Magnetoelectric effect in composites of piezoelectric and piezomagnetic phases

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The magnetoelectric effect in composites of piezoelectric and piezomagnetic phases is investigated theoretically. The magnetoelectric effect is totally absent in these two constituent phases, and so it is a new property of the composites. A generalized theoretical framework based on a Green's function method and perturbation theory is proposed to treat the coupled magnetoelectric behavior in the composites. Explicit relations for determining the effective magnetoelectric effect in the composites are derived, and the different approximate expressions for the magnetoelectric coefficient of the fibrous composites with 1-3 or 3-1 connectivity of phases are given. To illustrate the technique, numerical calculations of the magnetoelectric coefficients of the $BaTiO_3$-$CoFe_2O_4$ composites for various phase compositions and particle shapes are performed. The theoretical estimates are shown to be in agreement with available experimental results, and also show the interesting magnetoelectric behavior of the composites.

I. INTRODUCTION

The magnetoelectric effect is a coupled (or cross) two-field effect, in which the application of either a magnetic field or an electrical field induces an electrical polarization as well as a magnetization. Like other coupled-response effects in composites (e.g., the piezoelectric effect and pyroelectric effect in piezocomposites), the magnetoelectric effect in composites has recently attracted much attention owing to the significant interest in use of the magnetoelectric composites for broadband magnetic field probes which exhibit large magnetoelectric effects and an exceptionally flat frequency response.[1-3] Magnetoelectric composites with a surprisingly large magnetoelectric effect have been made from ferroelectric phases (e.g., $BaTiO_3$) and ferromagnetic phases (e.g., $CoFe_2O_4$).[2-5] When a magnetic field is applied to a composite of the piezoelectric perovskite and the spinel-structure phases, the ferrite particles change their shape because of magnetostriction, and the strain is passed along to the piezoelectric particles, resulting in an electrical polarization. The magnetoelectric effect obtained in this way can reach a hundred times larger than that in the single-phase magnetoelectric material Co_2O_3.

This magnetoelectric property of the ferroelectric-ferromagnetic composite is known as a product property of the composite,[6] and results from the interaction between different properties of the two phases in composites. Neither ferroelectric phase nor ferromagnetic phase has the magnetoelectric effect, but composites of these two phases have a remarkable magnetoelectric effect. Thus the magnetoelectric effect is a product of the piezomagnetic effect (magnetic-mechanical effect) in the ferromagnetic phase and the piezoelectric effect (mechanical-electrical effect) in the ferroelectric phase, namely,

$$\text{Magnetoelectric effect} = \frac{\text{magnetic}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{electrical}}$$

or

$$\text{Magnetoelectric effect} = \frac{\text{electrical}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}} ,$$

and is a coupled electrical and magnetic phenomenon by elastic interaction. Similarly, a coupled magnetoelectric effect can also be obtained by thermal interaction in a pyroelectric-pyromagnetic composite.

In spite of efforts in the development of magnetoelectric composites, the theoretical understanding of these materials is quite limited. As with most composites, studies on magnetoelectric composites are also concerned with the estimation of their effective properties in terms of details of their microstructures, i.e., phase properties, volume fraction, shape, connectivity. etc. A theoretical treatment is very necessary in order to design new magnetoelectric composites for applications. Recently, Milgrom and Shtrikman[7] gave a compatibility condition between the effective magnetoelectric coefficient and the dielectric and magnetic permeabilities for isotropic magnetoelectric composites of two magnetoelectric phases. Their technique is not suitable for ferroelectric-ferromagnetic composites because of the mechanical interaction of the problem and the nonmagnetoelectric effect in the two phases. More recently, Harshe, Dougherty, and Newnham[3] treated such a magnetoelectric effect of piezoelectric-piezomagnetic composites in terms of a simple approach. They assumed a relatively simple geometrical model, a cubes model, in which the so-called 0-3 or 3-0 composite with particles of one phase (denoted by 0) embedded in the matrix of the second phase (denoted by 3) was considered as consisting of small cubes, and then solved the fields in one cube for which the boundary-value problem involved is tractable. This simple cubes model is an elementary series-parallel-like model, and is lacking in theoretical rigor.

In this paper, a more rigorous treatment of the magnetoelectric behavior of piezoelectric-piezomagnetic composites will be performed in terms of a similar but somewhat different approach to the Green's function method and perturbation theory which have been widely em-

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ployed to treat the general linear-response properties of inhomogeneous media (see, for example, the recent review[8]). A theoretical approach has been developed recently to determine the coupled electroelastic behavior of piezoelectric composites and the coupled thermal-electrical-mechanical behavior of piezoelectric and pyroelectric composites by Nan and co-workers[9,10] In this paper, I will extend the theoretical method[9,10] to address the coupled magnetoelectric effect of piezoelectric-piezomagnetic composites.

Section II contains the theoretical framework derived by the Green's function method and the general solution to the effective coupled magnetoelectric coefficient of the composites. As a practical example, we consider specifically the case of aligned cylindrical fibers exhibiting transverse isotropic piezoelectricity (or piezomagnetism) embedded in a piezomagnetic (or piezoelectric) matrix with such transverse symmetry, which are the technologically important composites with 1-3 or 3-1 connectivity of phases. Two approximate solutions, namely, the so-called non-self-consistency and self-consistency effective-medium approximations, for the effective magnetoelectric coefficients of such 1-3 or 3-1 composites are given in Sec. III. The numerical results for the effective magnetoelectric properties of $BaTiO_3$-$CoFeO_4$ composites are presented and discussed in Sec. IV. The conclusions are summarized in Sec. V.

