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Chapter 12

Magnetoelectric Composites

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Abstract

Magnetoelectric composites provide an electrical output in response to a magnetic input, and vice versa. A mechanical input (deformation) also yields a magnetic and electric response. The composite combines two phases: piezoelectric and magnetostrictive. Neither phase has magnetoelectric response, but when combined into a composite, the new “material” displays strong magnetoelectric response at room temperature. The coupling is provided by deformation, which both phases share when combined into a composite material. The response can be quantified in terms of the properties of the phases, their relative volumetric participation, and the geometry of the device, as described in this chapter. Magnetoelectric composites are multifunctional in the sense that they can both sense and harvest energy, and they can do that from multiple sources, i.e., magnetic, electric, and deformation fields.

A review of major developments in this field is presented in Section 12.1, followed by a summary of the fundamental concepts and equations for the three physics involved in this chapter, namely electrostatics, magnetostatics, and elasticity. The nomenclature is presented in Table 12.1. Intrinsic and extrinsic properties are discussed in Section 12.6 and 12.7, respectively, followed by a summary and conclusions.

12.1 Introduction

Describing the behavior of *magnetoelectric* (ME) composites requires multiphysics, including electrostatics, magnetostatics, and elasticity.

12.1.1 Electrostatics

Consider two conductive plates, each with area A , separated by a distance x , in vacuum. Next, an *electric field* \mathbf{E} is introduced by applying a *direct current* (DC)

Symbol	Property or variable name	Units
σ	Stress tensor	Pa=N/m ²
s	Strain tensor	-
ϵ	Dielectric permittivity tensor	C/(V m)
μ	Magnetic permeability tensor	N/A ²
S	Elastic compliance tensor	Pa ⁻¹
d	Piezoelectric tensor	C/N
q	Piezomagnetic tensor	m/A
E	Electrical field vector	V/m
H	Magnetic field vector	A/m
D	Electrical displacement vector	C/m ²
B	Magnetic induction vector	N/(A m)
α	Magnetolectric voltage coefficient	V/A
β	Magnetolectric charge coefficient	C/(A m)
κ	ME, PE, PM coupling factor	-
V	Voltage	Volt
q	Charge	Coulomb
χ_e	Dielectric susceptibility tensor	-
χ_m	Magnetic susceptibility tensor	-
ME	Magnetolectric	
PE	Piezoelectric	
PM	Piezomagnetic	
($\hat{\quad}$)	Extrinsic properties	
f_m, f_e	Piezomagnetic and piezoelectric volume fractions	

Table 12.1: Nomenclature.

voltage V between the plates. As a result of the electric field, charge C accumulates on the plates. The *electric displacement* \mathbf{D} is a vector field defined as the charge per unit area (charge density). The constitutive equation relating electric vector field \mathbf{E} and electric displacement vector field \mathbf{D} in vacuum is

$$\mathbf{D} = \epsilon_0 \mathbf{E} \quad (12.1)$$

where $\epsilon_0 \approx 8.854 \times 10^{-12}$ C/(V m) is the dielectric permittivity in vacuum. Actually, the dielectric permittivity in vacuum is defined by $\epsilon_0 = c_0^{-2} \mu_0^{-1}$, where c_0, μ_0 , are the speed of light and magnetic permeability in vacuum, respectively.

If vacuum is replaced by a material, the new medium experiences some degree of dipole reorientation, which causes the permittivity value to change to

$$\epsilon = \epsilon_r \epsilon_0 \quad (12.2)$$

where the rank-two tensor ϵ_r is the relative permittivity of the material (dimensionless). The density of dipole moments can be represented by the polarization density \mathbf{P} by rewriting (12.1) as follows

$$\mathbf{D} = \boldsymbol{\epsilon} \cdot \mathbf{E} = \epsilon_0 \mathbf{E} + \mathbf{P} = (\mathbf{I} + \boldsymbol{\chi}_e) \epsilon_0 \cdot \mathbf{E} \quad (12.3)$$

where $\boldsymbol{\chi}_e$ is the rank-two dielectric susceptibility tensor, \mathbf{I} is the rank-two identity tensor, \cdot indicates the dot product, and

$$\mathbf{P} = \epsilon_0 \boldsymbol{\chi}_e \cdot \mathbf{E} \quad (12.4)$$

Since there are no dipoles in vacuum (12.3) reduces to (12.1) for vacuum. Furthermore, the capacitance $C = q/V$ measures the charge per unit voltage applied and the energy stored in the capacitor is $W_s = \frac{1}{2}CV^2$.

12.1.2 Magnetostatics

The *magnetization* \mathbf{M} is a vector field that represents the density of magnetic dipole moments. Just like the electric field produces an electric polarization, the *magnetic field* \mathbf{H} produces magnetization \mathbf{M} . *Diamagnets* and *paramagnets* can be modeled by the linear and reversible constitutive equation

$$\mathbf{M} = \boldsymbol{\chi}_m \cdot \mathbf{H} \quad (12.5)$$

where $\boldsymbol{\chi}_m$ is the magnetic susceptibility. However, magnetostrictive materials are ferromagnetic, and the constitutive equation is more complex because of hysteresis, but they can be approximated as linear over a small range, as it will be discussed in Section 12.1.6.

