

Influence of mechanical boundary conditions and microstructural features on magnetoelectric behavior in a three-phase multiferroic particulate composite

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We report theoretical calculations of the magnetoelectric properties in a three-phase multiferroic particulate composite of Terfenol-D, lead-zirconate-titanate (PZT), and polymer based on the Green's function technique. Our results show that the values of the magnetoelectric voltage coefficients are very sensitive to mechanical boundary conditions that the composite sample suffers, and that the polarization orientation in PZT particles and the inactive interface layer surrounding PZT particles have a significant effect on the magnetoelectric behavior of the composite. The calculations well describe the recent observations and provide a general guideline for experimentally achieving large ME response of such multiferroic composites.

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I. INTRODUCTION

Multiferroic composites combining ferroelectric and ferromagnetic substances have recently attracted much attention due to their multifunctionality and large magnetoelectric (ME) effect.¹ In particular, multiferroic composites containing a giant magnetostrictive rare-earth-iron alloy [e.g., $\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$ (Terfenol-D)] and a piezoelectric phase [e.g., lead-zirconate-titanate (PZT) or poly(vinylidene fluoride)-trifluoroethylene copolymer P(VDF-TrFE)] have been found to exhibit a giant magnetoelectric (GME) effect in theory² and subsequently in experiments.³⁻⁵ Among these reported ME materials, the laminated Terfenol-D/PZT composites show the highest ME response.^{3,5} However, the eddy current loss in bulk Terfenol-D is quite large at high frequency, which limits the applications of this laminated structure, and the GME response of the laminated composites is strongly influenced by the conductive epoxy binders used for gluing PZT and very brittle Terfenol-D thin disks together.⁶ In order to overcome these difficulties in Terfenol-D/PZT laminated composites, a three-phase composite of Terfenol-D, PZT, and a polymer has been developed.^{7,8} Such three-phase composites can be easily fabricated by a conventional low-temperature processing, and especially the three-phase particulate composites can be fabricated into a variety of forms such as thin sheets and molded shapes, and they exhibit improved mechanical properties.

In the three-phase multiferroic composites, the inactive polymer is just used as a binder, while PZT and Terfenol-D particles are embedded in the polymer matrix. The strain resulting from magnetostriction of Terfenol-D particles passes through the polymer matrix along to PZT particles, inducing the polarization. The effective magnetoelectric behavior of such three-phase particulate composites depends on

the composite microstructure. However, a theoretical description for the three-phase multiferroic composites is still lacking. In order to understand their ME behavior, in the present paper we present calculations of the effective ME properties of such three-phase composites based on the Green's function technique.²

II. MAGNETOELECTRIC EFFECT OF THREE-PHASE COMPOSITES

We denote such a three-phase particulate composite shown in Fig. 1 as f Terfenol-D/ $(1-f_m-f)$ PZT/ f_m polymer, where f and f_m are the volume fractions of Terfenol-D and polymer, respectively. As observed previously,⁷ the ME effect in the Terfenol-D/PZT/PVDF particulate composites is mainly limited by the concentration threshold of the Terfenol-D particles allowed in the composites due to the low resistance of Terfenol-D. Hence, here we consider the case of low f , e.g., $f < 0.1$. A low volume fraction of

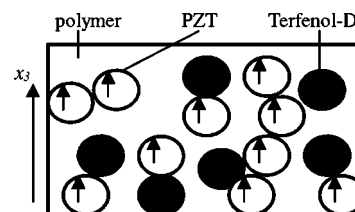


FIG. 1. Schematic representation of the particulate Terfenol-D/PZT/polymer composites. The black solid circles denote Terfenol-D particles and open circles denote PZT particles. All particles are randomly embedded in the polymer matrix. The polarization in PZT particles (denoted by the arrows within the open circles) is assumed to be parallel to the x_3 direction.

Terfenol-D particles is well dispersed in the PZT/polymer mixture matrix to keep the composite insulating. The Terfenol-D particles are assumed as randomly oriented crystallites as shown in Fig. 1, and are not in contact with each other while the PZT particles and the polymer are self-connected, thus forming a 0-3-3 connectivity of phases. After being poled along the x_3 axis, the three-phase particulate composite is transversely isotropic.