II. FORMALISM

Consider a perfectly bonded piezoelectric and piezomagnetic composite. For the piezoelectric phase in the composite, its *e*-type constitutive relations to describe the coupled interaction between electrical and elastic variables are

$$\begin{aligned} \sigma &= \mathbf{C}\mathbf{s} - \mathbf{e}^T\mathbf{E} \, , \\ \mathbf{D} &= \mathbf{e}\mathbf{s} + \varepsilon\mathbf{E} \, . \end{aligned} \tag{1}$$

For the piezomagnetic phase in the composite, its constitutive equations to describe the coupled mechanical-magnetic behavior are

$$\begin{aligned} \sigma &= \mathbf{C}\mathbf{s} - \mathbf{q}^T\mathbf{H} \, , \\ \mathbf{B} &= \mathbf{q}\mathbf{s} + \mu\mathbf{H} \, . \end{aligned} \tag{2}$$

Here σ, $\mathbf{s}$, $\mathbf{D}$, $\mathbf{E}$, $\mathbf{B}$, and $\mathbf{H}$, are the stress tensor, strain tensor, electrical displacement, electrical field intensity, magnetic induction (or flux density), and magnetic field intensity, respectively. $\mathbf{C}$, ε, and μ are the stiffness tensor (measured at a constant electrical and magnetic field) and dielectric and magnetic permeability tensors (measured at a constant strain), respectively. $\mathbf{e}$ and $\mathbf{q}$ are the piezoelectric and piezomagnetic coefficient tensors, respectively. $\mathbf{e}^T$ and $\mathbf{q}^T$ are the transposes of $\mathbf{e}$ and $\mathbf{q}$, respectively.

For a piezoelectric-piezomagnetic composite, because of the coupled interaction between the two phases, the constitutive relations to describe its coupled-response behavior turn into coupled magnetic-electrical-mechanical equations, namely,

$$\begin{aligned} \sigma &= \mathbf{C}\mathbf{s} - \mathbf{e}^T\mathbf{E} - \mathbf{q}^T\mathbf{H} \, , \\ \mathbf{D} &= \mathbf{e}\mathbf{s} + \varepsilon\mathbf{E} + \alpha\mathbf{H} \, , \\ \mathbf{B} &= \mathbf{q}\mathbf{s} + \alpha^T\mathbf{E} + \mu\mathbf{H} \, , \end{aligned} \tag{3}$$

where α is the magnetoelectric coefficient tensor and α^T is the transpose of α. The magnetoelectric property α is a new property of the composite, since it is entirely absent in the two phases making up the composite. Of these constitutive coefficient tensors, $\mathbf{C}$ is a fourth-rank tensor; $\mathbf{e}$ ($\mathbf{e}^T$) and $\mathbf{q}$ ($\mathbf{q}^T$) are three-rank tensors; and ε, μ, and α (α^T) are second-rank tensors. For simplicity of notation, we have used the direct notation for tensors, and dropped the often used superscripts $\mathbf{E}$, $\mathbf{H}$, and $\mathbf{s}$ on the constitutive coefficient tensors which are used to denote the constant-electrical-field, constant-magnetic-field, and constant-strain conditions. The tensors $\mathbf{C}$, $\mathbf{e}$, $\mathbf{q}$, ε, μ, and α are (6×6), (3×6), (3×6), (3×3), (3×3), and (3×3) matrices, respectively, by means of the compressive representation.

With the shorthand notation, Eq. (3) can be rewritten as

$$\begin{bmatrix} \sigma \\ \mathbf{D} \\ \mathbf{B} \end{bmatrix} = \begin{bmatrix} \mathbf{C} & -\mathbf{e}^T & -\mathbf{q}^T \\ \mathbf{e} & \varepsilon & \alpha \\ \mathbf{q} & \alpha^T & \mu \end{bmatrix} \begin{bmatrix} \mathbf{s} \\ \mathbf{E} \\ \mathbf{H} \end{bmatrix} . \tag{4}$$

The matrix of these constitutive coefficient tensors is a 12×12 matrix. This matrix formulation is to be interpreted simply as multiplication of matrices and will greatly simplify the resulting equations. For the composite, these quantities are local values depending on the spatial position $\mathbf{x}$. The effective constitute coefficient tensors of the piezoelectric-piezomagnetic composite are defined in terms of averaged fields, namely,

$$\begin{bmatrix} \langle \sigma \rangle \\ \langle \mathbf{D} \rangle \\ \langle \mathbf{B} \rangle \end{bmatrix} = \begin{bmatrix} \mathbf{C}^* & -\mathbf{e}^{T*} & -\mathbf{q}^{T*} \\ \mathbf{e}^* & \varepsilon^* & \alpha^* \\ \mathbf{q}^* & \alpha^{T*} & \mu^* \end{bmatrix} \begin{bmatrix} \langle \mathbf{s} \rangle \\ \langle \mathbf{E} \rangle \\ \langle \mathbf{H} \rangle \end{bmatrix} . \tag{5}$$

Therefore the problem essentially consists of the determination of the strain and electrical and magnetic fields in the composite under certain specified boundary conditions and then the performance of the averages.

The local principal constitutive coefficients $\mathbf{X}$, ($\mathbf{C}$, ε, and μ) can be written as

$$\mathbf{X} = \mathbf{X}^0 + \mathbf{X}' \, , \tag{6}$$

where the first term is the constitutive coefficient of a homogeneous comparison medium and the second term is the fluctuation on the first. Let the composite now be subjected on its external surface S to a homogeneous magnetic-electrical-mechanical boundary condition i.e.,

$$\begin{aligned} & u_i(S) = s_{ij}^0 x_j = u_i^0 , \quad \phi(S) = -E_i^0 x_i = \phi^0 \, , \\ & v(S) = -H_i^0 x_i = v^0 \, , \end{aligned}$$

where u_i, ϕ, and v denote elastic displacement, electrical potential, and magnetic potential, respectively. Consider a state of static equilibrium in the absence of body forces and free electrical charges so that

$$\begin{bmatrix} \sigma_{ij,j} \\ D_{i,i} \\ B_{i,i} \end{bmatrix} = 0 , \tag{7}$$

where the comma denotes partial differentiation. These are coupling equilibrium equations.

