Magnetoelectric effect of mildly conducting magnetostrictive/piezoelectric particulate composites

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A relatively simple model has been developed to study the magnetoelectric effect of magnetostrictive/piezoelectric dilute particulate composites. For illustrative purpose, we calculate the magnetoelectric voltage coefficients of particulate composites of $NiFe_2O_4$ and lead zirconate titanate. By treating the inclusion/matrix as mildly conducting materials, we have reproduced all the key experimental features of magnetoelectric behavior of the particulate composites. In addition, the qualitative dependence of the calculated magnetoelectric voltage coefficients on the constituent's electrical conductivity is also in good agreement with recent experimental observations. [DOI: 10.1063/1.2245194]

I. INTRODUCTION

The magnetoelectric (ME) effect is characterized by the appearance of dielectric polarization in a material under an applied magnetic field, which can be used in various applications such as magnetic-electric sensors and microwave electronics.[1] Several magnetoelectric single phase materials have been discovered since the experimental observation of linear ME effect in the antiferromagnetic Cr_2O_3 crystal in 1960.[2] However, these single phase materials have not found much technological uses currently due to the fact that they mostly exhibit a very weak ME effect, and most of them have Neél or Curie temperature far below room temperature. Recently, magnetostrictive-piezoelectric layered and bulk composites have attracted much interest because they can exhibit a much stronger ME effect in a wide temperature range than the single phase ME materials. Additionally, the composite ME effect is predetermined for microwave applications due to the fact that it is a "dynamic" effect in the microwave range: a pronounced ME response is only observed by applying an ac magnetic field superimposed upon a stronger dc bias field.[3] Interestingly, at low frequencies and away from the resonance values, it was found that the measured ME effects strongly depended on the conductivity of the inclusion/matrix materials or, alternatively, on the applied frequency. Laletin and Srinivasan and Srinivasan *et al.* reported an enhancement in the strength of ME effect by adding cobalt oxide to the nickel ferrite that resulted in orders of magnitude increase in the resistivity of the bulk nickel ferrite and barium lead zirconate titanate (BLZT) composites.[4,5] Nan and co-workers observed an increase in magnetoelectric voltage coefficient of Particulate composites of $NiFe_2O_4$ (NFO) and lead-zirconate-titante (PZT) with increasing frequency in the whole range of 1–500 kHz.[6,7]

As far as theory is concerned, the ME effects have been studied by many workers, motivated by a desire to understand and optimize the ME response.[3] Harshe and coworkers proposed a simplified approximation to calculate the longitudinal ME response of laminated PZT/ferrite composites.[8–10] Srinivasan *et al.* developed a theoretical model for ME coupling in layered magnetostrictive/piezoelectric samples.[11–15] Nan and co-workers investigated the coupled magnetic-mechanical-electric effects involving linearly and nonlinearly coupling interactions in ferroic layered composites by using the Green's function technique.[16–19] Bichurin and co-workers theoretically studied the frequency dependence of the ME voltage coefficient including the appearance of electromechanical resonances (EMRs) and its effects on the ME response.[20,21] However, most of the theoretical investigations of magnetoelectric effect are rather focused on layered structures than particulate composites. In addition, none of the suggested models have explicitly taken the effect of conductivity into account, and hence cannot discuss the influence of the constituent's electrical conductivity on the ME effect.

In this paper, we propose a relatively simple model to study the ME effect and its dependence on the conductivities of both inclusion and matrix phases of large-sized particulate composites, in which the interfacial effect should not become significant, at small volume fractions of inclusions. For illustration the ME voltage coefficients of NFO/PZT are calculated and compared with experimental results reported in Ref. 7.

II. THEORY AND MODELING

Consider the magnetostrictive spherical inclusion particles embedded in piezoelectric matrix, with a uniform magnetic field H applied along the z direction. Bulk and shear moduli for the inclusion (matrix) are $k_i(k_m)$ and $\mu_i(\mu_m)$, respectively. The magnetic permeabilities of the inclusion and matrix material are ξ_i and ξ_0 (the vacuum magnetic perme-

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ability), respectively. The volumetric averaging of quantities (such as magnetic flux density B) is defined by

$$\langle B_{gl}\rangle = \frac{1}{V}\int_V B_{gl} dV, \quad (1)$$

where $g=i,m$ denote inclusion and matrix, respectively; the subscript $l=x,y,z$ refers to the three coordinate directions and V is the volume.