For the three-phase multiferroic composites, the constitutive equation for coupling mechanical-electric-magnetic response can be still written by direct notation for tensors as²

$$\begin{aligned}\sigma &= \mathbf{c}\varepsilon - \mathbf{e}^T \mathbf{E} - \mathbf{c}\varepsilon^{ms}, \\ \mathbf{D} &= \mathbf{e}\varepsilon + \kappa \mathbf{E} + \alpha \mathbf{H}, \\ \mathbf{B} &= \mu(\varepsilon, \mathbf{E}, \mathbf{H})\mathbf{H},\end{aligned}\quad (1)$$

where σ , ε , \mathbf{D} , \mathbf{E} , \mathbf{B} , and \mathbf{H} are the stress, strain, electric displacement, electric field, magnetic induction, and magnetic field, respectively; \mathbf{c} and κ are respectively the stiffness at constant fields and the dielectric constant at constant strain; the permeability μ strongly depends on ε and electric and magnetic fields; \mathbf{e} (\mathbf{e}^T being the transpose of \mathbf{e}) is the piezoelectric coefficient; α is the ME coefficient; and ε^{ms} is the magnetostrictively induced strain related with the magnetic field dependent magnetostriction constants (λ_{100} and λ_{111} ⁹) of Terfenol-D, and can be expressed as¹⁰

$$\varepsilon_{ij}^{ms} = \begin{cases} \frac{3}{2}\lambda_{100}\left(\beta_{3i}^2 - \frac{1}{3}\right), & \text{for } i=j, \\ \frac{3}{2}\beta_{3i}\beta_{3j}\lambda_{111}, & \text{for } i \neq j, \end{cases}\quad (2)$$

where (β_{ij}) is the matrix transforming the local crystallographic axes, x'_j , to the material axes, x_i , in which an external magnetic field $\langle H_3 \rangle$ is applied along x_3 axis of the materials specimen (Fig. 1), namely, $x_i = \beta_{ij}x'_j$.¹⁰ Thus ε_{ij}^{ms} is nonlinearly dependent on \mathbf{H} .

The effective properties of the composite can be defined in terms of the averaged fields (denoted by angular brackets $\langle \rangle$), namely,

$$\begin{aligned}\langle \sigma \rangle &= \mathbf{c}^* \langle \varepsilon \rangle - \mathbf{e}^{T*} \langle \mathbf{E} \rangle - \mathbf{c}^* \varepsilon^{ms*}, \\ \langle \mathbf{D} \rangle &= \mathbf{e}^* \langle \varepsilon \rangle + \kappa^* \langle \mathbf{E} \rangle + \alpha^* \langle \mathbf{H} \rangle, \\ \langle \mathbf{B} \rangle &= \mu^* \langle \langle \varepsilon \rangle, \langle \mathbf{E} \rangle, \langle \mathbf{H} \rangle \rangle \langle \mathbf{H} \rangle,\end{aligned}\quad (3)$$

where the quantities with asterisks represent those of the composite. The local fields within the composite can be obtained in terms of the Green's function technique as before,² i.e.,

$$\begin{aligned}\varepsilon &= \varepsilon^o + \mathbf{G}^u(\mathbf{c} - \mathbf{c}^o)\varepsilon - \mathbf{G}^u \mathbf{e}^T \mathbf{E} - \mathbf{G}^u \mathbf{c} \varepsilon^{ms}, \\ \mathbf{E} &= \mathbf{E}^o + \mathbf{G}^\phi \mathbf{e} \varepsilon + \mathbf{G}^\phi (\kappa - \kappa^o) \mathbf{E} + \mathbf{G}^\phi \alpha \mathbf{H},\end{aligned}$$

$$\mathbf{H} = \mathbf{H}^o + \mathbf{G}^\psi (\mu - \mu^o) \mathbf{H},\quad (4)$$

where the quantities with superscript o represent those of a homogeneous reference medium; \mathbf{G}^u , \mathbf{G}^ϕ , and \mathbf{G}^ψ are the modified displacement, electric and magnetic potential Green's functions for the homogeneous medium.^{2,10,11} Iterative solutions of Eq. (4) yield

$$\begin{aligned}\varepsilon &= \mathbf{T}^{66} \varepsilon^o - \mathbf{T}^{63} \mathbf{E}^o - \mathbf{T}^{66} \mathbf{G}^u \mathbf{c} \varepsilon^{ms} - \mathbf{T}^{63} \mathbf{G}^\phi \alpha \mathbf{T}^{33m} \mathbf{H}^o, \\ \mathbf{E} &= \mathbf{T}^{36} \varepsilon^o + \mathbf{T}^{33e} \mathbf{E}^o - \mathbf{T}^{36} \mathbf{G}^u \mathbf{c} \varepsilon^{ms} + \mathbf{T}^{33e} \mathbf{G}^\phi \alpha \mathbf{T}^{33m} \mathbf{H}^o, \\ \mathbf{H} &= \mathbf{T}^{33m} \mathbf{H}^o,\end{aligned}\quad (5)$$