Substitution of Eqs. (4) and (6) into (7) yields

$$C^0_{ijkl} s_{kl,j} + (C'_{ijkl} s_{kl} - e_{nij} E_n - q_{nij} H_n)_{,j} = 0 , \tag{8a}$$

$$\varepsilon^0_{in} E_{n,i} + (e_{ijn} s_{jn} + \varepsilon'_{in} E_n + \alpha_{in} H_n)_{,i} = 0 , \tag{8b}$$

$$\mu^0_{in} H_{n,i} + (q_{ijn} s_{jn} + \alpha_{in} E_n + \mu'_{in} H_n)_{,i} = 0 . \tag{8c}$$

In terms of the elastic displacement u_k, electrical potential ϕ, and magnetic potential v, Eqs. (8) appear to be

$$C^0_{ijkl} u_{k,ij} + (C'_{ijkl} s_{kl} - e_{nij} E_n - q_{nij} H_n)_{i,j} = 0 , \tag{9a}$$

$$\varepsilon^0_{in} \phi_{,in} + (e_{ijn} s_{jn} + \varepsilon'_{in} E_n + \alpha_{in} H_n)_{,i} = 0 . \tag{9b}$$

$$\mu^0_{in} v_{,in} + (q_{ijn} s_{jn} + \alpha_{in} E_n + \mu'_{in} H_n)_{,i} = 0 . \tag{9c}$$

The solutions for $u_k(\mathbf{x})$, $\phi(\mathbf{x})$, and $v(\mathbf{x})$ can be obtained as

$$u_k(\mathbf{x}) = u^0_k + \int g^u_{ki}(\mathbf{x},\mathbf{x}') F_i(\mathbf{x}') d\mathbf{x}' , \tag{10a}$$

$$\phi(\mathbf{x}) = \phi^0 + \int g^\phi(\mathbf{x},\mathbf{x}') Y(\mathbf{x}') d\mathbf{x}' , \tag{10b}$$

$$v(\mathbf{x}) = v^0 + \int g^v(\mathbf{x},\mathbf{x}') Z(\mathbf{x}') d\mathbf{x}' , \tag{10c}$$

where F_i, Y, and Z represent the second terms in the left-hand sides of Eqs. (9a), (9b), and (9c), respectively. u^0_k, ϕ^0, and v^0 are the homogeneous solutions of Eqs. (9a), (9b), and (9c) under the given surface elastic displacement, surface electrical potential, and magnetic potential, depending only on $\mathbf{C}^0$, ε^0, and μ^0, respectively. $g^u_{ki}(\mathbf{x},\mathbf{x}')$, $g^\phi(\mathbf{x},\mathbf{x}')$, and $g^v(\mathbf{x},\mathbf{x}')$ are the elastic displacement, electrical potential, and magnetic potential Green's functions for the homogeneous comparison medium $(\mathbf{C}^0,\varepsilon^0,\boldsymbol{\mu}^0)$.[11] The solutions of the local fields within the composite can be obtained by differentiating (10) and then integrating by parts:

$$\mathbf{s}(\mathbf{x}) = \mathbf{s}^0 + \int \mathbf{G}^u(\mathbf{x},\mathbf{x}')[\mathbf{C}'(\mathbf{x}')\mathbf{s}(\mathbf{x}') - \mathbf{e}^T(\mathbf{x}')\mathbf{E}(\mathbf{x}') - \mathbf{q}^T(\mathbf{x}')\mathbf{H}(\mathbf{x}')] d\mathbf{x}' , \tag{11a}$$

$$\mathbf{E}(\mathbf{x}) = \mathbf{E}^0 + \int \mathbf{G}^\phi(\mathbf{x},\mathbf{x}')[\mathbf{e}(\mathbf{x}')\mathbf{s}(\mathbf{x}') + \varepsilon'(\mathbf{x}')\mathbf{E}(\mathbf{x}') + \boldsymbol{\alpha}(\mathbf{x}')\mathbf{H}(\mathbf{x}')] d\mathbf{x}' , \tag{11b}$$

$$\mathbf{H}(\mathbf{x}) = \mathbf{H}^0 + \int \mathbf{G}^v(\mathbf{x},\mathbf{x}')[\mathbf{q}(\mathbf{x}')\mathbf{s}(\mathbf{x}') + \boldsymbol{\alpha}^T(\mathbf{x}')\mathbf{E}(\mathbf{x}') + \boldsymbol{\mu}'(\mathbf{x}')\mathbf{H}(\mathbf{x}')] d\mathbf{x}' . \tag{11c}$$

These equations can be expressed in the operator form

$$\begin{bmatrix} \mathbf{s} \\ \mathbf{E} \\ \mathbf{H} \end{bmatrix} = \begin{bmatrix} \mathbf{s}^0 \\ \mathbf{E}^0 \\ \mathbf{H}^0 \end{bmatrix} + \begin{bmatrix} \mathbf{G}^u & 0 & 0 \\ 0 & \mathbf{G}^\phi & 0 \\ 0 & 0 & \mathbf{G}^V \end{bmatrix} \times \begin{bmatrix} \mathbf{C}' & -\mathbf{e}^T & -\mathbf{q}^T \\ \mathbf{e} & \varepsilon' & \boldsymbol{\alpha} \\ \mathbf{q} & \boldsymbol{\alpha}^T & \boldsymbol{\mu}' \end{bmatrix} \begin{bmatrix} \mathbf{s} \\ \mathbf{E} \\ \mathbf{H} \end{bmatrix} , \tag{12}$$

where $\mathbf{G}^u$, $\mathbf{G}^\phi$, and $\mathbf{G}^v$ are the modified elastic displacement, electrical potential, and magnetic potential Green's functions for the homogeneous comparison medium $(\mathbf{C}^0,\varepsilon^0,\boldsymbol{\mu}^0)$, respectively,[11] and $(\mathbf{s}^0,\mathbf{E}^0,\mathbf{H}^0)$ are the homogeneous fields in the homogeneous medium.