The constitutive magnetostatic equations are

$$\langle B_{iz}\rangle = \xi_i\langle H_{iz}\rangle + \langle M_{iz}\rangle, \quad (2a)$$

$$\langle B_{mz}\rangle = \xi_0\langle H_{mz}\rangle, \quad (2b)$$

where $\langle H\rangle$, $\langle M\rangle$, and $\langle B\rangle$ are the volumetric averaged magnetic field, magnetization, and flux density.

The volumetric averaged magnetic field and flux density of the composite are calculated by

$$\langle H_z\rangle = \phi\langle H_{iz}\rangle + (1-\phi)\langle H_{mz}\rangle, \quad (3a)$$

$$\langle B_z\rangle = \phi\langle B_{iz}\rangle + (1-\phi)\langle B_{mz}\rangle, \quad (3b)$$

where ϕ denotes the inclusion volume fraction.

The boundary value problem gives the following equation:[22]

$$\langle B_{iz}\rangle - \langle B_{mz}\rangle = -2\xi_0(\langle H_{iz}\rangle - \langle H_{mz}\rangle). \quad (4)$$

From Eqs. (2)–(4), we get

$$[2+\phi+\xi_i(1-\phi)/\xi_0]\langle H_{iz}\rangle + (1-\phi)\langle M_{iz}\rangle = 3\langle H_z\rangle, \quad (5)$$

which relates the inclusion magnetic field to the applied magnetic field.

The magnetostrictive inclusion particles will deform under the application of external magnetic field, thus exerting forces on the piezoelectric matrix material, giving a pizoelectric signal. The strain-stress relationships can be solved by employing elastic theory in the inclusion and matrix and matching boundary conditions at the interface. Since we assume that the composite is subjected to a magnetic field in the z direction in our problem, we only need to be concerned with the variables in the z direction and (say) x direction due to the transverse isotropy since $T_{ix}=T_{iy}$, $T_{mx}=T_{my}$, $e_{ix}=e_{iy}$, and $e_{mx}=e_{my}$, where T and e are the stress and strain, respectively. The constitutive equations including magnetostriction effect for the two materials are given by[22]

$$\langle T_{gl}\rangle = \left(k_g - \frac{2}{3}\mu_g\right)\langle 2e_{gx}+e_{gz}\rangle + 2\mu_g\langle e_{gl}\rangle - f_{gl}(H_g), \quad (6)$$

where $f_{gl}(H_g)$ denotes the magnetic field induced stresses perpendicular ($l=x$) and parallel ($l=z$) to the applied field in the magnetostrictive inclusions if $g=i$; $f_{gl}(H_g)$ is assumed to be zero for $g=m$ since we have assumed that the pure matrix material is nonmagnetostrictive.

The elasticity equations are

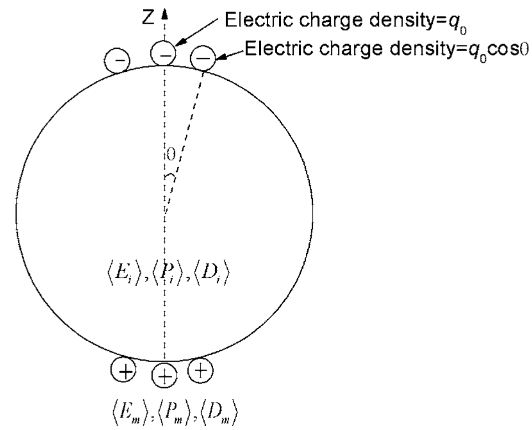

FIG. 1. The polarized sphere covered with "compensating" electric charge.

$$\langle T_{ix}\rangle - \langle T_{mx}\rangle = (A+B)(\langle e_{ix}\rangle - \langle e_{mx}\rangle) + B(\langle e_{iz}\rangle - \langle e_{mz}\rangle), \quad (7a)$$

$$\langle T_{iz}\rangle - \langle T_{mz}\rangle = 2B(\langle e_{ix}\rangle - \langle e_{mx}\rangle) + A(\langle e_{iz}\rangle - \langle e_{mz}\rangle), \quad (7b)$$

and the coefficients A and B are given by[22]

$$A = \frac{10}{9}\mu_m\left(-3 + \frac{2\mu_m}{k_m+2\mu_m}\right), \quad (8a)$$

$$B = \frac{1}{9}\mu_m\left(-3 - \frac{10\mu_m}{k_m+2\mu_m}\right). \quad (8b)$$

Since the composite in our ME effect problem is assumed to be free from external mechanical stresses, although it may be subjected to an external magnetic field, we also have

$$\phi\langle T_{il}\rangle + (1-\phi)\langle T_{ml}\rangle = 0. \quad (9)$$

For the electric part of our problem, the constitutive electrostatic equations for the elastically isotropic constitutents are

$$\langle D_{iz}\rangle = \varepsilon_i\langle E_{iz}\rangle + \langle P_{iz}\rangle, \quad (10a)$$

$$\langle D_{mz}\rangle = \varepsilon_m\langle E_{mz}\rangle + \langle P_{mz}\rangle, \quad (10b)$$

where $\langle E\rangle$, $\langle P\rangle$, and $\langle D\rangle$ are the volumetric averaged electric field, polarization, and displacement.

