is dependent on the volume fraction v_m/v_p.

We now use the above model for the theoretical calculation of $\alpha_\mathbf{E}$ for comparison with the data. The following material parameters were used for the constituent phases:[11,15,16]

$$\text{PZ,}\quad s_{11}^p = 14\times10^{-12}\ \text{m}^2/\text{N},\quad s_{12}^p = -8\times10^{-12}\ \text{m}^2/\text{N},$$

$$\varepsilon_{33}^{T,p} = 17\times10^{-9}\ \text{F/m},$$

$$\text{NiFe}_2\text{O}_4\quad s_{11}^m = 6.5\times10^{-12}\ \text{m}^2/\text{N},$$

$$s_{12}^m = -2.4\times10^{-12}\ \text{m}^2/\text{N}.$$

Measured values of the piezoelectric coupling coefficient d_{33} for the multilayers ranged from 70–170 pm/V at 100 Hz and an average value of $d_{31}=d_{33}/2=60$ pm/V was used. The other required parameter, $q=\delta\lambda/\delta\mathbf{H}$ was determined from parallel (λ_{11}) and perpendicular (λ_{13}) magnetostriction data in Fig. 1. Theoretical values[19] of $\alpha_{\mathbf{E},33}$ and $\alpha_{\mathbf{E},31}$ were estimated from Eqs. (2) and (3).

In Fig. 7 calculated transverse and longitudinal ME voltage coefficients for $v_m/v_p=1$ are compared with the data for the bilayer and multilayer (in Figs. 2 and 3). One observes an overall agreement for both the magnitude and field dependence. Recall that $\alpha_\mathbf{E}$ is frequency dependent and the agreement between theory and data improves at high frequencies since $\alpha_\mathbf{E}$ values are 15% higher at 10 kHz than at 1 kHz. The $\mathbf{H}$ dependence of $\alpha_\mathbf{E}$ essentially tracks the slope of λ vs $\mathbf{H}$. Once the magnetostriction attains the saturation value, the loss of pseudopiezomagnetic coupling leads to the absence of ME effects. It is clear from Fig. 7 that for the bilayer there is good agreement between low-field data and theory. However, it is necessary to explore the reason for the rapid drop in $\alpha_{\mathbf{E},31}$ at high fields. For the multilayer (i) the expected order of magnitude difference in $\alpha_{\mathbf{E},33}$ and $\alpha_{\mathbf{E},31}$ agrees with the data, (ii) the estimated $\mathbf{H}$ value corresponding to maximum in $\alpha_{\mathbf{E},31}$ is smaller than observed experimentally, and (iii) there is exceptionally good agreement between theory and data for the longitudinal coefficient $\alpha_{\mathbf{E},33}$.

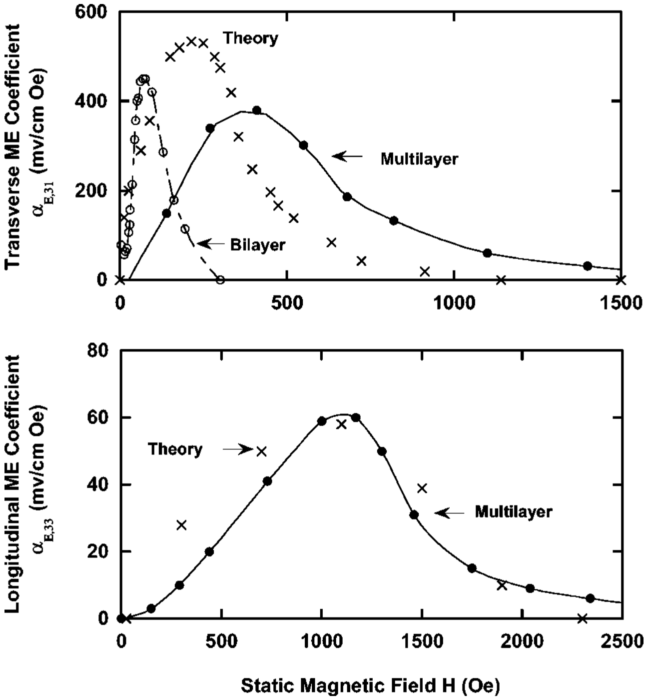

FIG. 7. Comparison of $\mathbf{H}$ dependence of theoretical ME coefficients estimated for a simple two-layer NFO-PZT structure with the data for the bilayer and multilayer composites in Figs. 2 and 3. The open (filled) circles are data points for the bilayer (multilayer). The crosses are the theoretical values estimated using Eqs. (2) and (3), $v_m/v_p=1$, material parameters given in the text, and the slope $d\lambda/d\mathbf{H}$ of magnetostriction λ vs $\mathbf{H}$ data in Fig. 1.