We iterate Eq. (12) and obtain an explicit solution for the local fields as

$$\begin{bmatrix} \mathbf{s} \\ \mathbf{E} \\ \mathbf{H} \end{bmatrix} = \begin{bmatrix} \mathbf{T}^{11} & \mathbf{T}^{12} & \mathbf{T}^{13} \\ \mathbf{T}^{21} & \mathbf{T}^{22} & \mathbf{T}^{23} \\ \mathbf{T}^{31} & \mathbf{T}^{32} & \mathbf{T}^{33} \end{bmatrix} \begin{bmatrix} \mathbf{s}^0 \\ \mathbf{E}^0 \\ \mathbf{H}^0 \end{bmatrix} , \tag{13}$$

with

$$\begin{aligned}
\mathbf{T}^{11} &= [\mathbf{I} - \mathbf{G}^u\mathbf{C}' + \mathbf{G}^u\mathbf{e}^T(\mathbf{I} - \mathbf{G}^\phi\varepsilon')^{-1}\mathbf{G}^\phi\mathbf{e} + \mathbf{G}^u\mathbf{q}^T(\mathbf{I} - \mathbf{G}^v\boldsymbol{\mu}')^{-1}\mathbf{G}^v\mathbf{q}]^{-1} , \\
\mathbf{T}^{12} &= -\mathbf{T}^{11}\mathbf{G}^u\mathbf{e}^T(\mathbf{I} - \mathbf{G}^\phi\varepsilon')^{-1} , \\
\mathbf{T}^{13} &= -\mathbf{T}^{11}\mathbf{G}^u\mathbf{q}^T(\mathbf{I} - \mathbf{G}^v\boldsymbol{\mu}')^{-1} , \\
\mathbf{T}^{21} &= (\mathbf{I} - \mathbf{G}^\phi\varepsilon')^{-1}\mathbf{G}^\phi\mathbf{e}\mathbf{T}^{11} , \\
\mathbf{T}^{22} &= (\mathbf{I} - \mathbf{G}^\phi\varepsilon')^{-1}(\mathbf{I} + \mathbf{G}^\phi\mathbf{e}\mathbf{T}^{12}) , \\
\mathbf{T}^{23} &= (\mathbf{I} - \mathbf{G}^\phi\varepsilon')^{-1}\mathbf{G}^\phi\mathbf{e}\mathbf{T}^{13} , \\
\mathbf{T}^{31} &= (\mathbf{I} - \mathbf{G}^v\boldsymbol{\mu}')^{-1}\mathbf{G}^v\mathbf{q}\mathbf{T}^{11} , \\
\mathbf{T}^{32} &= (\mathbf{I} - \mathbf{G}^v\boldsymbol{\mu}')^{-1}\mathbf{G}^v\mathbf{q}\mathbf{T}^{12} , \\
\mathbf{T}^{33} &= (\mathbf{I} - \mathbf{G}^v\boldsymbol{\mu}')^{-1}(\mathbf{I} + \mathbf{G}^v qT^{13}) ,
\end{aligned} \tag{14}$$

where $\mathbf{I}$ is the unit tensor, and the terms containing the magnetoelectric coefficient $\boldsymbol{\alpha}$ have been ignored because the two phases making up the composite do not exhibit the magnetoelectric effect. By first substituting Eq. (13) into (4) and averaging, then eliminating $\mathbf{s}^0$, $\mathbf{E}^0$, and $\mathbf{H}^0$ from those equations obtained by averaging, and finally comparing them with Eq. (5), we get the general solutions to the six effective constitutive coefficient tensors of the composite:

$$\mathbf{C}^* = \langle(\mathbf{C}\mathbf{T}^{11} - \mathbf{e}^T\mathbf{T}^{21} - \mathbf{q}^T\mathbf{T}^{31})\rangle\mathbf{A}^{11} + \langle(\mathbf{C}\mathbf{T}^{12} - \mathbf{e}^T\mathbf{T}^{22})\rangle\mathbf{A}^{12} + \langle(\mathbf{C}\mathbf{T}^{13} - \mathbf{q}^T\mathbf{T}^{33})\rangle\mathbf{A}^{13} , \tag{15}$$

$$\mathbf{e}^{T*} = \langle[(\mathbf{C}^* - \mathbf{C})\mathbf{T}^{12} + \mathbf{e}^T\mathbf{T}^{22}]\rangle\langle\mathbf{T}^{22}\rangle^{-1} , \tag{16}$$

$$\mathbf{q}^{T*} = \langle[(\mathbf{C}^* - \mathbf{C})\mathbf{T}^{13} + \mathbf{q}^T\mathbf{T}^{33}]\rangle\langle\mathbf{T}^{33}\rangle^{-1} , \tag{17}$$

$$\varepsilon^* = \langle[(\mathbf{e} - \mathbf{e}^*)\mathbf{T}^{12} + \varepsilon\mathbf{T}^{22}]\rangle\langle\mathbf{T}^{22}\rangle^{-1}, \tag{18}$$

$$\boldsymbol{\alpha}^* = \langle(\mathbf{e} - \mathbf{e}^*)\mathbf{T}^{13}\rangle\langle\mathbf{T}^{33}\rangle^{-1} , \tag{19}$$

$$\boldsymbol{\mu}^* = \langle[(\mathbf{q} - \mathbf{q}^*)\mathbf{T}^{13} + \boldsymbol{\mu}\mathbf{T}^{33}]\rangle\langle\mathbf{T}^{33}\rangle^{-1} , \tag{20}$$

where

$$\begin{aligned}
\mathbf{A}^{11} &= [\langle\mathbf{T}^{11}\rangle - \langle\mathbf{T}^{12}\rangle\langle\mathbf{T}^{22}\rangle^{-1}\langle\mathbf{T}^{21}\rangle - \langle\mathbf{T}^{13}\rangle\langle\mathbf{T}^{33}\rangle^{-1}\langle\mathbf{T}^{31}\rangle]^{-1} , \\
\mathbf{A}^{12} &= -\langle\mathbf{T}^{22}\rangle^{-1}\langle\mathbf{T}^{21}\rangle\mathbf{A}^{11} , \\
\mathbf{A}^{13} &= -\langle\mathbf{T}^{33}\rangle^{-1}\langle\mathbf{T}^{31}\rangle\mathbf{A}^{11} .
\end{aligned}$$