The boundary value problem gives the following equation (see Fig. 1):[23]

$$\langle D_{iz}\rangle - \langle D_{mz}\rangle = -2\varepsilon_m(\langle E_{iz}\rangle - \langle E_{mz}\rangle) + q_0. \quad (11)$$

Herein we assume that the polarized charge at the inclusion-matrix spherical interface is fully compensated by free charges with an angular distribution given by $q=q_0\cos\theta$, where q_0 is the surface charge density along the z direction (see Fig. 1).

As mentioned earlier there are experimental indications that electrical conductivity may play a subtle role in the ME effect of mildly conducting magnetoelectric composites; we therefore include conductivity effects in our present model. The conduction current densities j in the constituents are

$$\langle j_{iz}\rangle = \sigma_i \langle E_{iz}\rangle, \tag{12a}$$

$$\langle j_{mz}\rangle = \sigma_m \langle E_{mz}\rangle, \tag{12b}$$

where σ is electric conductivity. Following similar calculation of obtaining the D and E relation as shown in Eq. (11), we can get the analogous equation relating the conduction current densities to the electric fields of the constituents:[23]

$$\langle j_{iz}\rangle - \langle j_{mz}\rangle = -2\sigma_m(\langle E_{iz}\rangle - \langle E_{mz}\rangle) - \partial q_0/\partial t. \tag{13}$$

The z component of the volumetric averaged electric field of the composite $\langle E_z\rangle$ is calculated by

$$\langle E_z\rangle = \phi\langle E_{iz}\rangle + (1-\phi)\langle E_{mz}\rangle. \tag{14}$$

Using Eqs. (10)–(14), after some mathematical manipulation, the time evolution of $\langle E_{iz}\rangle$ is written as[23]

$$\frac{\partial\langle E_{iz}\rangle}{\partial t} = \frac{3(\sigma_m\langle E_z\rangle + \varepsilon_m\partial\langle E_z\rangle/\partial t) + (1-\phi)\partial\langle P_{mz}\rangle/\partial t - [\phi 3\sigma_m + (1-\phi)(\sigma_i + 2\sigma_m)]\langle E_{iz}\rangle}{\phi 3\varepsilon_m + (1-\phi)(\varepsilon_i + 2\varepsilon_m)}, \tag{15}$$

where $\langle P_{mz}\rangle = d_{33}\langle T_{mz}\rangle + 2d_{31}\langle T_{mx}\rangle$ is the electric polarization induced by stresses in the piezoelectric matrix. d_{33} and d_{31} are the longitudinal and transverse piezoelectric constants of the matrix material, respectively.

There are usually two kinds of methods for measuring the ME voltage coefficient $\alpha_E \equiv \delta E/\delta H$ when an ac magnetic field $H_{\text{ac}}\sin(2\pi ft)$ superimposed on a dc magnetic field H_{dc} is applied on the sample, where f is the applied frequency. One is measuring the charge $Q=\int_0^t J(t)dt$ generated from the sample under a short circuit condition, where $J(t)$ is the total current flowing through the circuit; the output voltage is obtained from the charge and the capacitance of the composite using $V=Q/C$, and α_E is given by the measured voltage divided by the thickness of the sample and amplitude of the ac magnetic field. The other method measures the open circuit voltage across the sample, and the output voltage divided by the thickness and the ac magnetic field gives the ME voltage coefficient of the sample. Under the short circuit condition, $E=0$, and in the open circuit condition, $J=0$. The longitudinal ME voltage coefficient is calculated by

$$\alpha_{E_{33}} = -\frac{\{(\varepsilon_i + 2\varepsilon_m)(1-\phi)\partial\langle P_m\rangle/\partial t + 3\phi(\varepsilon_m\sigma_i - \varepsilon_i\sigma_m)E_i\}_{\cos 2\pi ft}}{\varepsilon[(1-\phi)\varepsilon_i + (2+\phi)\varepsilon_m]2\pi f H_{\text{ac}}} \tag{16a}$$

for short circuit and

$$\alpha_{E_{33}} = -\frac{\{(\varepsilon_i + 2\varepsilon_m)(1-\phi)\partial\langle P_m\rangle/\partial t + [(1+2\phi)\varepsilon_i + 2(1-\phi)\varepsilon_m]\sigma_m E + 3\phi(\varepsilon_m\sigma_i - \sigma_m\varepsilon_i)E_i\}_{\cos 2\pi ft}}{\varepsilon_m[(1+2\phi)\varepsilon_i + 2(1-\phi)\varepsilon_m]2\pi f H_{\text{ac}}} \tag{16b}$$

for open circuit, where $\{\ \}_{\cos 2\pi ft}$ is the $\cos 2\pi ft$ Fourier component of the function within the bracket.