The *magnetic induction* \mathbf{B} is a vector field as well, computed as

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) = \mu \cdot \mathbf{H} \quad (12.6)$$

where μ_0 is the magnetic permeability in vacuum. A ferromagnetic material can be magnetized (made into a magnet) by applying a strong enough magnetic field \mathbf{H}_0 .

For magnetic materials, the demagnetization effect is important when the magnetic field is applied at a certain distance.

While the electric field is applied/harvested at the boundary of the device, the magnetic field to be detected/harvested is usually present at a distance from the device. Since the material has a different magnetic permeability μ than the surroundings (μ_0), the magnetic and induction fields will not be homogeneous. The demagnetizing effect is postulated to take into account the inhomogeneity of the resulting magnetic field inside the device, as it is discussed in Section 12.7.

12.1.3 Elasticity

The state of stress at a point in any medium is completely defined by the symmetric, rank-two stress tensor $\boldsymbol{\sigma}$. The traction \mathbf{t} (force per unit area) in any direction of interest indicated by the unit vector $\hat{\mathbf{n}}$ can be calculated using Cauchy's law

$$\mathbf{t} = \boldsymbol{\sigma} \cdot \hat{\mathbf{n}} \quad (12.7)$$

The state of deformation at a point in any medium is completely defined by the symmetric, rank-two strain tensor \mathbf{s} . Additional relationships are developed in the Section 12.4, in the particular context of piezoelectric and magnetostrictive materials.

12.1.4 Direct magnetoelectric effect

Direct *magnetoelectric* (ME) coupling is the manifestation of an electrical polarization \mathbf{P} (as in (12.3)) or an electric field \mathbf{E} when a magnetic field \mathbf{H} is applied, i.e.,

$$d\mathbf{E} = \boldsymbol{\alpha} \cdot d\mathbf{H} \quad ; \quad \alpha_{ij} = \left. \frac{\partial E_i}{\partial H_j} \right|_{\mathbf{D}=0} \quad (12.8)$$

$$d\mathbf{P} = \boldsymbol{\beta} \cdot d\mathbf{H} \quad ; \quad \beta_{ij} = \left. \frac{\partial D_i}{\partial H_j} \right|_{\mathbf{E}=0} \quad (12.9)$$

where $d\mathbf{E}$, $d\mathbf{P}$, are the change in *electric field* and *magnetic polarization*, respectively, $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, are the ME voltage and charge coefficients, respectively. Conversely, ME effect is the manifestation of magnetization \mathbf{M} as a result of an applied electric field, i.e.,

$$d\mathbf{M} = \boldsymbol{\gamma} \cdot d\mathbf{E} \quad (12.10)$$

Considering linear effects only (as it will be justified later in this chapter), the polarization can be calculated as

$$\mathbf{P}(\mathbf{E}, \mathbf{H}) = \mathbf{P}^S + \epsilon_0 \boldsymbol{\chi}_e \cdot \mathbf{E} + \boldsymbol{\beta} \cdot \mathbf{H} + \dots \quad (12.11)$$

and the magnetization

$$\mathbf{M}(\mathbf{E}, \mathbf{H}) = \mathbf{M}^S + \boldsymbol{\chi}_m \cdot \mathbf{H} + \boldsymbol{\gamma} \cdot \mathbf{E} + \dots \quad (12.12)$$

where \dots denotes higher order terms, $\boldsymbol{\beta}$, $\boldsymbol{\gamma}$, are coupling tensors, and \mathbf{P}^S , \mathbf{M}^S , denote the spontaneous polarization and magnetization, respectively. Note that the second term in (12.11)–(12.12) represent the uncoupled effects described by (12.4) and (12.5).

12.1.5 Historical review

The first important achievement in the area of ME effect was made by Rontgen [1] in 1888, showing that a moving dielectric¹ material can be magnetized by the application of an electric field. This effect is known as direct ME effect. The converse

¹A dielectric is a material that can be polarized by an applied electric field. While a dielectric has low electrical conductivity, it differs from an insulator in that it can be polarized.

ME effect was observed by Wilson [2] in 1905. He measured the electric polarization of a dielectric material (ebonite) while rotating in a magnetic field parallel to the axis of revolution, finding that the induced polarization is proportional to the applied magnetic field. In 1894 Pierre Curie [3] proposed that the ME effect was possible in materials at rest, using crystal symmetry considerations, i.e., an asymmetric molecule may become magnetically polarized if placed in an electric field. He was not able to quantify the effect, and did not know if it was feasible to measure the effect or under what conditions (e.g., temperature).