with

$$\begin{aligned}\mathbf{T}^{66} &= \{\mathbf{I} - \mathbf{G}^u(\mathbf{c} - \mathbf{c}^o) + \mathbf{G}^u \mathbf{e}^T [\mathbf{I} - \mathbf{G}^\phi (\kappa - \kappa^o)]^{-1} \mathbf{G}^\phi \mathbf{e}\}^{-1}, \\ \mathbf{T}^{33e} &= \{\mathbf{I} - \mathbf{G}^\phi (\kappa - \kappa^o) + \mathbf{G}^\phi \mathbf{e} [\mathbf{I} - \mathbf{G}^u(\mathbf{c} - \mathbf{c}^o)]^{-1} \mathbf{G}^u \mathbf{e}^T\}^{-1}, \\ \mathbf{T}^{63} &= \mathbf{T}^{66} \mathbf{G}^u \mathbf{e}^T [\mathbf{I} - \mathbf{G}^\phi (\kappa - \kappa^o)]^{-1}, \\ \mathbf{T}^{36} &= \mathbf{T}^{33e} \mathbf{G}^\phi \mathbf{e} [\mathbf{I} - \mathbf{G}^u(\mathbf{c} - \mathbf{c}^o)]^{-1}, \\ \mathbf{T}^{33m} &= [\mathbf{I} - \mathbf{G}^\psi (\mu - \mu^o)]^{-1},\end{aligned}\quad (6)$$

where \mathbf{I} is the unit tensor. Substitution of Eq. (5) into (1) directly gives explicit solutions for the local σ , \mathbf{D} , and \mathbf{B} , also as a function of ε^o , \mathbf{E}^o , and \mathbf{H}^o . By averaging these solutions for the local field quantities and eliminating ε^o , \mathbf{E}^o , and \mathbf{H}^o from them, and further by considering that $\mathbf{e}(\mathbf{e}^T) = 0$ for the Terfenol-D and polymer phases, $\varepsilon^{ms} = 0$ for the PZT and polymer phases, and $\alpha = 0$ for these three phases, the general solutions to the effective properties of the composite can be derived as²

$$\mathbf{c}^* = \langle \mathbf{c} \mathbf{T}^{66} - \mathbf{e}^T \mathbf{T}^{36} \rangle \mathbf{A} + \langle \mathbf{c} \mathbf{T}^{63} + \mathbf{e}^T \mathbf{T}^{33e} \rangle \mathbf{B},\quad (7)$$

$$\mathbf{e}^{T*} = \langle (\mathbf{c} - \mathbf{c}^*) \mathbf{T}^{63} + \mathbf{e}^T \mathbf{T}^{33e} \rangle \langle \mathbf{T}^{33e} \rangle^{-1},\quad (8)$$

$$\kappa^* = \langle (\mathbf{e}^* - \mathbf{e}) \mathbf{T}^{63} + \kappa \mathbf{T}^{33e} \rangle \langle \mathbf{T}^{33e} \rangle^{-1},\quad (9)$$

$$\mu^* = \langle \mu \mathbf{T}^{33m} \rangle \langle \mathbf{T}^{33m} \rangle^{-1},\quad (10)$$

$$\varepsilon^{ms*} = (\mathbf{c}^*)^{-1} \langle [(\mathbf{c} - \mathbf{c}^*) \mathbf{T}^{66} \mathbf{G}^u + \mathbf{I}] \mathbf{c} \varepsilon^{ms} \rangle,\quad (11)$$

$$\alpha^* \langle \mathbf{H} \rangle = \mathbf{e}^* \langle \mathbf{T}^{66} \mathbf{G}^u \mathbf{c} \varepsilon^{ms} \rangle,\quad (12)$$

with $\mathbf{A} = [\langle \mathbf{T}^{66} \rangle + \langle \mathbf{T}^{63} \rangle \langle \mathbf{T}^{33e} \rangle^{-1} \langle \mathbf{T}^{36} \rangle]^{-1}$ and $\mathbf{B} = \langle \mathbf{T}^{33e} \rangle^{-1} \langle \mathbf{T}^{36} \rangle \mathbf{A}$. Because they are general and independent of the models assumed for the composite, these solutions are also applicable to the three-phase multiferroic composite. Here the angular brackets denote the microstructural averages, which mainly includes the common volume average directly related to the volume fractions and orientation average¹² over all possible orientations of the Terfenol-D and PZT particles in the composite.² Such an average of a local tensor \mathbf{X} is expressed as