Herein, we briefly describe the procedures for numerically calculating $\alpha_{E_{33}}$. The relevant magnetostriction response functions $f(H)$'s of the inclusion material have to be determined. We use experimental longitudinal and transverse strains of the pure inclusion material under zero external stresses to determine the magnetostriction response functions $f(H_i)$'s by Eq. (6). The electric polarization $\langle P_m\rangle$ induced by stresses in the piezoelectric matrix can then be calculated from Eqs. (5)–(9). Finally, the longitudinal ME voltage coefficient $\alpha_{E_{33}}$ is numerically solved from Eqs. (15) and (16) for a given composite system.

III. RESULTS AND DISCUSSION

To verify our model, we perform numerical calculations for the particulate NFO/PZT composites reported in Ref. 7 and compare with experimental data for $\phi=0.07$, 0.2, and 0.32 therein. The following parameters are adopted:[7,24–28] $k_i=197$ GPa, $\mu_i=56$ GPa, $k_m=62.3$ GPa, $\mu_m=27.1$ GPa, $d_{33}=375$ pC/N, $d_{31}=-175$ pC/N, $\varepsilon_i=10\varepsilon_0$, $\varepsilon_m=1560\varepsilon_0$, $\xi_i=3\xi_0$, $H_{\text{ac}}=2$ Oe, $f=1$ kHz, $\sigma_i=6\times10^{-6}\ \Omega^{-1}\,\text{m}^{-1}$, and $\sigma_m=5\times10^{-12}\ \Omega^{-1}\,\text{m}^{-1}$. The magnetostriction response functions are found by using data on the longitudinal and transverse magnetostrictive strain responses of polycrystalline NFO taken from Ref. 29 (Fig. 2). Figure 3 shows a comparison between the calculations by Eq. (16a) and reported experimental data[7] for the longitudinal magnetoelectric voltage coefficients of particulate NFO/PZT composites obtained by measuring the charge generated from the composites under short circuit condition. Good agreement up to 32% volume fraction of NFO with the experimental data is shown. Some key experimental features are reproduced by our calculation: $\alpha_{E_{33}}$ increases with the volume fraction of NFO in the range of $0\% < \phi < 32\%$, and the magnetic field values correspond-

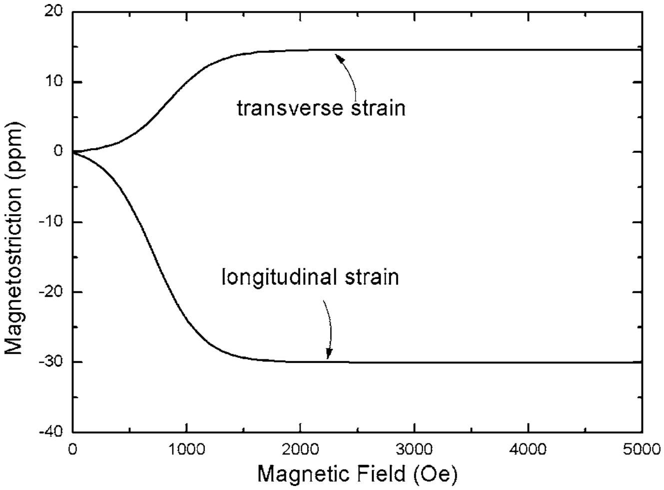

FIG. 2. The experimental longitudinal and transverse strains of NFO subjected to magnetic fields under zero external stresses.

ing to maximum $\alpha_{E_{33}}$ are about 1 kOe. It is noted that our calculation will give a much larger value, e.g., a peak value of 130 mV/cm Oe for the sample with 32% volume fraction of NFO, if no conductivity is considered.