Herein the terms containing $\mathbf{T}^{23}$ or $\mathbf{T}^{32}$ are ignored, since $\mathbf{e} = \mathbf{0}$ for the piezomagnetic phase and $\mathbf{q} = \mathbf{0}$ for the piezoelectric phase. These results are general and independent of the models assumed for the composite, and also provide the interrelationships between these effective coefficient tensors. Obviously, the three principal effective moduli tensors, i.e., the effective elastic stiffness $\mathbf{C}^*$, the effective dielectric constant tensor $\boldsymbol{\varepsilon}^*$, and the effective magnetic permeability $\boldsymbol{\mu}^*$, all contain the coupled magnetic-electrical-mechanical effect. After ignoring these coupled terms, Eqs. (15), (18), and (20) become

$$C^* = \langle \mathbf{C}\mathbf{T}^{11} \rangle \langle \mathbf{T}^{11} \rangle^{-1} , \quad (21)$$

$$\boldsymbol{\varepsilon}^* = \langle \boldsymbol{\varepsilon}\mathbf{T}^{22} \rangle \langle \mathbf{T}^{22} \rangle^{-1} , \quad (22)$$

$$\boldsymbol{\mu}^* = \langle \boldsymbol{\mu}\mathbf{T}^{33} \rangle \langle \mathbf{T}^{33} \rangle^{-1} , \quad (23)$$

where the $\mathbf{T}$ tensors are simplified as

$$\mathbf{T}^{11} = (\mathbf{I} - \mathbf{G}^u \mathbf{C}')^{-1} ,$$

$$\mathbf{T}^{22} = (\mathbf{I} - \mathbf{G}^\phi \boldsymbol{\varepsilon}')^{-1} ,$$

$$\mathbf{T}^{33} = (\mathbf{I} - \mathbf{G}^v \boldsymbol{\mu}')^{-1} .$$

These results are the same as those for general linear-response problems. Numerical results show that the influence of the coupled effects on $\mathbf{C}^*$, $\boldsymbol{\varepsilon}^*$, and $\boldsymbol{\mu}^*$ is generally weak, so Eqs. (21)–(23) are applicable for the determination of the principal effective moduli ($\mathbf{C}^*$, $\boldsymbol{\varepsilon}^*$, and $\boldsymbol{\mu}^*$) of the composite.

The effective piezoelectric tensor $\mathbf{e}^{T^*}$, Eq. (16), contains the piezomagnetic effect. If the piezomagnetic effect in Eq. (16) is ignored, Eq. (16) also becomes the known result[9] for piezoelectric composites. The effective piezomagnetic tensor $\mathbf{q}^{T*}$ is similar to the effective piezoelectric tensor $\mathbf{e}^{T*}$. If the piezoelectric term in Eq. (17) is ignored, Eq. (17) is the result for piezomagnetic composites. The behavior of $\mathbf{q}^{T*}$ for the piezomagnetic composites is similar to that of $\mathbf{e}^{T*}$ for the piezoelectric composites.

Equation (19) for the effective magnetoelectric coefficient tensor $\boldsymbol{\alpha}^*$ for the piezoelectric-piezomagnetic composite is an important result, and this is the product property of piezoelectric and piezomagnetic effects. The composite, indeed, has a nonzero magnetoelectric effect, though the magnetoelectric effect is absent in the two constituent phases. Next we mainly discuss the magnetoelectric effect of the piezoelectric-piezomagnetic composite.

III. MAGNETOELECTRIC COEFFICIENT OF 1-3 AND 3-1 COMPOSITES

As a practical example, first consider a 1-3 or 3-1 transversely isotropic composite composed of a transversely isotropic matrix and aligned but randomly located fibers also exhibiting transverse isotropic symmetry. The fibers, the matrix, and the composite are transversely isotropic about the x_3 axis, and x_1-x_2 is the basal plane of transverse symmetry. In the limiting case that the aspect ratio of the constituent particles approaches infinity, we can obtain the following simple approximate result for the important component α_{33}^* of the magnetoelectric tensor $\boldsymbol{\alpha}^*$:

$$\alpha_{33}^* = \left\langle \frac{2(e_{31} - e_{31}^*) q_{31}}{k + m^0} \right\rangle , \quad (24)$$

from Eq. (19), where $k = C_{11} + C_{12}$ and $m = C_{11} - C_{12}$. Depending upon the choices of the homogeneous comparison medium, Eq. (24) can give different approximate results.

For the 1-3 piezoelectric-piezomagnetic composite with piezoelectric fibers embedded in a continuous piezomagnetic matrix, we can approximately take the continuous piezomagnetic matrix as the comparison medium. In this case, Eq. (24) becomes

$$\alpha_{33}^* = -\frac{2f(1-f)\,{}^e e_{31}\,{}^m q_{31}}{{}^e k + {}^m m - f({}^e k - {}^m k)} , \quad (25)$$

where f is the volume fraction of the piezoelectric phase, and the superscripts e and m denote the piezoelectric phase and the piezomagnetic phase, respectively.