$$\langle \mathbf{X} \rangle = f \langle \mathbf{X}(Ter) \rangle_{orientT} + f_m \mathbf{X}(Polymer) + (1 - f - f_m) \times \langle \mathbf{X}(PZT) \rangle_{orientP} \quad (13)$$

where the local quantities in $\mathbf{X}(Ter)$ are those for the Terfenol-D phase and $\langle \mathbf{X}(Ter) \rangle_{orientT}$ denotes averaging over all possible orientations of the Terfenol-D particles in the composite; the local quantities in $\mathbf{X}(Polymer)$ are those for the isotropic polymer; and the local quantities in $\mathbf{X}(PZT)$ are those for the PZT phase and $\langle \mathbf{X}(PZT) \rangle_{orientP}$ denotes averaging over all possible orientations of the PZT particles in the composite. For example, Eq. (12) can be rewritten as

$$\alpha^* \langle \mathbf{H} \rangle = f \mathbf{e}^* \langle \mathbf{T}^{66} \mathbf{G}^u \mathbf{c} \boldsymbol{\varepsilon}^{ms} \rangle_{orientT}, \quad (14)$$

since $\boldsymbol{\varepsilon}^{ms} = 0$ for the PZT and polymer phases. Here the local quantities on the right side of Eq. (14) are those for Terfenol-D in the composite frame of reference x_i , and are related to those corresponding to the individual Terfenol-D particles through the usual geometric transformations (β_{ij}). After performing the usual geometric transformations for these tensors via direction cosines (β_{ij}), these orientation averages can be obtained in the matrix notation easily suited for numerical computation.¹²

The macroscopically averaged magnetic field $\langle \mathbf{H} \rangle$ is related to the local magnetic field \mathbf{H} through¹⁰

$$\mathbf{H} = [(\mathbf{I} - \mathbf{G}^\psi(\mu - \mu^o))^{-1} [(\mathbf{I} - \mathbf{G}^\psi(\mu - \mu^o))^{-1}]^{-1} \langle \mathbf{H} \rangle]. \quad (15)$$

This equation also gives the relation between the macroscopically applied magnetic field $\langle \mathbf{H} \rangle$ and the local magnetic field \mathbf{H} within the Terfenol-D phase.

On applying an external magnetic field $\langle H_3 \rangle$ along the symmetric x_3 axis of the poled composite sample (Fig. 1), a ME output voltage $\langle E_3 \rangle$ across the sample can be produced in the x_3 direction. Thus the ME voltage coefficient along this direction can be defined as

$$\alpha_{E33} = \langle E_3 \rangle / \langle H_3 \rangle, \quad (16)$$

which is the figure of merit used to assess the performance of a ME material for a magnetic device. Under the open circuit measurement condition, $\langle \mathbf{D} \rangle = 0$. Furthermore, we consider two different mechanical boundary conditions. The first one is a completely mechanically clamped boundary condition, i.e., $\langle \boldsymbol{\varepsilon} \rangle = 0$. In this case, we obtain the ME output voltage from Eq. (3) as

$$\langle \mathbf{E} \rangle = -\boldsymbol{\kappa}^{*-1} \alpha^* \langle \mathbf{H} \rangle = \alpha_E^{true} \langle \mathbf{H} \rangle, \quad (17)$$

$$\alpha_{E33}^{true} = \langle E_3 \rangle / \langle H_3 \rangle = -\alpha_{33}^* / \kappa_{33}^*. \quad (18)$$

This is the primary (“true”) ME effect, and α_{E33}^{true} is the primary ME voltage coefficient.

To the other extreme, there is a mechanical free boundary condition, i.e., $\langle \boldsymbol{\sigma} \rangle = 0$. In this case the ME output voltage can be expressed from Eq. (3) as

$$\langle \mathbf{E} \rangle^{free} = -[\boldsymbol{\kappa}^* + \mathbf{e}^* \mathbf{c}^{*-1} \mathbf{e}^{T*}]^{-1} (\alpha^* \langle \mathbf{H} \rangle + \mathbf{e}^* \boldsymbol{\varepsilon}^{ms*}), \quad (19)$$

TABLE I. Properties of PZT, Terfenol-D, and polymer taken in the present numerical calculations.