The term *magnetoelectric* was introduced by Debye [4] and experimentally demonstrated by Rado et al. [5] in 1961 using single crystal Cr_2O_3 . The voltage produced was proportional to the applied magnetic field. ME charge coefficient β as a function of temperature can be seen in Figure 12.1. A clear disadvantage of this material is that does not present ME response at temperatures higher than 318 K. Another drawback of single-phase (not composite) ME materials is that the ME coupling is too small for practical applications such as sensors or harvesters. The maximum value in Figure 12.1 is $\beta = 4.13pC/(Am)$ at 263K according to [6, 7].

In an effort to increase the ME coefficient, about 80 materials were found that display ME effect [8]. The three largest coefficients have been observed for $LiCoPO_4$, *Yttrium Iron garnet* (YIG), and $TbPO_4$. Rivera [7] measured ME coupling in $LiCoPO_4$, obtaining² 30.6 ps/m at 4.2 K, and a Néel temperature³ of 21.9 K. For YIG, an ME coupling of 30 ps/m was reported by Krichevtsov et al. [9]. Rado et al. [10] reported 36.7 ps/m for $TbPO_4$ at 2 K. The data is summarized in Table 12.2

After these investigations with single-phase materials, interest in ME coupling phenomena decreased, since the achievable coupling of about 10 ps/m was deemed to be too low for practical applications. Furthermore, the Curie temperature⁴ or Néel temperature below which these materials show ME coupling is far below room temperature, thus making them impractical. The discovery of ME composite materials increased the interest in ME materials again because the drawbacks of single-phase materials were mostly removed and more design degrees of freedom became available to pursue practical applications.

12.1.6 ME effect in composite materials

The properties of a composite material are determined by the properties of the constituents, their volumetric participation, and the interaction among themselves and with the applied fields (magnetic, electric, or deformation) [24]. Traditionally, composites enhance one or more properties that are already available in both constituents, approximately according to the sum of the contributions from the constituents weighed by their volume fraction f_i [26, §4.1].

Consider an effect σ (e.g., stress) described by $\sigma_i = E_i s$, where E_i is a material *property* (e.g., modulus) and s (e.g., strain) is the common driver for the effect

²ps/m=pC/(A m).

³Néel temperature is the highest temperature at which the magnetic ordering of ferrimagnetic and anti-ferromagnetic materials is preserved.

⁴Curie temperature is the highest temperature at which the magnetic ordering of ferromagnetic materials is preserved.

Composition	β [ps/m]	Neel/Curie temp [K]	Source
Single-phase			
<i>Nb₂Mn₄O₉</i>	0.02	110	[11]
<i>Mn₃B₇O₁₃I</i>	0.02	26	[11]
<i>MnGeO₃</i>	0.02	16	[11]
<i>Cu₃B₇O₁₃Cl</i>	0.03	8.4	[11]
<i>MnNb₂O₆</i>	0.03	4.4	[11]
<i>Ta₂Mn₄O₉</i>	0.10	104	[11]
<i>CrTiNdO₅</i>	0.10	13	[11]
<i>Nb₂Co₄O₉</i>	0.21	27	[11]
<i>LiMnPO₄</i>	0.21	35	[11]
<i>TbCoO₃</i>	0.31	3.3	[11]
<i>Fe₂TeO₆</i>	0.31	219	[11]
<i>LiNiPO₄</i>	0.42	23	[11]
<i>GdAlO₃</i>	1.05	4	[11]
<i>Cr₂O₃</i>	4.13	263	[6, 7]
<i>Ta₂Co₄O₉</i>	1.05	21	[11]
<i>LiFePO₄</i>	1.05	50	[11]
<i>DyOOH</i>	1.05	7.2	[11]
<i>Gd₂CuO₄</i>	1.05	6.5	[11]
<i>CoGeO₃</i>	1.05	31	[11]
<i>HoPO₄</i>	2.09	1.4	[11]
<i>Ni₃B₇O₁₃I</i>	2.09	61.5	[11]
<i>GdVO₄</i>	3.14	2.4	[11]
<i>Co₃B₇O₁₃CI</i>	3.14	12	[11]
<i>Ni₃B₇O₁₃CI</i>	3.14	9	[11]
<i>Cr₂O₃</i>	4.13	203	[5, 12, 13]
<i>FeGaO₃</i>	4.19	305	[11]
<i>TbOOH</i>	4.19	10	[11]
<i>ErOOH</i>	5.24	4.1	[11]
<i>LiCoPO₄</i>	7.33	22	[11]
<i>TbAlO₃</i>	10.47	4	[11]
<i>DyPO₄</i>	10.47	3.4	[11]
<i>Co₃B₇O₁₃I</i>	10.47	38	[11]
<i>DyAlO₃</i>	20.94	3.5	[11]
<i>Co₃B₇O₁₃Br</i>	20.94	17	[11]
<i>YIG</i>	30	573	[9, 14]
<i>LiCoPO₄</i>	30.6	21.9	[6]
<i>TbPO₄</i>	36.7	2.29	[10]
Particulates			
<i>CoFe₂O₄/BaTiO</i>	720		[15, 16]

Table 12.2: Single phase magnetoelectric composites, compared to *CoFe₂O₄/BaTiO* particulate composite. The particulate outperforms the best single-phase material (in this table) by 20X.