For the 3-1 piezoelectric-piezomagnetic composite with piezomagnetic fibers embedded in a continuous piezoelectric matrix, which is an inversion of the 1-3 composite, α_{33}^* is

$$\alpha_{33}^* = -\frac{2f(1-f)\,{}^e e_{31}\,{}^m q_{31}}{{}^m k + {}^e m - (1-f)({}^m k - {}^e k)} . \quad (26)$$

Equations (25) and (26) are non-self-consistency (NSC) approximations, and valid for matrix-based composites with dispersive microstructure. Another important approximation is to take $C^0 = C^*$, which is the self-consistent effective-medium theory (SCEMT). In this case, α_{33}^* is determined by

$$\alpha_{33}^* = -\frac{2f(1-f)\,{}^e e_{31}\,{}^m q_{31}(k^* + m^*)}{({}^e k + m^*)({}^m k + m^*)} , \quad (27)$$

where k^* and m^* are determined by their self-consistency equations[11]

$$f\frac{{}^e k - k^*}{{}^e k + m^*} + (1-f)\frac{{}^m k - k^*}{{}^m k + m^*} = 0 , \quad (28)$$

$$f\frac{{}^e m - m^*}{{}^e m(k^* + 2m^*) + 3k^* m^*} + (1-f)\frac{{}^m m - m^*}{{}^m m(k^* + 2m^*) + 3k^* m^*} = 0 . \quad (29)$$

Although the results of α_{33}^* predicted by these three equations are different, obviously, $\alpha_{33}^* = 0$ at $f = 0$ or $f = 1$, and there is a nonzero α_{33}^* only in the piezoelectric-piezomagnetic composite ($f \neq 0$ or 1). This nonzero α_{33}^* results from the product interaction between the piezoelectric (${}^e e_{31}$) and piezomagnetic (${}^m q_{31}$) effects.

IV. NUMERICAL RESULTS AND DISCUSSIONS

In order to have a better understanding for the theoretical results above, we perform a numerical computation for a two-phase transversely isotropic piezoelectric-piezomagnetic composite with $6mm$ symmetry, such as the $BaTiO_3$-$CoFe_2O_4$ composite. Piezoelectric-piezomagnetic composites of this type have been intro-

TABLE I. Properties of $BaTiO_3$ and $CoFe_2O_4$ to be taken for numerical calculations of the magnetoelectric coefficients of the composites.

	$BaTiO_3$	$CoFe_2O_4$
C_{11} (GPa)	166.2	286.0
C_{12} (GPa)	76.5	173.0
C_{13} (GPa)	77.4	170.5
C_{33} (GPa)	161.4	269.5
$\varepsilon_{33}/\varepsilon^0$	1350	10
μ_{33}/μ^0	8	125
e_{31} (C/m^2)	−4.22	0
e_{33} (C/m^2)	18.6	0
q_{31} (N/A m)	0	580.3
q_{33} (N/A m)	0	699.7

duced in recent years to obtain enhanced performance in magnetic field sensors. An important quantity used to assess the performance of the composite for a typical device is given by

$$\alpha_{E33} = -\alpha_{33}^*/\varepsilon_{33}^* , \quad (30)$$

which is the magnetoelectric voltage coefficient of the composite.

For computations, $BaTiO_3$-$CoFe_2O_4$ composites are considered. The properties of the two phases used for calculations of the magnetoelectric effect in the composite are given in Table I. For the sake of comparison with experiments and theoretical results predicted by using the cubes model (CM) of Harshe, Dougherty, and Newnham,[3] the available experimental data[3,4] for the magnetoelectric voltage coefficient for the $BaTiO_3$-$CoFe_2O_4$ composite and the CM approximate results[3] for the 0-3 and 3-0 composites are also shown.

Some theoretical predictions of the effective magnetoelectric coefficients of the composites are shown in Figs. 1–5. These predictions show that the numerical values of the magnetoelectric coefficient α_{33}^* and voltage coefficient α_{E33} of the composites with various connectivities of phases increase from zero to the maxima with increasing volume fraction f of the piezoelectric phase because of the continuous enhancement in the elastic interaction, and then approach zero at $f=1$. The maximum numerical values of α_{33}^* lie in the intermediate

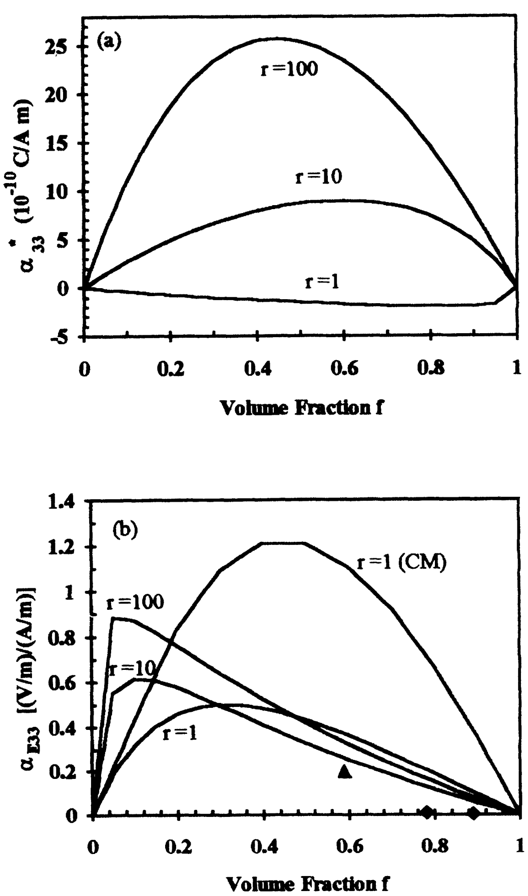

FIG. 1. (a) Magnetoelectric coefficient α_{33}^* and (b) magnetoelectric voltage coefficient α_{E33} of 0-3 or 1-3 composites for various aspect ratios of the piezoelectric phase (denoted by 0 or 1) calculated by using the NSC approach. The CM results (Ref. 3) of α_{E33} for the 0-3 composite and three available experimental data points (Refs. 3,4) (solid triangle and diamonds) are also shown.