Properties	Terfenol-D ^a	PZT-5A	Polymer
c_{11} (GPa)	82	121	4.84
c_{12} (GPa)	40	75.4	2.72
c_{13} (GPa)	40	75.2	2.72
c_{33} (GPa)	82	111	4.84
c_{44} (GPa)	38	21.1	1.06
$\varepsilon_{33}/\varepsilon_o$		830	8
μ_{33}/μ_o	5	1	1
e_{31} (C/m ²)	0	-5.4	0
e_{33} (C/m ²)	0	15.8	0
e_{15} (C/m ²)	0	12.3	0
λ_{111} (ppm)	1700	0	0
λ_{100} (ppm)	100	0	0

^aTerfenol-D exhibits a cubic symmetry, and its properties are taken by referring to Refs. 2 and 9. Its $\mu_{33}/\mu_o = 5$ at zero magnetic field and decreases about linearly with increasing the magnetic field to 1.8 in the saturation; the magnetic field dependences of λ_{111} and λ_{100} are shown in Fig. 3(c).

$$\alpha_{E33}^{free} = \langle E_3 \rangle^{free} / \langle H_3 \rangle. \quad (20)$$

The first term on the right side of Eq. (19) corresponds to the primary ME response, and the second term is the secondary ME response measuring the additional ME response produced by the magnetostrictive strain of the composite ($\boldsymbol{\varepsilon}^{ms*}$) through the piezoelectric effect of the composite (\mathbf{e}^*). α_{E33}^{free} is the ME voltage coefficient under completely mechanical free boundary condition. Obviously, the ME response of the multiferroic composites is quite sensitive to what boundary condition the composite samples are suffering.

However, the composite samples are often tested under the condition that the boundary is partly free. The samples are normally not completely clamped or completely free, but between these two boundary conditions. For example, we nearly clamp a composite sample in the x_3 direction (i.e., measurement direction), but let the transverse direction be free in actual measurement. The experimentally measured ME response is within the bounds limited by α_{E33}^{true} and α_{E33}^{free} .

For quantitative purpose, next we perform numerical calculations on the Terfenol-D/PZT/polymer composites. The properties of each phase used for calculations are listed in Table I. The ME properties of the three-phase particulate composites are calculated by a generalized self-consistent effective medium approximation as before,² i.e., the three constituent phases are considered to be embedded in an effective medium that corresponds to the overall composite itself but with the moduli that must be determined self-consistently, which means $\mathbf{c}^o = \mathbf{c}^*$, $\boldsymbol{\kappa}^o = \boldsymbol{\kappa}^*$, and $\boldsymbol{\mu}^o = \boldsymbol{\mu}^*$. Phenomenologically, this approximation corresponds to the Bruggeman–Landauer self-consistent approximation for the transport problem or the Hill–Budiansky self-consistent approximation for the elastic problem. The good quantitative agreement of previous results of the Green’s function based theory and

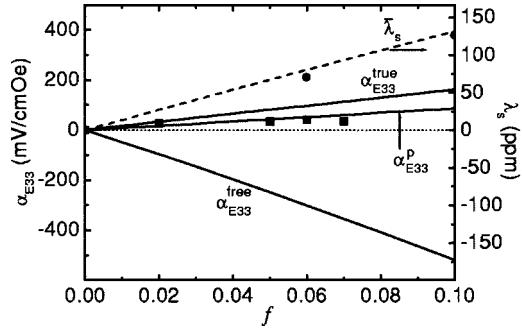


FIG. 2. Calculated ME coefficients (α_{E33}^{true} , α_{E33}^{free} , and α_{E33}^p) and engineering magnetostriction $\bar{\lambda}_s$ at high field saturation for the f Terfenol-D/(0.7- f)PZT/0.3 polymer composites. For comparison, the measured α_{E33} (solid squares) and $\bar{\lambda}_s$ (solid circles) are also shown.⁷

experiment for piezoelectric and magnetostrictive composites^{10,11} has demonstrated the predictive power of the theoretical approach. In order to perform numerical calculations, we adopt an iterative scheme. \mathbf{c}^* , \mathbf{e}^* , and κ^* are calculated from Eqs. (7)–(9).^{10,11} A value for $\langle H_3 \rangle$ is selected from which the value of H_3 in the Terfenol-D phase is calculated using Eqs. (10) and (15).¹⁰ These values are then used to determine ε^{ms*} from Eq. (11)¹⁰ and α^* from Eq. (12).² With these values, the ME voltage coefficients under different mechanical boundary conditions can be finally obtained.