Theoretical values of the transverse ME coefficient are shown in Fig. 6 as a function of the volume of the constituentphases and there is good agreement with the data. Increase in the volume of the MS phase leads to an enhancement in the strain due to magnetostriction and an increase in the ME coefficient. Our recent theoretical modeling of the reciprocal effect, i.e., shift in the ferromagnetic resonance field of the MS phase due to piezoelectric effects in the PE-phase, indicates increasing resonance-field shift with increasing volume of the PE phase.[20] Thus, although the theory is based on a simple two-layer structure, it accounts very well for both the magnitude and volume and $\mathbf{H}$ dependence. It is worth noting that data in Figs. 6 and 7 are to our knowledge the first ever theoretical analysis of $\alpha_\mathbf{E}$ for composites.

Next we address an important question that arises from the study. What is the cause of giant ME effects in NFO-PZT? The large $\alpha_{\mathbf{E},31}$ is in part due to inherent advantages in ML geometry: efficient poling and the total absence of leakage currents. But other systems such as CFO-PZT also have the same advantages. In ferrites, domains are spontaneously deformed in the magnetization direction and the Joule magnetostriction is caused by domain-wall motion and domain rotation in the presence of **H**. Since ME effects involve dynamic magnetoelastic coupling, key requirements for the ferrite phase are unimpeded domain motion and a large λ. A soft, high initial permeability (low coercivity), and high-λ ferrite, such as NFO used here, is the main ingredient for strong ME effects. In magnetically hard cobalt ferrite, however, one has the disadvantage of a large coercive field that limits domain rotation. Since the ME effect originates at the interface, it is important to consider the influence of growth-induced stress and its effect on magnetic anisotropy and the dynamics of domain motion. The interface coupling is also influenced by a variety of other factors such as defects, inhomogeneities, and grain boundaries that pin the domain and limit wall motion and rotation. In the absence of detailed studies on NFO-PZT and other ferrite-PZT interfaces, we could only speculate on possible reasons for a unique and favorable interface bonding in the present system. Important factors that affect the interface properties during the high-temperature processing are the thermal-expansion coefficients (2 ppm for PZT vs 10 ppm for most ferrites), thermal conductivity (an order of magnitude higher in CFO compared to PZT or NFO) (Refs. 15 and 16), and the sintering temperature. Differential thermal expansion and thermal conductivity could result in built-in strain and interface microcracks. The sintering temperature of 1425–1500 K is much closer to the melting temperature of cobalt ferrite (1840 K) than NFO (2020 K) and it is quite likely that the highly reactive lead compound (PZT) could easily form both structural and chemical inhomogeneities at the interface with cobalt ferrite.[15] Studies show extensive microcracks and loss of Fe from the ferrite in bulk composites of CFO-BaTiO$_3$.[8,9] So it is reasonable to conclude that the giant ME effect in NFO-PZT is most likely due to an interface free of growth-induced stress or defects and a favorable domain dynamics. Investigations on the microscopic nature of the NFO-PZT interface with techniques such as high-resolution X-ray diffraction, electron microscopy, and magnetic-force microcopy are critically important for an understanding of the current observations.

V. CONCLUSION

Thick-film bilayers and multilayers of nickel ferrite–PZT prepared by tape casting techniques show the strongest magnetoelectric effects reported to date in any system. The effect is of the same strength in bilayers and multilayers for the same effective thickness of the constituent phases. A general increase in $\alpha_{\mathbf{E}}$ is observed with increasing volume of the magnetostrictive phase. A theoretical model that assumes ideal interface conditions accounts very well for the magnitude, and volume and field dependence of ME parameters and, therefore, implies a perfectly bonded defect-free interface. We anticipate considerable future activities related to the physics and chemistry of the NFO-PZT interface. The field-conversion efficiency for the composite is well within the range needed for practical applications.

ACKNOWLEDGMENT

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