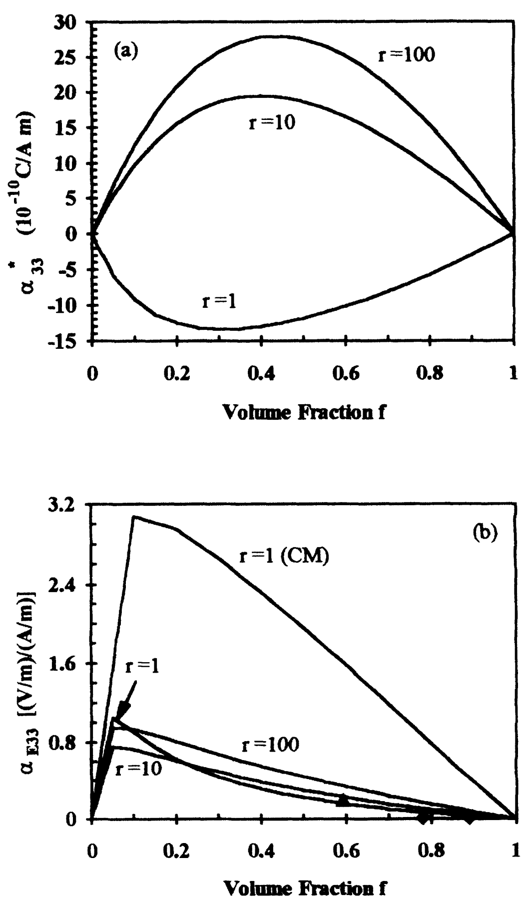

FIG. 2. (a) Magnetoelectric coefficient α_{33}^* and (b) magnetoelectric voltage coefficient α_{E33} of 3-0 or 3-1 composites for various aspect ratios of the piezomagnetic phase (denoted by 0 or 1) calculated by using the NSC approach. The CM results (Ref. 3) of α_{E33} for the 0-3 composite and three available experimental data points (Refs. 3,4) (solid triangle and diamonds) are also shown.

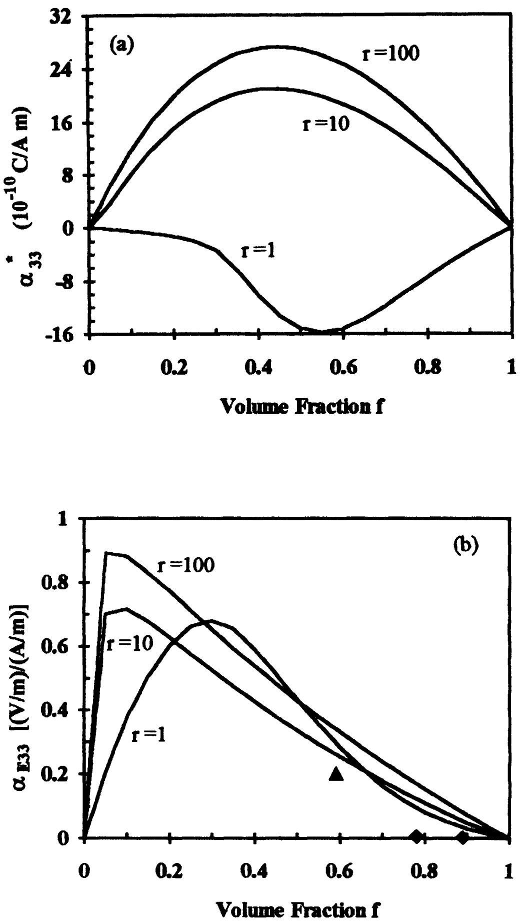

FIG. 3. (a) Magnetoelectric coefficient α^*_{33} and (b) magnetoelectric voltage coefficient α_{E33} of the composites for various aspect ratios calculated by using the SCEMT. Solid triangle and diamonds are three available experimental data points (Refs. 3,4).

composition range near $f=0.5$, because the stiffnesses of the two phases are comparable in magnitude and the elastic interaction between the two phases is strongest near $f=0.5$. The maximum numerical values of α_{E33}, which is a combination property of α^*_{33} and ε^*_{33}, however, lie in the low-volume-fraction f range, which is due to the fact that the dielectric permittivity of the piezoelectric phase is at least two orders of magnitude larger than that of the piezomagnetic phase.

The aspect ratio r of the dispersive-phase particles has a pronounced effect on the effective magnetoelectric properties. With increase in the aspect ratio r of the dispersive phase, the values of the magnetoelectric coefficient α^*_{33} of the $BaTiO_3$-$CoFe_2O_4$ composite change from negative to positive values, and correspondingly the values of α_{E33} change from positive to negative values, at about $r=3$, as shown in Fig. 5. For the sake of clear illustration, the values of α_{E33} on α_{E33} vs f curves for $r>10$ have been shown with their positive numerical values. As the aspect ratio is less than about 3, the numerical values of the effective magnetoelectric coefficients of the composites rapidly decrease with incrêasing r. In the range $10>r>3$ the numerical values of the effective magnetoelectric coefficients rapidly increase with increasing r. For $r>10$, the numerical values of the effective magnetoelectric coefficients change slightly with r and finally approach the values in the limiting case of aligned fibers ($1/r=0$), predicted by Eqs. (25)–(27). The changes in the magnetoelectric coefficients with the aspect ratio r predicted theoretically are interesting consequences, and remain to be experimentally verified.