III. NUMERICAL RESULTS AND DISCUSSION

For convenience, the volume fraction of the polymer f_m is fixed as $f_m=0.3$ as in the previous experiment,⁷ so the composite can be denoted as f Terfenol-D/(0.7- f)PZT/0.3 polymer. In the Terfenol-D/PZT/PVDF particulate composites, Terfenol-D particles are randomly oriented, and the polarization in the PZT particles are assumed to be perfectly parallel to the sample x_3 axis after poled. In this case, the orientation average is only taken for randomly oriented Terfenol-D particles [see, for example, Eq. (14)].¹³

As shown in Fig. 2, in the low volume fraction range of $f < 0.1$, the values of the ME voltage coefficients α_{E33} and engineering magnetostriction² $\bar{\lambda}_s$ at high-magnetic-field saturation increase approximately linearly with increasing f , i.e., $\alpha_{E33}^{true} \propto f$, $\alpha_{E33}^{free} \propto f$, and $\bar{\lambda}_s \propto f$. Comparison in Fig. 2 shows that there is a good agreement between the experimental and calculated $\bar{\lambda}_s$; however, there are large discrepancies between the values of α_{E33}^{true} , α_{E33}^{free} , and measured α_{E33} , especially between α_{E33}^{free} and measured α_{E33} . The absolute value of α_{E33}^{free} is about three times larger than that of α_{E33}^{true} . As discussed above, α_{E33}^{true} and α_{E33}^{free} give a pair of bounds for any other cases. The values of the measured ME voltage coefficient fall between the values of α_{E33}^{true} and α_{E33}^{free} , and are closer to the values of α_{E33}^{true} . For illustration, we also calculate the ME coefficient (see α_{E33}^p in Fig. 2) of the composite under the following boundary condition, i.e., completely mechanically clamped in the x_3 direction but free in the transverse direction. This boundary condition is more similar to the actual

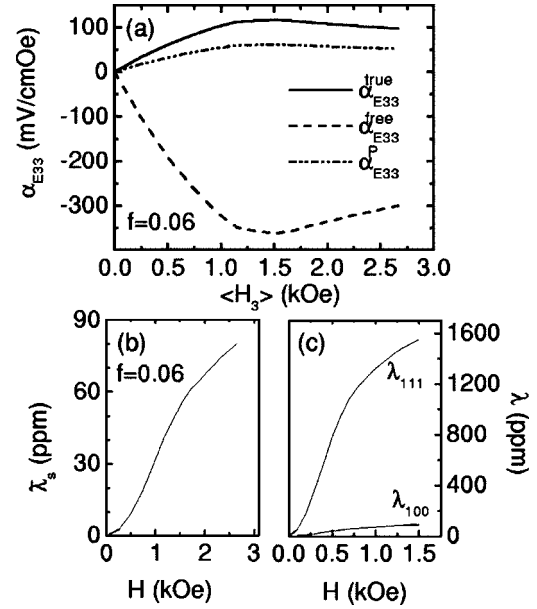


FIG. 3. (a) The calculated ME coefficients of the f Terfenol-D/(0.7- f)PZT/0.3 polymer composite with $f=0.06$ as a function of the applied magnetic field. (b) The calculated magnetostriction $\bar{\lambda}_s$ for this composite. (c) The magnetic-field-dependent magnetostriction constants^{2,9} (λ_{100} and λ_{111}) used for the present numerical calculations.

measurement condition in experiment,⁷ where the sample is mechanically clamped between the sample holder (along the x_3 direction) but free deformed in the transverse direction.⁷ Obviously, the α_{E33}^p values are in quite good agreement with the values of the measured ME coefficient.

Figure 3 shows nonlinear dependence of the ME response [Fig. 3(a)] and magnetostriction [Fig. 3(b)] of the composite on the magnetic field, calculated by using field-dependent λ_{100} and λ_{111} for Terfenol-D [Fig. 3(c)]. The ME sensitivity of the composite increases with increasing $\langle H_3 \rangle$ due to increasing magnetostriction, after reaching a maximum value, and then decreases at high magnetic field saturation. For the composite with $f=0.06$, the maximum α_{E33}^{true} , α_{E33}^p , and α_{E33}^{free} values are 117, 62, and -362 mV/cm Oe, respectively. Thus such three-phase particulate composites are expected to have a remarkable ME response for technological applications.