In recent experiments,[4,5] it is found that the measured ME voltage coefficients depended on the constituent's conductivity or, alternatively, the applied frequency for bulk composites of NFO/PZT, nickel zinc ferrite $Ni_{1-x}Zn_xFe_2O_4(x=0-0.5)$ (NZFO)/PZT, and NFO/BLZT by measuring the voltage induced under a small ac magnetic field. Figure 4 elucidates the effects of electrical conductivity of the inclusion and matrix, respectively; the calculation is performed on the NFO/PZT system with $\phi=10\%$. It is shown from the figure that the ME voltage coefficients decrease as the conductivity of the constituent materials increases. The resistivity of the composite will decrease with increasing conductivity of either inclusion or matrix, or both. Our calculation therefore demonstrates that larger resistance of the composite will enhance the ME effect and that the range over which notable ME effect is observed becomes

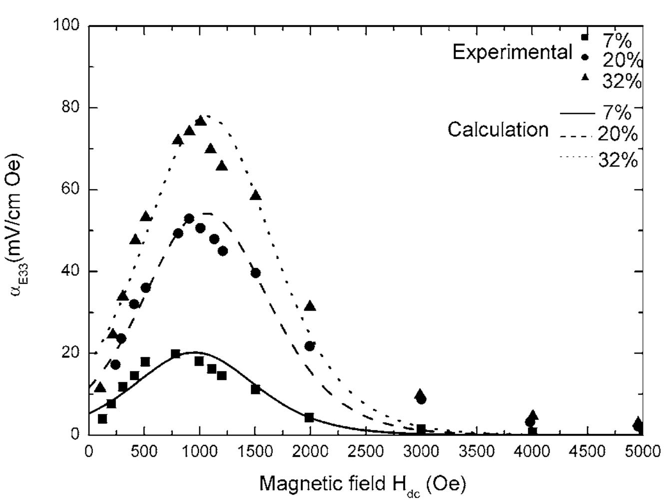

FIG. 3. Measured (denoted by ■, ●, and ▲) and calculated (denoted by—, --, and ……) longitudinal magnetoelectric voltage coefficients $\alpha_{E_{33}}$ of NFO/PZT composites vs applied magnetic field for inclusion volume fractions of $\phi=0.07$, 0.2, and 0.32.

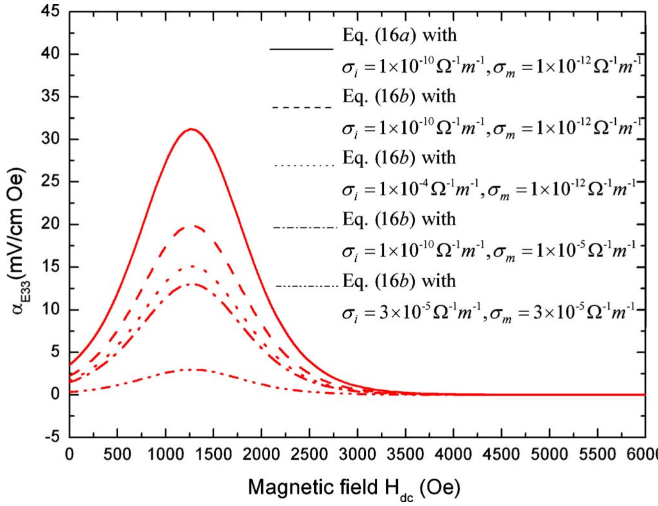

FIG. 4. The effects of inclusion and matrix conductivities (denoted by σ_i and σ_m) on the calculated ME voltage coefficients by using different measurement methods.

smaller when decreasing the resistivity of the composites. These trends are observed in recent experiments with particulate composites of NZFO/PZT and NFO/BLZT.[4,5] The solid line in Fig. 4 represents the calculated ME voltage coefficients by considering short circuit condition, which is about 1.5 times as large as the value under open circuit condition with the same electrical conductivities of constituents (the dashed line in Fig. 4). The absence of finite electrical conductivity in the materials should give the same values under the two different methods of calculation. Interesting to note, the calculated $\alpha_{E_{33}}$ will gradually increase with increasing frequency f, a trend also experimentally observed in particulate composites.[6] From the above calculation results, we can see that the conductivity of either inclusion or matrix material is one of the possible key factors determining the magnetoelectric behavior of particulate composites.

In conclusion, we have proposed a relatively simple model to include the effect of electric conductivity in mildly conducting inclusion and matrix phases on the magnetoelectric effect of large-sized particulate composites comprising a dilute suspension of spherical magnetostrictive particles uniformly distributed in a piezoelectric matrix, for which our model has reproduced some key characteristic experimental features. Our results may stimulate further interest in these kinds of materials for various applications. The study of particulate magnetoelectric composites with high inclusion volume fractions is very interesting because then the effective conductivity may increase rapidly with ϕ, implying the tendency of a decreasing α_E with higher ϕ; this is currently being investigated.

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