The trend of change of α_{E33} predicted by the NSC approach is similar to that predicted by the series-parallel-like CM for the 0-3 and 3-0 composites [Figs. 1(b) and 2(b)]. The NSC predictions are in agreement with experimental results, but there exists large deviation of the CM

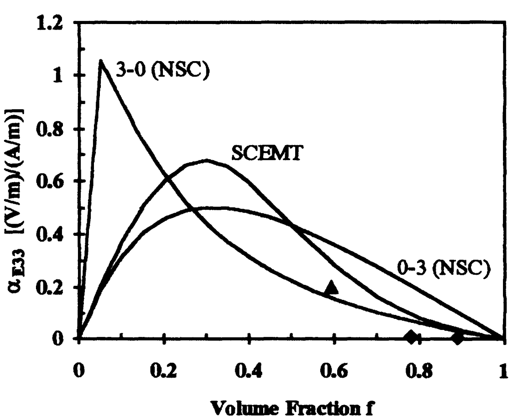

FIG. 4. Comparison between the NSC and SCEMT predictions of the magnetoelectric voltage coefficient α_{E33} for the 0-3 or 3-0 composites. Solid triangle and diamonds are three available experimental data points (Refs. 3,4).

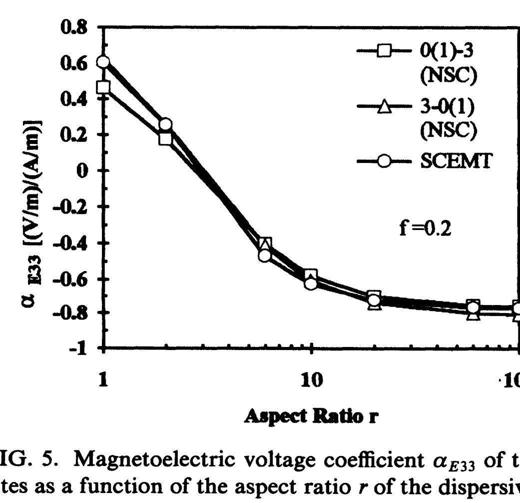

FIG. 5. Magnetoelectric voltage coefficient α_{E33} of the composites as a function of the aspect ratio r of the dispersive-phase particles.

predictions from the experimental results. The large discrepancy between the CM predictions and experiments results from the inherent shortcoming of the simplified cubes model, which overestimates the values of α_{E33} and can be considered as an upper bound of α_{E33} of composites.

For the 0-3 ($r=1$) or 1-3 composite in which in piezoelectric phase is the dispersive phase and the piezomagnetic phase is the continuous matrix, the characteristic volume fractions corresponding to the maximum α_{E33} and α_{33}^{*} decrease with increase in the aspect ratio of the piezoelectric particles (Fig. 1). For the 3-0 or 3-1 composites with the inverse structures of the 0-3 or 1-3 composites, the characteristic volume fractions corresponding to the maximum α_{E33} and α_{33}^{*} increase with increasing aspect ratio of the piezomagnetic particles (Fig. 2). In these cases, the large α_{E33} is always obtained at low volume fractions of the piezoelectric phase. An important consequence is that the 3-0 or 3-1 piezoelectric-piezomagnetic composite exhibits a larger magnetoelectric effect than the 0-3 or 1-3 piezoelectric-piezomagnetic composite.

The difference between the NSC approach and the SCEMT for the magnetoelectric coefficient lies in which SCEMT expression for the effective magnetoelectric coefficient contains the effective stiffnesses of the composites estimated by self-consistency equations. Unlike the effective piezoelectric properties of piezoelectric-polymer composites,[11] there is no remarkable difference between the NSC and SCEMT estimations of the effective magnetoelectric coefficient of the piezoelectric-piezomagnetic composites because these two phases have comparable stiffnesses (Figs. 1–3). In the $BaTiO_3$-rich and $CoFe_2O_4$-rich composition regions, the behavior of the effective magnetoelectric coefficients predicted by the SCEMT is similar to that for the 3-0 (or 3-1) composite and for the 0-3 (or 1-3) composite estimated by the NSC approach, respectively, as shown in Fig. 4. Close to $f=0$ and $f=1$, the results predicted by the SCEMT are in agreement with those obtained from the NSC estimations.

V. CONCLUSIONS

Although the piezoelectric and piezomagnetic phases have no magnetoelectric effect, their composites have coupled magnetic-electrical effects as a result of the elastic interaction between these two phases. The magnetoelectric effect which can be observed as the product property of the composites has been treated first in terms of rigorous theoretical modeling based on the developed Green's function method and perturbation theory. For transversely isotropic fibrous piezoelectric-piezomagnetic composites, explicit approximate expressions for the magnetoelectric coefficient have been given by means of the NSC approach and the SCEMT. As a practical example, explicit numerical calculations for the magnetoelectric effect in $BaTiO_3$-$CoFe_2O_4$ composites with various connectivities of phases have been performed over the whole range of compositions following the NSC approximation and the SCEMT of the theory. In comparison with the recent CM results, our theoretical predictions are in good agreement with the available experimental results, and the CM results can be considered as upper bounds of the magnetoelectric coefficients of the composites. The effective magnetoelectric coefficients of the composites can be strongly influenced by the connectivity, the volume fraction, and the aspect ratio of the particles. At low volume fractions of the piezoelectric phase $BaTiO_3$, a large magnetoelectric voltage coefficient of the composites can be obtained. The maximum magnetoelectric effect in 0(1)-3 piezoelectric-piezomagnetic composites is smaller than that in 3-0(1) piezoelectric-piezomagnetic composites. These numerical results show the interesting behavior of the composites, which can provide a general guideline for the evaluation of more composite systems and the selection of the best combination with an efficient coupling of piezoelectric and piezomagnetic properties. The present theoretical framework can also be directly generalized to the modeling of the magnetoelectric effect in composites of a pyroelectric phase and a pyromagnetic phase.

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