As shown in Fig. 3, the magnetic-field dependence of the ME response of the multiferroic composites is dominated by Terfenol-D. For further illustration, we consider two different magnetostrictive behaviors of Terfenol-D used in the composite, as shown in Fig. 4(b), i.e., (1) one with low saturation field and (2) another with high saturation field. The calculations show totally different ME responses for these two cases [Fig. 4(a)]. For the multiferroic composites containing Terfenol-D with low saturation field, their ME response reaches a maximum value at low field and then decreases at high field saturation. For the composites containing Terfenol-D with high saturation field, the ME response gradually increases with the field. Terfenol-D with large saturation magnetostriction in low magnetic field range is quite desirable for achieving high ME response of the composites.

In the calculations above, the polarization in each PZT particle is assumed to be perfectly oriented along the x_3 di-

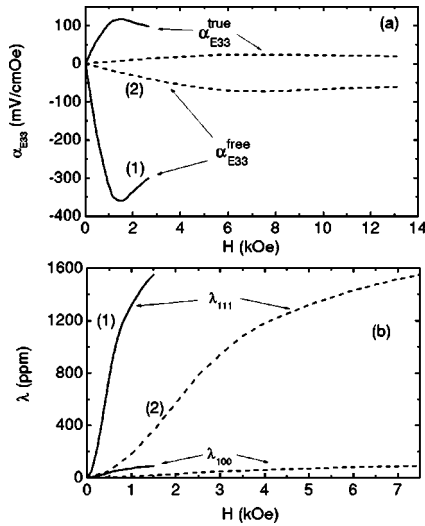


FIG. 4. (a) The ME coefficients (α_{E33}^{true} and α_{E33}^{free}) calculated for the f Terfenol-D/(0.7- f)PZT/0.3 polymer composite with $f=0.06$ containing two different magnetostrictive properties of Terfenol-D as shown in (b).

rection (Fig. 1). However, in practice, PZT particles in the particulate composites might not be easily completely polarized, since the electric field distributed on PZT particles is less than the applied electric field.¹⁴ In order to evaluate the effect of the orientations of the polarization in PZT particles, we assume that the local polarization orientations in PZT particles are uniformly distributed between $\theta=0$ and θ_{cutoff} with respect to the sample x_3 axis as shown in Fig. 5(a). $\theta_{cutoff}=0$ corresponds to the case in Fig. 1, and at $\theta_{cutoff}=180^\circ$, the polarization orientations in PZT particles are random. In this case, the orientation average over the PZT phase also needs to be taken.^{15,16} The calculations [Fig.

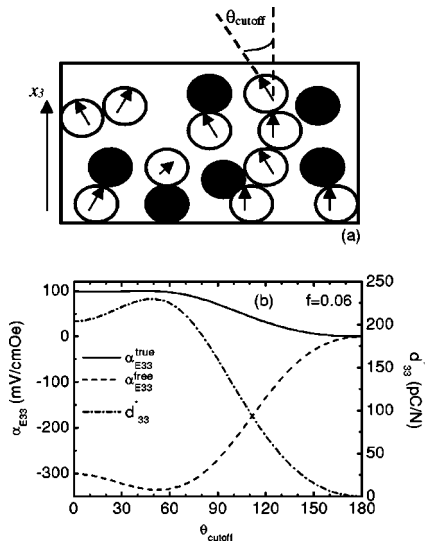


FIG. 5. (a) Orientations of the polarization (denoted by the arrows within the open circles) in the PZT particles are assumed to distribute uniformly with a cutoff angle θ_{cutoff} about the x_3 axis. (b) Effect of the cutoff angle on the ME coefficients and the effective piezoelectric constant d_{33}^* of the composites.

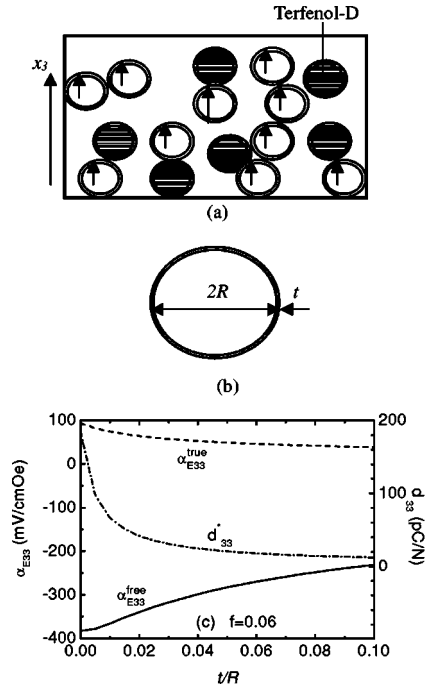


FIG. 6. Schematic representation of (a) the interface layer surrounding the particles in the composites and (b) a single particle of R in radius coated with an interface layer of t in thickness. (c) The calculated ME coefficients and piezoelectric constant d_{33}^* of the composites as a function of the relative ratio t/R .

5(b)] show that the dependence of α_{E33}^{true} and α_{E33}^{free} on θ_{cutoff} is quite similar to that of the effective piezoelectric coefficient d_{33}^* . d_{33}^* slightly increases with θ_{cutoff} as θ_{cutoff} is less than 60° but quickly decreases as $\theta_{cutoff} > 60^\circ$,¹⁵ and so do α_{E33}^{true} and α_{E33}^{free} . When $\theta_{cutoff}=180^\circ$, entirely random orientations of the polarization in PZT particles result in the disappearance of piezoelectricity in the composites, thereby the disappearance of the extrinsic ME effect, i.e., $\alpha_{E33}=0$.

The interface in the multiferroic composites is another important feature which has an effect on the ME response of the composites, and the existence of an inactive interface layer would alter the ME behavior of composites. In order to evaluate the interface effect, we consider the particles in the composites to be surrounded by a thin interfacial layer, as shown in Fig. 6(a). For convenience, we take the elastic parameters of the electrically/magnetically inactive interface layer to be equal to those of the polymer matrix. Terfenol-D particles are randomly oriented, and the polarizations in the PZT particles are assumed to be perfectly parallel to the sample x_3 axis again. Our numerical results (not present here) show that the ME voltage coefficient of the composites is only slightly influenced by the thin interface layer surrounding the Terfenol-D particles, since the thin interface layer with the same elastic constants as the polymer matrix has only a slight effect on the effective magnetostriction of the composites. However, the piezoelectric effect is strongly influenced by the interface layer surrounding the PZT particles. The effective piezoelectric coefficient d_{33}^* of the composites rapidly drops first with increasing t/R [see Fig. 6(b)], and then slowly decreases [Fig. 6(c)]. Accordingly, the ME coefficients of the multiferroic composites are also sensitive

to t/R due to the large degradation of the piezoelectric effect of the composites.

IV. CONCLUSIONS

Using the successful Green's function technique, we have calculated the effective properties of three-phase multiferroic particulate composites of Terfenol-D/PZT/polymer. The results show that the ME response of the composites strongly depends on the mechanical boundary conditions on the composites, and the calculated ME coefficients α_{E33}^{true} and α_{E33}^{free} under two extreme cases, i.e., completely mechanically clamped or free, set a pair of bounds for those under any other cases. The calculated results are in good agreement with the observed. The dependence of the ME coefficients on the applied field is mainly dominated by the magnetostrictive behavior of the ferromagnetic constituent, and a large ME

response can be achieved with a ferromagnetic substance with high saturation magnetostriction and low saturation field. The calculations also illustrate that the polarization orientation in PZT particles and the inactive interface between PZT particles and matrix polymer have a significant effect on the effective behavior of the multiferroic composites. The three-phase particulate composites are promising ME materials because of their easy fabrication, low eddy current loss and large ME response.

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¹²For example, the orientation average of a four-rank tensor X_{ijkl} for the transversely isotropic composite is expressed as $\langle X_{ijkl} \rangle_{orient} = \int \sum_{m,n,p,q=1}^3 \beta_{im} \beta_{jn} \beta_{kp} \beta_{lq} X'_{mnpq} F(\theta) \sin \theta d\theta / \int F(\theta) \sin \theta d\theta$, where $F(\theta)$ is a distribution function describing the variation in the Euler angle θ of the local x'_3 axis with respect to the sample x_3 axis, and X'_{mnpq} are the corresponding quantities in the individual particles.

¹³In this case, Eq. (13) becomes $\langle \mathbf{X} \rangle = f \langle \mathbf{X}(Ter) \rangle_{orientT} + f_m \mathbf{X}(Polymer) + (1-f-f_m) \mathbf{X}(PZT)$, and the integration over θ is from 0 to π with $F(\theta)=1$.

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